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# Syntheses of methylene-bridged *ansa*-zirconocene complexes and copolymerization studies of ethylene and norbornene

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**Abstract**

Methylene-bridged *ansa*-metallocene complexes bearing substituents on the cyclopentadienyl (Cp) and fluorenyl (Flu) moieties, namely methylene[9-(2,7-di-*tert*-butyl)fluorenyl(2-(1,3-dimethylcyclopentadienyl))]zirconium dichloride (**1a**) and its analogue, methylene[(9-(2,7-di-*tert*-butyl)fluorenyl(2-(1-methyl-3-phenyl)cyclopentadienyl))]zirconium dichloride (**2a**), have been prepared from (2,7-di-*tert*-butyl)-9-prop-2-ynyl-9H-fluorene (**2**). This procedure includes the use of 3-bromo-1-propyne which affords the methylene bridging unit by way of an intermolecular Pauson–Khand reaction in which norbornadiene and a pendant alkyne cyclize to form a ring that later becomes a substituted cyclopentadienyl group. Ethylene–norbornene (E–N) copolymerization was then carried out using these new complexes (**1a** and **1b**) in the presence of methylaluminoxane (MAO) as a cocatalyst; these activities can be compared to that of isopropylene[9-fluorenyl-cyclopentadienyl]zirconium dichloride (**3a**). The activity of catalyst **1a** was comparable to that of **3a** but much higher than that of **2a**. In addition, **1a** shows higher norbornene insertion performance, and gives an E–N copolymer with a higher glass transition temperature ($T_g$) than **2a** under identical conditions; both **1a** and **2a** give a lower $T_g$ polymer than **3a** does.

*Keywords:* *ansa*-Zirconocene; Ethylene–norbornene copolymerization; Glass transition temperature ($T_g$); