

# The effect that 6-*tert*-butoxyhexyl functionalization has on ethylene polymerization in *ansa*-zirconocene dichlorides

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## Abstract

New *ansa*-zirconocene dichloride derivatives have been prepared, which have a 6-*t*-butoxyhexyl pendant introduced either on a Cp-ring-carbon or at the silicon and carbon *ansa*-bridging atom. Ethylene polymerization studies have been carried out with novel precatalysts of the type:  $[(\eta^5\text{-C}_{13}\text{H}_8)\text{-X}(t\text{-BuOC}_6\text{H}_{12})\text{Me}-(\eta^5\text{-C}_5\text{H}_4)]\text{ZrCl}_2$  [X = C **[1a]**, Si **[2a]**],  $[(\eta^5\text{-C}_{13}\text{H}_8)\text{-XMe}_2-(\eta^5\text{-}(t\text{-BuOC}_6\text{H}_{12}\text{C}_5\text{H}_3))]\text{ZrCl}_2$  [X = C **[3a]**, Si **[4a]**] in the presence of excess methylalumoxane (MAO) to compare their catalytic activity and to delineate the effect of the 6-*t*-butoxyhexyl functionality on ethylene polymerization. The precatalysts **[1a]** and **[2a]** with the bridge functionality showed higher activity in ethylene polymerization than the corresponding complexes **[3a]** and **[4a]** which have it on the Cp ring moiety. On the other hand the silyl bridged complexes **[2a]** and **[4a]** produced a higher molecular weight polyethylene than the carbon-bridged one, regardless of the location of functional group.

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**Keywords:** *Ansa*-zirconocene; Fluorenyl; 6-*t*-Butoxyhexyl pendant; Ethylene polymerization; MAO

## 1. Introduction

A large variety of *ansa*-metallocene precursors have been synthesized, characterized and used industrially, not only for the purpose of  $\alpha$ -olefin polymerization catalysts [1], but also for systematic mechanistic studies [2] since Kaminsky coworkers [3] discovered catalytic  $\alpha$ -olefin polymerization by metallocene complexes in the presence of methylalumoxane (MAO). Silyl-bridged cyclopentadienyl (Cp)-fluorenyl (Flu) ligand based metallocenes [4], along with half-sandwich metallocenes of “constrained geometry” catalysts (CGCs) [5], are especially attractive with respect to producing high molecular weight polyethylene, microstructure-controlled polypropylene, and  $\alpha$ -olefin copolymers [6]. However, regarding these studies, most metallocene precatalysts have been designed with a dialkylsilyl or diarylsilyl bridging unit [7], or a pendant hydrocarbyl or aryl group attached to one of the Cp rings to monitor the steric and electronic effects of such substitution [8]. Marks and coworkers [9] introduced a chiral

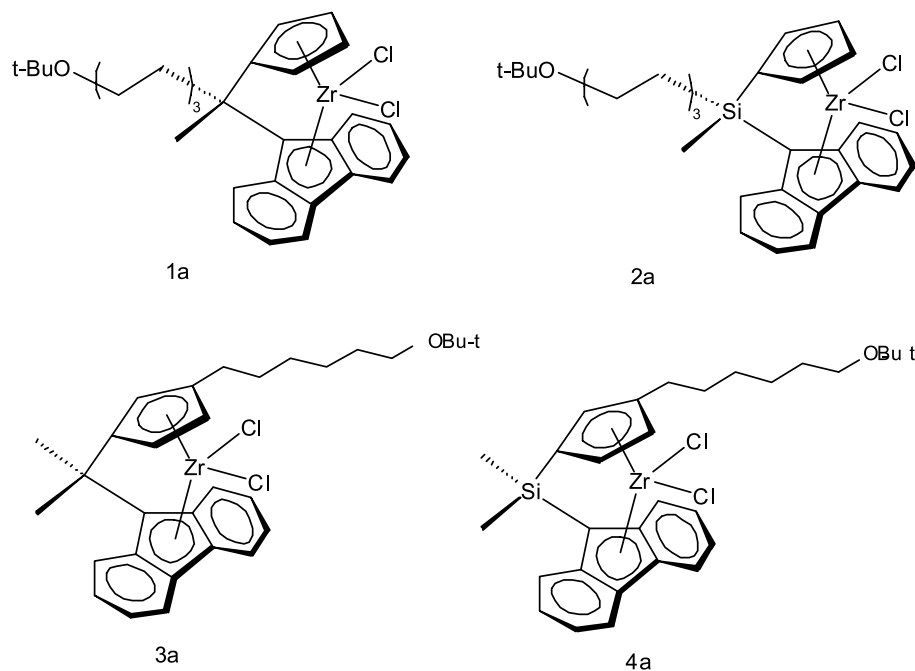
ancillary on the Cp ring in an *ansa*-metallocene to determine the role that this constraint plays on the stereoregularity of  $\alpha$ -olefin polymerization.

Recently, Jutzi et al. [10,11] reported a functionalized cyclopentadienyl complex which shows intra- or intermolecular donor–acceptor interaction between the functional group and the metal center. Specifically, the  $[\text{Me}_2\text{Si}]$ -bridged (Cp)–(Flu) zirconocene containing an  $-(\text{CH}_2)_2\text{NR}_2$  (R = methyl or isopropyl) pendant group on the Cp ring, with MAO as the cocatalyst, has produced a bimodal polyethylene (a mixture of high and low molecular weight polymers) by the presence of two catalytically active sites, i.e., the metal center and the N-donor functionality interacting with MAO [12].

A large number of group 4 metallocenes and *ansa*-metallocenes have been reported with an  $-\text{OR}$  or  $-(\text{CH}_2)_n\text{OR}$  functional group on the side chain [13,14], which participates in metal binding as a hemi-labile ligand. However, examples of metallocenes in which the  $-\text{OR}$  functional groups on the bridging unit or Cp pendants in silicon and/or carbon-bridged (Cp)–(Flu) zirconocenes have not been reported to date (Scheme 1). In this paper we report the synthetic preparations of new

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Scheme 1. New *ansa*-zirconocene dichlorides with 6-*t*-butoxyhexyl pendant groups.

*ansa*-metallocene complexes and the activities of these precatalysts in ethylene polymerization with MAO, to better understand the effect of O-donor pendant arm location.

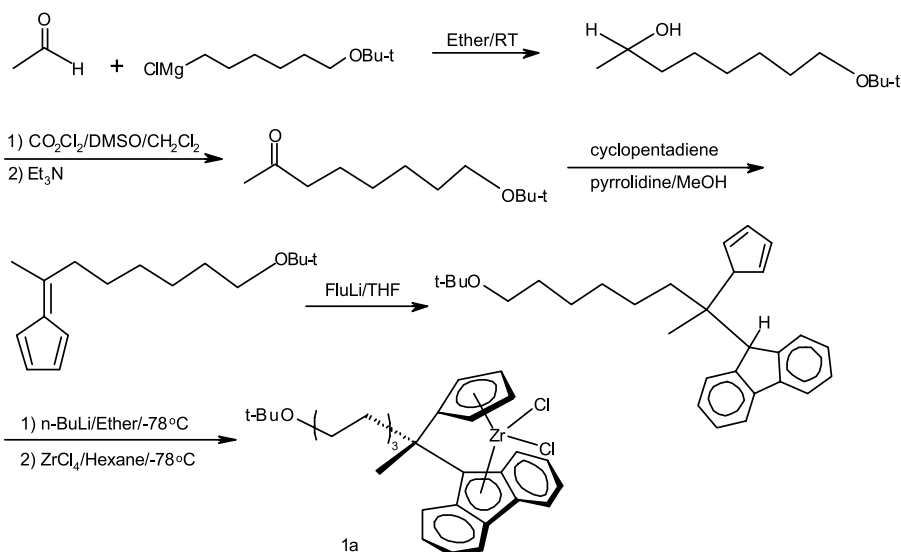
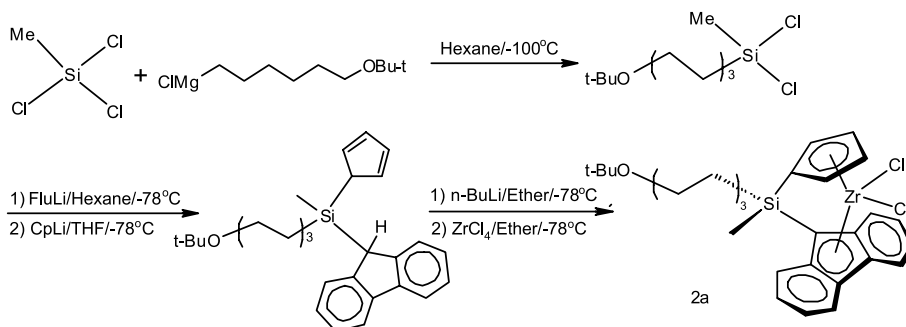
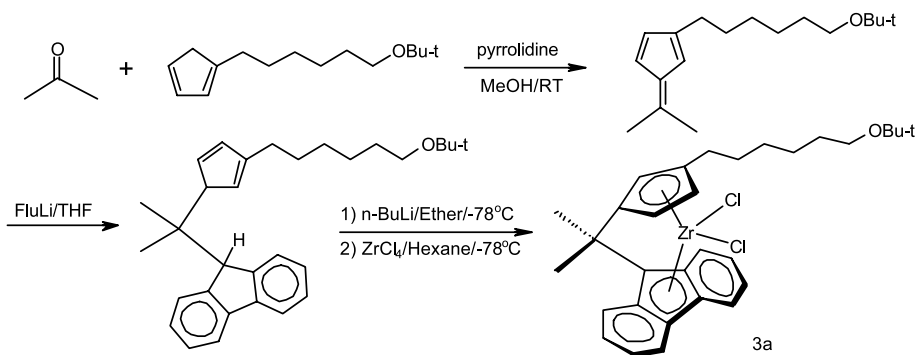
## 2. Results and discussion

### 2.1. Preparation and characterization of complexes [1a]–[4a]

We have synthesized various metallocene catalyst precursors that have a functional pendant arm on the ancillary ligand in order to attach them to a modified or unmodified silica surface [15]. Thus, the heterogenized catalysts [16] can be delivered to a slurry or gas-phase process free of “reactor fouling” in industry. Previously mentioned, the *ansa*-metallocene complexes of group 4, especially [dialkylsilyl(Cp)(Flu)] and [isopropylene(Cp)(Flu)] zirconium complexes have been used as precatalysts to produce high molecular weight polyethylene and stereoregulated polypropylene [17] with reasonable catalytic activity. With these advantages in zirconocene chemistry, however syntheses of these *ansa*-metallocene derivatives are not trivial. Such obstacles for use of these complexes on an industrial scale include, multiple steps in preparing pure ligands, difficulty in ligand purification and sensitivity to polar reaction solvents such as THF during metallation step with the desired ligand. These difficulties generally lead to low preparative yields. The syntheses of *ansa*-zirconocene dichlorides, with the functional pendant, 6-*t*-butoxyhexyl is illustrated in Scheme 2. The 6-*t*-butoxyhexyl

group was introduced at the carbon and silicon bridge of (Cp)(Flu)zirconium dichlorides in Schemes 2 and 3, respectively. Schemes 4 and 5 illustrate the routes to prepare the *ansa*-(Cp)(Flu)zirconium dichlorides with the corresponding Cp-ring pendant group.

The syntheses of all substituted complexes were very sensitive to the purity of the ligand dianion salt, solvents of metallation, reaction temperature and reaction time. Washing the dianion salt with hydrocarbon solvent, after generating the dianion with two equivalents *n*-BuLi in diethyl ether or THF, was very important in the success of this preparation. Another reason for washing the dilithium salt of the *ansa*-bridged ligand is that more polar solvents lead to decomposition in the metallation step. All excess THF needs to be removed; this is effected by washing and subsequent trituration. During the metallation step, hydrocarbon solvents such as pentane or hexane were used as the reaction solvent for the carbon bridged complexes; for the silicon-bridged complexes, the metallation was found best to be performed in diethyl ether. Shorter reaction times and low temperature proved to be the best conditions for this metallation as well. For the preparation of carbon-bridged complexes, the intermediate fulvene compounds were employed efficiently [18]. Complexes [Me(*t*-BuOC<sub>6</sub>H<sub>12</sub>)C(Flu)(Cp)]ZrCl<sub>2</sub> [1a] and [Me(*t*-BuOC<sub>6</sub>H<sub>12</sub>)Si(Flu)(Cp)]ZrCl<sub>2</sub> [2a] were both obtained as a racemic mixture. Enantiomeric and diastereomeric species are possible for complexes 1a–4a, due to the presence of one or two stereogenic centers involving the bridging atom and Cp ring; all of the appropriate diastereomers were identified by <sup>1</sup>H NMR spectroscopy.

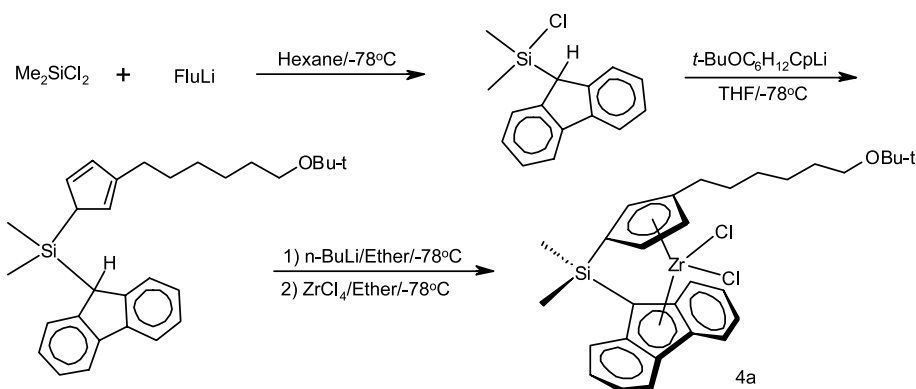
Scheme 2. Synthesis of  $[\text{Me}(t\text{-BuOC}_6\text{H}_{12})\text{C}(\text{Flu})(\text{Cp})]\text{ZrCl}_2$  [**1a**].Scheme 3. Synthesis of  $[\text{Me}(t\text{-BuOC}_6\text{H}_{12})\text{Si}(\text{Flu})(\text{Cp})]\text{ZrCl}_2$  [**2a**].Scheme 4. Synthesis of  $[\text{Me}_2\text{C}(\text{Flu})(t\text{-BuOC}_6\text{H}_{12}\text{Cp})]\text{ZrCl}_2$  [**3a**].

Compared to the *ansa*-metallocene complexes **1a** and **2a** that have the functionality to the bridge unit, the corresponding metallocene **3a** and **4a** with the side chain functionality more easily decompose. In addition all new complexes have shown an increased solubility in hydrocarbon solvent compared to the parent complexes that have no functional pendant. However, the metallocenes **2a** and **4a** appear to be much more stable than

the parent complex  $[\text{Me}_2\text{Si}(\text{Cp})(\text{Flu})]\text{ZrCl}_2$  towards decomposition.

## 2.2. Polymerization of ethylene with MAO

Ethylene polymerization was carried out with complexes **1a–4a** in combination with MAO at  $60^\circ\text{C}$  in toluene under ethylene pressure (30 psi). To ensure re-

Scheme 5. Synthesis of  $[\text{Me}_2\text{Si}(\text{Flu})(t\text{-BuOC}_6\text{H}_{12}\text{Cp})]\text{ZrCl}_2$  [**4a**].

producibility, these polymerizations were repeated twice for each catalyst precursor, summarized in Table 1. The polyethylene that is produced by **1a–4a** was analyzed by gel permeation chromatography (GPC). Exceptionally, complex **2a** demonstrated the highest polyethylene productivity among the rest of the catalysts by 2–4 fold. Precatalysts **1a** and **2a** showed higher activity in ethylene polymerization than the corresponding complexes **3a** and **4a**. Furthermore, the silyl-bridged metallocenes produced higher molecular weight polyethylene ( $M_w/M_n$  value) than the carbon-bridged analog did, regardless of whether the pendant was attached to the Cp ring or to the bridge. Although this phenomenon has already been observed in other catalyst systems, determining the degree of electronic richness or poorness imparted to the metal center by the Cp-type ligand [19,20], as well as discovering the relationship between the electron density of the metal center and the nature of the resulting polymer are both ongoing challenges [21,22].

*Ansa*-bridges with single-atom linkers were demonstrated as having an electron withdrawing effect through experiment and calculations [23], thus *ansa*-bridges  $[\text{Me}(t\text{-BuOC}_6\text{H}_{12})\text{Si}]$  and  $[\text{Me}(t\text{-BuOC}_6\text{H}_{12})\text{C}]$  are believed to possess some degree of an electron withdrawing effect. The other apparent difference between complex **1a** and **2a** is the size of the bridging atom. A comparison of the crystal structures of parent complexes  $[\text{Me}_2\text{Si}(\text{Cp})(\text{Flu})]\text{ZrCl}_2$  and  $[\text{Me}_2\text{C}(\text{Cp})(\text{Flu})]\text{ZrCl}_2$  reveals that the geometry at the carbon atom is more tetrahedral

than for that of silicon [24]. Also, the amount that the Cp or Flu group coordination is leaning from  $\eta^5$  coordination towards  $\eta^5$  coordination is similar in the two structures. Specifically, the  $\text{Cp}(\text{cent})\text{-Zr-Flu}(\text{cent})$  angles in  $[\text{Me}_2\text{Si}(\text{Cp})(\text{Flu})]\text{ZrCl}_2$  and  $[\text{Me}_2\text{C}(\text{Cp})(\text{Flu})]\text{ZrCl}_2$  are  $128^\circ$  and  $119^\circ$ , respectively. These facts suggest the ligand  $[\text{Me}_2\text{Si}(\text{Cp})(\text{Flu})]$  may be able to better donate electron density to the metal center than  $[\text{Me}_2\text{C}(\text{Cp})(\text{Flu})]$  can, which may influence the kind of polyethylene that is formed.

The polydispersities ( $M_w/M_n$ , PDI) of 2 or 3 for polyethylene, which is characteristic of single site metallocene catalysts, indicated that these precatalyst produced polyethylene with unimodal molecular weight distribution at the polymerization temperature  $60^\circ\text{C}$ . This observation is quite different from that involving complexes in which there is an N-donor functional group anchored to the Cp moiety such as in  $[\text{Me}_2\text{Si}(\eta^5\text{-}(\text{Pr}_2\text{NC}_2\text{H}_4)\text{C}_5\text{H}_3)_2]\text{ZrCl}_2$  and the more closely related complex,  $[(\eta^5\text{-C}_{13}\text{H}_8)\text{-Me}_2\text{C}(\eta^5\text{-(Et}_2\text{NC}_2\text{H}_4)\text{C}_5\text{H}_3)]\text{ZrCl}_2$ , which shows PDI values of about 18 and 15 in which the shoulder of GPC curve occurs at 60 and  $50^\circ\text{C}$ , respectively [12].

### 3. Conclusion

In summary, we have synthesized four new *ansa*-zirconocene dichlorides which have a 6-*t*-butoxyhexyl

Table 1

Ethylene polymerization results<sup>a</sup> for  $[(\eta^5\text{-C}_{13}\text{H}_8)\text{-X}(t\text{-BuOC}_6\text{H}_{12})\text{Me}(\eta^5\text{-C}_5\text{H}_4)]\text{ZrCl}_2$  [X = C [**1a**], Si [**2a**]] and  $[(\eta^5\text{-C}_{13}\text{H}_8)\text{-XMe}_2\text{-}\eta^5\text{-(}t\text{-BuOC}_6\text{H}_{12})\text{C}_5\text{H}_3)]\text{ZrCl}_2$  [X = C [**3a**], Si [**4a**]]

Complex	Yield (g)	Time (min)	$M_w$	$M_w/M_n$	Activity <sup>b</sup>
<b>1a</b>	6.76	30	606,000	2.8	4.5
<b>2a</b>	4.46	8	1,208,000	3.0	11.2
<b>3a</b>	4.30	30	478,000	2.5	2.9
<b>4a</b>	4.40	30	998,000	2.7	2.9

<sup>a</sup> Polymerization conditions: zirconocene: 3  $\mu\text{mol}$ , Al/Zr = 1000, toluene 200 mL,  $T_p = 60^\circ\text{C}$ ,  $P = 30$  psi.

<sup>b</sup> Activity in  $10^3$  kg PE/mol of Zr h.

pendant introduced at the ring-carbon or at the silicon and carbon *ansa*-bridge. Also we studied their catalytic activity for ethylene polymerization in the presence of excess MAO. The precatalysts [1a] and [2a] with the bridge functionality showed higher activity in ethylene polymerization than the corresponding complexes [3a] and [4a] which have it on the Cp ring moiety. Also, the silyl bridged complexes [2a] and [4a] produced higher molecular weight polyethylene than the carbon-bridged one, regardless of the location of functional group. The temperature dependence of the production of polyethylene with a bimodal molecular weight distribution is very distinctive for the N-donor functionalized metallocene complexes; however it is not yet clear at this point whether this same trend is true for the O-donor functionalized metallocenes described here, and this is a subject for further study.

## 4. Experimental

### 4.1. General techniques and reagents

All manipulations were performed using the combination of glove box, high vacuum, and Schlenk techniques [25]. Solvents were purified and degassed by standard procedures prior to use. All available reagents were purchased commercially and used as received unless otherwise noted in the experimental procedure. Elemental analyses were performed using a Perkin–Elmer 2400 CHN Elemental Analyzer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Advance 400DRX spectrometer operating at 399.9 and 100.6 MHz, respectively.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR chemical shifts are reported in ppm relative to  $\text{SiMe}_4$  ( $\delta = 0$ ) and were referenced internally, relative to the protio solvent impurity ( $\delta = 7.26$  ppm and  $\delta = 77.0$  ppm for  $\text{CDCl}_3$ ). All coupling constants are reported in hertz. Gel permeation chromatography (GPC) for the polyethylene was obtained using a Waters 150C plus apparatus in 1,2,4-trichlorobenzene at 140 °C. Calibration was performed by narrow distributed linear polystyrene standards.

### 4.2. 8-*t*-Butoxy-2-octanol (1)

*t*-Butoxyhexylmagnesium chloride in diethyl ether (200 mL, ca. 0.14 mol) was slowly added to a diethyl ether solution of acetaldehyde (20 mL, 0.36 mol) in a 1 L 3-neck round-bottom flask at 0 °C. After stirring the reaction mixture at room temperature for 5 h, it was quenched with 1 N HCl solution. The crude product was extracted with diethyl ether ( $2 \times 100$  mL). The clear liquid product was dried over  $\text{MgSO}_4$  and concentrated in vacuo to afford 27.7 g of the product (98% based on 0.14 mol of the Grignard reagent).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,

7.26 ppm): 1.17 (*t*-BuO, 9H, s), 3.31 (*t*-BuOCH<sub>2</sub>, 2H, t,  $^3J_{\text{H-H}} = 6.5$  Hz), 1.31, 1.41, 1.50 (CH<sub>2</sub>, MeC(OH)H, 13H, m), 3.75 (MeC(OH)H, sextet).

### 4.3. 8-*t*-Butoxy-2-octanone (2)

Oxalyl chloride (1.5 eq. with respect to DMSO, 18 mL, 0.21 mol) was added to DMSO (3 eq. with respect to alcohol, 30 mL, 0.42 mol) in 150 mL anhydrous methylene chloride at  $-78$  °C. After the reaction mixture was stirred at  $-60$  °C for 30 min, this reagent was added slowly to 8-*t*-butoxy-2-octanol (27.7 g, 0.14 mol) in 50 mL methylene chloride in a 1 L round-bottom flask at  $-60$  °C. The reaction mixture was stirred at  $-60$  °C for 3 h and was quenched by  $\text{Et}_3\text{N}$  (102 mL, 0.73 mol, 3 eq. of oxalyl chloride) at  $-40$  °C. The mixture was stirred at  $-40$  °C for an additional 30 min at room temperature giving a brown oil crude product. The crude product was washed with water ( $2 \times 100$  mL) and concentrated to give a brown liquid product that was vacuum (75 °C at 600 mTorr) distilled to afford 20.1 g of pure product (75%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 7.26 ppm): 1.16 (*t*-BuO, 9H, s), 3.30 (*t*-BuOCH<sub>2</sub>, 2H, t,  $^3J_{\text{H-H}} = 7$  Hz), 2.40 (CH<sub>3</sub>COCH<sub>2</sub>, 2H, t,  $^3J_{\text{H-H}} = 8$  Hz), 2.11 (CH<sub>3</sub>CO, 3H, s), 1.49 (CH<sub>2</sub>, 4H, m), 1.31 (CH<sub>2</sub>, 4H, m).

### 4.4. 6-Methyl-6-(6-*t*-butoxyhexyl)fulvene, Me(*t*-BuOC<sub>6</sub>H<sub>12</sub>)C=(C<sub>5</sub>H<sub>4</sub>) (3)

To a solution of 8-*t*-butoxy-2-octanone (13.5 g, 0.067 mol) and cyclopentadiene (9.0 g, 0.14 mol) in dry methanol (200 mL), pyrrolidine (12.5 mL, 0.15 mol) was added at room temperature. The reaction mixture was stirred overnight at room temperature. Acetic acid (12 g, 0.2 mol, in 200 mL water) was added to the reaction mixture and stirred for 1 h. The reaction solution was diluted with 300 mL of diethyl ether and 200 mL of water. The organic layer was then extracted, washed with brine (200 mL), dried over  $\text{MgSO}_4$ , and concentrated in vacuo to give orange oil as a crude product. Pure pale yellow product (6.5 g) was obtained by vacuum distillation (100 °C and ca. 500 mTorr) (39%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 7.26 ppm): 1.17 (*t*-BuO, 9H, s), 3.31 (*t*-BuOCH<sub>2</sub>, 2H, t,  $^3J_{\text{H-H}} = 7$  Hz), 2.53 (CH<sub>3</sub>CpCH<sub>2</sub>, 2H, t,  $^3J_{\text{H-H}} = 7.6$  Hz), 2.20 (CH<sub>3</sub>Cp, 3H, s), 6.52–6.47 (Cp, 4H, m), 1.40–1.30 (CH<sub>2</sub>, 4H, m), 1.60–1.52 (CH<sub>2</sub>, 4H, m).

### 4.5. 2-Methyl-2'-6-*t*-butoxyhexylmethylene[cyclopentadienyl-fluorene-9-yl], [(CpH)Me(*t*-BuOC<sub>6</sub>H<sub>12</sub>)C(FluH)] (4)

The above fulvene derivative (3) (6.5 g, 0.026 mol) in THF (50 mL) was added to fluorenyllithium (1 Et<sub>2</sub>O bound: 6.5 g, 0.026 mol) in THF (100 mL) at  $-78$  °C slowly. TLC (developing solvent EtOAc:hexane = 5:95 v/v%) was carried to confirm reaction completion after the

red reaction mixture was stirred at room temperature overnight. The reaction mixture was quenched by a saturated solution of  $\text{NH}_4\text{Cl}$  (30 mL) and followed by adding 300 mL water. A yellow crude product was extracted with diethyl ether and then purified by column chromatography (silica, starting with 100% hexane, after fluorene separation, with 10% EtOAc and 90% hexane) to give 10.5 g of the product as a yellow oil (97%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 7.26 ppm): 1.19 (*t*-BuO, 9H, s), 0.58, 0.89 (MeC, 3H, s), 1.90 ( $\text{CH}_2$ , 2H, m), 1.49 ( $\text{CH}_2$ , 2H, m), 1.30 ( $\text{CH}_2$ , 4H, m), 1.27 ( $\text{CH}_2$ , 2H, m), 3.31 (*t*-BuOCH<sub>2</sub>, 2H, t,  $^3J_{\text{H-H}} = 7$  Hz), 6.88, 6.62, 5.87 (CpH, 3H, brs), 3.07 (methyleneCpH, 2H, brs), 4.15 (FluH, 1H, s), 7.72 (FluH, 1H, m), 7.67 (FluH, 1H, m), 7.55 (FluH, 1H, m), 7.36 (FluH, 1H, m), 7.28 (FluH, 1H, m), 7.24 (FluH, 1H, m), 7.04 (FluH, 1H, m), 6.76 (FluH, 1H, m).

4.6. *2-Methyl-2'-6-t-butoxyhexylmethylene[cyclopentadienyl-fluorene-9-yl]-zirconocenedichloride, [( $\eta^5$ -C<sub>13</sub>H<sub>8</sub>)-Me(*t*-BuOC<sub>6</sub>H<sub>12</sub>)C-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)]ZrCl<sub>2</sub> (1a)*

*n*-BuLi (1.6 M hexane solution, 10 mL, 0.016 mol) was added slowly to a solution of [(*t*-BuOC<sub>6</sub>H<sub>12</sub>)MeC(FluH)(CpH)] (4) (3.2 g, 0.008 mol) in THF (50 mL) at  $-78$  °C. After stirring the red reaction mixture at room temperature for 5 h, the solvent was removed in vacuo. A crude red solid was washed with hexane (2 × 30 mL) to give 3 g of the dianion [(*t*-BuOC<sub>6</sub>H<sub>12</sub>)MeC(Flu)(Cp)]Li<sub>2</sub> (88%) that is used for the next metallation step. This ligand solution of [(*t*-BuOC<sub>6</sub>H<sub>12</sub>)MeC(Flu)(Cp)]Li<sub>2</sub> (2.5 g, 0.0044 mol) in hexane (50 mL) was added to the solution of ZrCl<sub>4</sub> (1.02 g, 0.0045 mol) in hexane (50 mL) at  $-78$  °C. The reaction solvent was removed after stirring at room temperature for 12 h. The solid residue was dried and extracted with toluene 100 mL using a frit. The bright red solid was washed with 10 mL of hexane to give 0.8 g of pure product (31%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 7.26 ppm): 1.18 (*t*-BuO, 9H, s), 2.39 (MeC, 3H, s), 1.82 ( $\text{CH}_2$ , 2H, m), 1.59 ( $\text{CH}_2$ , 4H, m), 1.46 ( $\text{CH}_2$ , 2H, m), 1.22 ( $\text{CH}_2$ , 2H, m), 3.34 (*t*-BuOCH<sub>2</sub>, 2H, t,  $^3J_{\text{H-H}} = 7$  Hz), 6.33 (CpH, 2H, t,  $^3J_{\text{H-H}} = 2$  Hz), 5.80–5.75 (CpH, 2H, m), 7.27 (FluH, 2H, m), 7.56 (FluH, 2H, m), 7.63 (FluH, 1H, d,  $^3J_{\text{H-H}} = 9$  Hz), 7.82 (FluH, 1H, d,  $^3J_{\text{H-H}} = 9$  Hz), 8.14 (FluH, 2H, m).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 77 ppm): 27.5 (Me<sub>3</sub>CO, q,  $^1J_{\text{C-H}} = 124$  Hz), 27.6 (MeC, q,  $^1J_{\text{C-H}} = 124$  Hz), 44.4 (Me<sub>3</sub>C, s), 26.3 (MeC, s), 72. (ipsoC, s), 78.9 (ipsoC, s), 115.0, 122.1, 123.3, 123.6 (4C, s), 61.5 (Me<sub>3</sub>COCH<sub>2</sub>, t,  $^1J_{\text{C-H}} = 139$  Hz), 40.6 (ipsoCCH<sub>2</sub>, t,  $^1J_{\text{C-H}} = 124$  Hz), 30.6, 30.0, 26.6, 23.5 (4C, t,  $^1J_{\text{C-H}} = 124$  Hz,  $^3J_{\text{C-H}} = 10$  Hz), 101.6, 102.5, 118.7, 119.7, 129.3, 129.1, 125.2, 125.0, 124.9, 124.8, 123.4, 122.9 (FluC and CpC, 12C, d,  $^1J_{\text{C-H}} = 171$  Hz,  $^3J_{\text{C-H}} = 10$  Hz). Analysis calculated for C<sub>30</sub>H<sub>36</sub>OZrCl<sub>2</sub>: C, 62.69; H, 6.31. Found: C, 61.33; H, 5.97%.

4.7. *6-t-Butoxyhexyldichloromethylsilane (5)*

A solution of *t*-butoxyhexylmagnesium chloride (ca. 100 mL, 0.14 mol in diethyl ether solution) was added to the solution of trichloromethylsilane (24.7 mL, 0.21 mol) in hexane (100 mL) dropwise at  $-100$  °C over 3 h. The clear solution was filtered and the solid residue was extracted with additional hexane after stirring at room temperature for 3 h. The solvent was removed in vacuo to get rid of excess trichloromethylsilane and to give 32 g of colorless product (ca. 84%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 7.26 ppm): 0.75 (Si–Me, 3H, s), 1.17 (*t*-BuO, 9H, s), 3.55 (*t*-BuOCH<sub>2</sub>, 2H, t,  $^3J_{\text{H-H}} = 8$  Hz), 1.51 ( $\text{CH}_2$ , 4H, m), 1.40 ( $\text{CH}_2$ , 4H, m), 1.13 (Si–CH<sub>2</sub>, 2H, m).

4.8. *6-t-Butoxyhexylchloromethyl-(9-fluorenyl)silane, (t-BuOC<sub>6</sub>H<sub>12</sub>)MeSi(FluH)Cl (6)*

A solution of solid fluorenyllithium (1 Et<sub>2</sub>O bound: 7 g, 0.028 mol) in hexane (150 mL) was added to a solution of Me(*t*-BuOC<sub>6</sub>H<sub>12</sub>)SiCl<sub>2</sub> (7.71 g, 0.028 mol) in hexane (50 mL) dropwise at  $-78$  °C over the period of 2 h. The reaction solvent was dried in vacuo after stirring at room temperature for 5 h. The solid residue was extracted with hexane (100 mL) to give a pale yellow oil product.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 7.26 ppm): 0.12 (Si–Me, 3H, d), 1.18 (*t*-BuO, 9H, s), 3.28 (*t*-BuOCH<sub>2</sub>, 2H, t,  $^3J_{\text{H-H}} = 8$  Hz), 1.46 ( $\text{CH}_2$ , 4H, m), 1.27 ( $\text{CH}_2$ , 4H, m), 1.0 (Si–CH<sub>2</sub>, 2H, m), 4.12 (FluH, 1H, s), 7.88–7.85 (FluH, 2H, m), 7.67–7.66 (FluH, 2H, m), 7.41–7.38 (FluH, 2H, m), 7.35–7.33 (FluH, 2H, m).

4.9. *6-t-Butoxyhexylmethyl-(cyclopentadienyl)-(9-fluorenyl)silane, [(CpH)(t-BuOC<sub>6</sub>H<sub>12</sub>)MeSi(FluH)] (7)*

A solution of solid cyclopentadienyllithium (2.02 g, 0.028 mol) in THF (50 mL) was slowly added to a mixture of (*t*-BuOC<sub>6</sub>H<sub>12</sub>)MeSi(FluH)Cl (11.2 g, 0.028 mol) in THF (50 mL) at room temperature. The solvent was pumped off after stirring at room temperature for 3 h. The solid residue was extracted with hexane (100 mL) to give an orange oily product (11.5 g, 95%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 7.26 ppm): 1.17, 1.15 (*t*-BuO, 9H, s),  $-0.15$ ,  $-0.36$  (MeSi, 3H, s), 0.35, 0.27 ( $\text{CH}_2$ , 2H, m), 0.60, 0.70 ( $\text{CH}_2$ , 2H, m), 1.40, 1.26 ( $\text{CH}_2$ , 4H, m), 1.16, 1.12 ( $\text{CH}_2$ , 2H, m), 3.26 (*t*-BuOCH<sub>2</sub>, 2H, t,  $^3J_{\text{H-H}} = 7$  Hz), 2.68 (methyleneCpH, 2H, brs), 6.60, 6.52, 6.10 (CpH, 3H, brs), 4.10, 4.00 (FluH, 1H, s), 7.86 (FluH, 2H, m), 7.78 (FluH, 1H, m), 7.53 (FluH, 1H, m), 7.43–7.22 (FluH, 4H, m).

4.10. *6-t-Butoxyhexylmethylsilanediy[cyclopentadienyl-fluorene-9-yl]-zirconocenedichloride, [( $\eta^5$ -C<sub>13</sub>H<sub>8</sub>)-Me(*t*-BuOC<sub>6</sub>H<sub>12</sub>)Si-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)]ZrCl<sub>2</sub> (2a)*

*n*-BuLi (1.6 M of hexane, 35 mL, 0.056 mol) was added slowly to a solution of [(*t*-BuOC<sub>6</sub>H<sub>12</sub>)MeSi-

(FluH)(CpH)] (7) (12 g, 0.028 mol) in THF (100 mL) at  $-78^{\circ}\text{C}$ . After stirring the red reaction mixture at room temperature for 4 h, the solvent was removed in vacuo. A crude orange solid was washed with hexane ( $2 \times 50$  mL) to give 10 g of dianion [(*t*-BuOC<sub>6</sub>H<sub>12</sub>)MeSi(Flu)(Cp)]Li<sub>2</sub> that is used for the next metallation (81%). The ligand solution of [(*t*-BuOC<sub>6</sub>H<sub>12</sub>)MeSi(Flu)(Cp)]Li<sub>2</sub> (2 g, 0.0045 mol) in a diethyl ether (30 mL) was added to the solution of ZrCl<sub>4</sub> (1.05 g, 0.0045 mol) in diethyl ether (30 mL) at  $-78^{\circ}\text{C}$ . The reaction solution was filtered after stirring at room temperature for 3 h and the solid residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL) using a frit. The dark red solid was washed with 10 mL hexane to give 1.44 g of pure product (54%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 7.26 ppm): 1.19 (*t*-BuO, 9H, s), 1.13 (MeSi, 3H, s), 1.79 (CH<sub>2</sub>, 4H, m), 1.60 (CH<sub>2</sub>, 4H, m), 1.48 (CH<sub>2</sub>, 2H, m), 3.35 (*t*-BuOCH<sub>2</sub>, 2H, t, <sup>3</sup>J<sub>H-H</sub> = 7 Hz), 6.61 (CpH, 2H, t, <sup>3</sup>J<sub>H-H</sub> = 3 Hz), 5.76 (CpH, 2H, d, <sup>3</sup>J<sub>H-H</sub> = 3 Hz), 8.13 (FluH, 1H, m), 7.83 (FluH, 1H, m), 7.78 (FluH, 1H, m), 7.65 (FluH, 1H, m), 7.54 (FluH, 1H, m), 7.30 (FluH, 2H, m), 7.06 (FluH, 1H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 77 ppm): 27.5 (Me<sub>3</sub>CO, q, <sup>1</sup>J<sub>C-H</sub> = 124 Hz), -3.3 (MeSi, q, <sup>1</sup>J<sub>C-H</sub> = 121 Hz), 64.6, 66.7, 72.4, 103.3, 127.6, 128.4, 129.0 (7C, s), 61.4 (Me<sub>3</sub>COCH<sub>2</sub>, t, <sup>1</sup>J<sub>C-H</sub> = 135 Hz), 14.5 (*ipso* SiCH<sub>2</sub>, t, <sup>1</sup>J<sub>C-H</sub> = 122 Hz), 33.1, 30.4, 25.9, 22.7 (4C, t, <sup>1</sup>J<sub>C-H</sub> = 119 Hz), 110.7, 111.4, 125.0, 125.1, 128.8, 128.1, 126.5, 125.9, 125.3, 125.1, 125.0, 123.8 (FluC and CpC, 12C, d, <sup>1</sup>J<sub>C-H</sub> = 171 Hz, <sup>3</sup>J<sub>C-H</sub> = 10 Hz). Analysis calculated for C<sub>29</sub>H<sub>36</sub>OSiZrCl<sub>2</sub>: C, 58.96; H, 6.14. Found: C, 58.68; H, 6.27%.

#### 4.11. 6-*t*-Butoxyhexylcyclopentadiene (*t*-BuOC<sub>6</sub>H<sub>12</sub>CpH)

A clear liquid 6-*t*-butylhexylchloride (305 g, 1.58 mol) was added to a solution of lithium cyclopentadienylide (814 mL, 1.63 mol, 2.0 M of THF solution) dropwise at  $0^{\circ}\text{C}$ . The reaction was exothermic and kept at ice bath temperature for 2 h and stirred overnight at room temperature. The reaction mixture was transferred into a separatory funnel and washed with water ( $3 \times 300$  mL) to give a red burgundy solution. The reaction solvent was pumped off and the residue was vacuum distilled (120  $^{\circ}\text{C}$ , 600 mTorr) to give a clear oily product (300 g, 83%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 7.26 ppm): 1.18 (*t*-BuO, 9H, s), 1.45 (CH<sub>2</sub>, 2H, m), 1.35 (CH<sub>2</sub>, 4H, m), 1.53 (CH<sub>2</sub>, 4H, m), 2.35 (CH<sub>2</sub>, 2H, m), 3.32 (*t*-BuOCH<sub>2</sub>, 2H, t, <sup>3</sup>J<sub>H-H</sub> = 7 Hz), 6.00 (CpH, 1H, brs), 6.15 (CpH, 1H, brs), 6.32 (CpH, 1H, brs), 6.40 (CpH, 1H, brs), 2.94 (CpH, 1H, brs), 2.87 (CpH, 1H, brs).

#### 4.12. 6,6-Dimethyl-3-(6-*t*-butoxyhexyl)fulvene, Me<sub>2</sub>C=C<sub>5</sub>H<sub>4</sub>(*t*-BuOC<sub>6</sub>H<sub>12</sub>)

To a solution of anhydrous acetone (14.7 mL, 0.2 mol) and *t*-butoxyhexylcyclopentadiene (22.3 g, 0.1 mol) in a dried methanol (200 mL), pyrrolidine (21 mL, 0.25

mol) was added slowly at  $-78^{\circ}\text{C}$ . The reaction mixture was stirred at room temperature overnight. Acetic acid (18 g, 0.3 mol, in 200 mL water) was then added to the reaction mixture and stirred for an hour. The reaction solution was diluted with 300 mL diethyl ether and 200 mL water and the organic layer was extracted. The organic layer was washed with brine (200 mL), dried over MgSO<sub>4</sub>, and concentrated in vacuo to give an orange oil crude product. 15.9 g of orange oil product was obtained by vacuum distillation (110  $^{\circ}\text{C}$ , 500 mTorr) (59%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 7.26 ppm): 1.18 (*t*-BuO, 9H, s), 2.14 (Me<sub>2</sub>C, 3H, s), 3.32 (*t*-BuOCH<sub>2</sub>, 2H, t, <sup>3</sup>J<sub>H-H</sub> = 7 Hz), 1.54 (CH<sub>2</sub>, 4H, m), 1.35 (CH<sub>2</sub>, 4H, m), 2.38 (CpCH<sub>2</sub>, 2H, t, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz), 6.49 (CpH, 1H, m), 6.35 (CpH, 1H, m), 6.16 (CpH, 1H, m).

#### 4.13. 2-(6-*t*-Butoxyhexylcyclopentadienyl)-2-(fluorenyl)propane, [(*t*-BuOC<sub>6</sub>H<sub>12</sub>CpH)Me<sub>2</sub>C(FluH)] (10)

The above fulvene derivative (9) (8 g, 0.03 mol) in THF (50 mL) was added slowly to fluorenyllithium (1 Et<sub>2</sub>O bound: 10 g, 0.041 mol) in THF (100 mL) at  $-78^{\circ}\text{C}$ . TLC (developing solvent EtOAc:hexane = 5:95 v/v%) was carried out to confirm reaction completion after the red reaction mixture was stirred at room temperature overnight. The reaction mixture was quenched by first adding a portion of a saturated solution of NH<sub>4</sub>Cl (20 mL), followed by adding a portion of water (200 mL). A yellow crude product was extracted with diethyl ether and then purified by column chromatography (silica, starting with 100% hexane, after fluorene separation with 10% EtOAc and 90% hexane) to give 9.0 g of yellow oil as the pure final product (70%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 7.26 ppm): 1.19, 1.20 (*t*-BuO, 9H, s), 1.06, 1.05, 1.02 (Me<sub>2</sub>C, 6H, s), 1.27 (CH<sub>2</sub>, 2H, m), 1.41 (CH<sub>2</sub>, 2H, m), 1.58 (CH<sub>2</sub>, 4H, m), 2.50, 2.46, 2.36 (Cp-CH<sub>2</sub>, 2H, t, <sup>3</sup>J<sub>H-H</sub> = 7 Hz), 3.36 (*t*-BuOCH<sub>2</sub>, 2H, d of t, <sup>3</sup>J<sub>H-H</sub> = 7 Hz), 6.53, 6.10, 6.00, 5.97, 5.69 (CpH, 5H, brs), 3.07 (methyleneCpH, 2H, brs), 4.14, 4.11, 4.10 (FluH, 1H, s), 7.70 (FluH, 2H, m), 7.33 (FluH, 2H, m), 7.23–7.10 (FluH, 4H, m).

#### 4.14. Isopropylidene[3-(6-*t*-butoxyhexyl)-cyclopentadienyl-fluorene-9-yl]-zirconocenedichloride, [(η<sup>5</sup>-C<sub>13</sub>H<sub>8</sub>)Me<sub>2</sub>C-(η<sup>5</sup>-(*t*-BuOC<sub>6</sub>H<sub>12</sub>C<sub>5</sub>H<sub>3</sub>))]ZrCl<sub>2</sub> (3a)

*n*-BuLi (1.6 M of hexane, 26.3 mL, 0.042 mol) was slowly added to a solution of [Me<sub>2</sub>C(FluH)(*t*-BuOC<sub>6</sub>H<sub>12</sub>CpH)] (10) (9.0 g, 0.021 mol) in THF (200 mL) at  $-78^{\circ}\text{C}$ . After stirring the red reaction mixture at room temperature for 5 h, the solvent was removed in vacuo. A crude red solid was washed with hexane ( $2 \times 50$  mL) to give 11.1 g of the dianion [Me<sub>2</sub>C(Flu)(*t*-BuOC<sub>6</sub>H<sub>12</sub>Cp)]Li<sub>2</sub> that is used for the next metallation (90%). The ligand solution of [Me<sub>2</sub>C(Flu)(*t*-BuOC<sub>6</sub>H<sub>12</sub>Cp)]Li<sub>2</sub> (2.5

g, 0.0042 mol) in pentane (50 mL) was added to the solution of  $ZrCl_4$  (0.98 g, 0.0042 mol) in pentane (50 mL) at  $-78^\circ C$ . The pentane was removed after stirring at room temperature for 12 h. The solid residue was dried and extracted into toluene (100 mL) by use of a frit. The pink solid was washed with 10 mL hexane to give 1.55 g of pure product (63%).  $^1H$  NMR ( $CDCl_3$ , 7.26 ppm): 1.16 (*t*-BuO, 9H, s), 2.35 ( $Me_2C$ , 3H, s), 2.40 ( $Me_2C$ , 3H, s), 1.46 ( $CH_2$ , 4H, m), 1.27 ( $CH_2$ , 4H, m), 1.20 ( $CH_2$ , 2H, m), 2.52 (Cp- $CH_2$ , 2H, m), 3.27 (*t*-BuOCH<sub>2</sub>, 2H, t,  $^3J_{H-H} = 7$  Hz), 5.43 (CpH, 1H, t,  $^3J_{H-H} = 3$  Hz), 5.67 (CpH, 1H, t,  $^3J_{H-H} = 3$  Hz), 6.01 (CpH, 1H, t,  $^3J_{H-H} = 3$  Hz), 8.15 (FluH, 2H, m), 7.80 (FluH, 2H, m), 7.54 (FluH, 2H, m), 7.26 (FluH, 2H, m).  $^{13}C$  NMR ( $CDCl_3$ , 77 ppm): 27.5 ( $Me_3CO$ , q,  $^1J_{C-H} = 124$  Hz), 15.3 ( $Me_2C$ , q,  $^1J_{C-H} = 124$  Hz), 40.4 ( $Me_3C$ , s), 25.9 ( $Me_2C$ , s), 68.1, 72.4, 78.8, 113.8, 122.6, 136.4, 142.0 (7C, s), 61.5 ( $Me_3COCH_2$ , t,  $^1J_{C-H} = 140$  Hz), 65.8 (CpCH<sub>2</sub>, t,  $^1J_{C-H} = 138$  Hz), 30.5, 29.7, 29.2, 27.6 (4C, t,  $^1J_{C-H} = 124$  Hz), 103.0, 103.1, 117.2, 128.9, 128.2, 125.3, 124.9, 124.8, 123.4, 123.2, 123.1 (FluC and CpC, 11C d,  $^1J_{C-H} = 171$  Hz,  $^3J_{C-H} = 10$  Hz). Analysis calculated for  $C_{31}H_{38}OZrCl_2$ : C, 63.24; H, 6.51. Found: C, 61.53; H, 6.40%.

#### 4.15. Chlorodimethyl-(9-fluorenyl)silane, $Me_2Si(FluH)Cl$ (11)

A solution of solid fluorenyllithium (1 Et<sub>2</sub>O bound : 9.64 g, 0.056 mol) in hexane (300 mL) was added to a solution of  $Me_2SiCl_2$  (16 mL, 0.13 mol) in hexane (100 mL) dropwise at  $-78^\circ C$  for 2 h. The reaction solvent was dried in vacuo after stirring at room temperature for 5 h. The solid residue was extracted with hexane (100 mL) to give a pale yellow solid.  $^1H$  NMR ( $C_6D_6$ , 7.15 ppm):  $-0.08$  ( $Me_2Si$ , 6H, s), 3.77 (FluH, 1H, s), 7.67 (FluH, 2H, d,  $^3J_{H-H} = 8$  Hz), 7.55 (FluH, 2H, d,  $^3J_{H-H} = 8$  Hz), 7.23 (FluH, 2H, t,  $^3J_{H-H} = 8$  Hz), 7.18 (FluH, 2H, t,  $^3J_{H-H} = 8$  Hz).

#### 4.16. *t*-Butoxyhexylcyclopentadienyl-(9-fluorenyl)dimethylsilane, $[(t-BuOC_6H_{12}CpH)Me_2Si(FluH)]$ (12)

*n*-BuLi (1.6 M of hexane, 10.2 mL, 0.016 mol) was added to a solution of  $[(t-BuOC_6H_{12})(CpH)]$  (3.64 g, 0.016 mol) in THF (30 mL) at  $-78^\circ C$  slowly. After stirring the red reaction mixture at room temperature for 4 h, the yellow solution turned into clear. The reaction solvent was removed in vacuo to give an oil product that was used for the next reaction without further purification. A solution of *t*-butoxyhexylcyclopentadienyllithium in THF (50 mL) was added dropwise to a solution of chlorodimethylfluorenylsilane (11) (4.14 g, 0.016 mol) in THF (50 mL) at room temperature. After stirring a yellow reaction mixture at room temperature for 4 h, the reaction solvent was removed in

vacuo. The solid residue was extracted with hexane (100 mL) and the volatiles were pumped off to give a yellow oil product (99%).  $^1H$  NMR ( $C_6D_6$ , 7.15 ppm): 1.09 (*t*-BuO, 9H, s),  $-0.09$ ,  $-0.13$  ( $Me_2Si$ , 6H, s), 1.25 ( $CH_2$ , 2H, m), 1.24 ( $CH_2$ , 2H, m), 1.41 ( $CH_2$ , 4H, m), 2.25 (CpCH<sub>2</sub>, 2H, m), 3.23 (*t*-BuOCH<sub>2</sub>, 2H, d of t,  $^3J_{H-H} = 7$  Hz), 6.35, 6.05, 5.70 (CpH, 5H, m, brs), 3.05 (methyleneCpH, 2H, brs), 4.20, 4.00, 3.85 (FluH, 1H, s), 7.80 (FluH, 2H, m), 7.45 (FluH, 2H, m), 7.29–7.20 (FluH, 4H, m).

#### 4.17. Dimethylsilyl[3-(6-*t*-butoxyhexyl)-cyclopentadienyl-fluorene-9-yl]-zirconocenedichloride, $[(\eta^5-C_{13}H_8)-SiMe_2-(\eta^5-(t-BuOC_6H_{12}C_5H_3))]ZrCl_2$ (4a)

*n*-BuLi (1.6 M of hexane, 20 mL, 0.032 mol) was added slowly to a solution of  $[Me_2Si(FluH)(t-BuOC_6H_{12}CpH)]$  (7.12 g, 0.016 mol) in diethyl ether (100 mL) at  $-78^\circ C$ . After stirring the red reaction mixture at room temperature for 12 h, the volatiles were removed in vacuo to give a sticky red solid. The ligand solution of  $[Me_2Si(Flu)(t-BuOC_6H_{12}Cp)]Li_2$  (7.31 g, 0.016 mol) in diethyl ether (50 mL) was added to the solution of  $ZrCl_4$  (3.73 g, 0.016 mol) in diethyl ether (30 mL) at  $-78^\circ C$ . The reaction solution was filtered after stirring at room temperature for 5 h and the solid residue was extracted with  $CH_2Cl_2$  (50 mL) using a frit. The orange solid was washed with 10 mL hexane to give 2.4 g of pure product (25%).  $^1H$  NMR ( $CDCl_3$ , 7.26 ppm): 1.16 (*t*-BuO, 9H, s), 1.11 ( $Me_2Si$ , 3H, s), 1.13 ( $Me_2Si$ , 3H, s), 1.43 ( $CH_2$ , 4H, m), 1.25 ( $CH_2$ , 4H, m), 2.45 (Cp- $CH_2$ , 2H, m), 3.26 (*t*-BuOCH<sub>2</sub>, 2H, t,  $^3J_{H-H} = 7$  Hz), 5.41 (CpH, 1H, t,  $^3J_{H-H} = 3$  Hz), 5.70 (CpH, 1H, t,  $^3J_{H-H} = 3$  Hz), 6.28 (CpH, 1H, t,  $^3J_{H-H} = 3$  Hz), 8.13 (FluH, 2H, m), 7.67–7.49 (FluH, 4H, m), 7.29 (FluH, 2H, m).  $^{13}C$  NMR ( $CDCl_3$ , 77 ppm): 27.5 ( $Me_3CO$ , q,  $^1J_{C-H} = 125$  Hz),  $-3.3$  ( $Me_2Si$ , q,  $^1J_{C-H} = 121$  Hz), 27.6, 66.3, 72.4, 102.6, 113.8, 128.8, 129.1, 141.9 (9C, s), 61.5 ( $Me_3COCH_2$ , t,  $^1J_{C-H} = 141$  Hz), 30.5, 30.2, 30.0, 29.2, 25.9 (5C, t,  $^1J_{C-H} = 124$  Hz), 111.6, 112.0, 119.7, 123.8, 123.9, 125.0, 126.3, 126.5, 128.0, 128.1, 128.7 (FluC and CpC, 11C d,  $^1J_{C-H} = 161$  Hz,  $^3J_{C-H} = 10$  Hz). Analysis calculated for  $C_{30}H_{38}OSiZrCl_2$ : C, 59.57; H, 6.33. Found: C, 59.32; H, 6.09%.

#### 4.18. General procedure for the polymerization of ethylene

A zirconocene complex (3  $\mu$ mol) in toluene was placed in a 500 mL glass reactor that is equipped with a mechanical stirrer and pressure controller. After activating the precatalyst by MAO ( $Zr/Al = 1:1000$ , 1.11 mL, 3.0 mmol Al, 8.2 wt% in toluene) dry toluene (200 mL) was added to the reactor. The reactor was placed in a  $60^\circ C$  oil bath for 2 min while it was degassed and saturated with ethylene for 3 min without agitation. The polymerization time was measured at the moment the



stirring started. Ethylene feeding was constant (30 psi) during the polymerization. The polymerization was terminated by cutting ethylene feeding and adding methanol. Additionally the polymer solution was quenched by the addition of a portion of 1 N HCl solution and was then filtered, washed with hexane and acetone, and dried in vacuo.

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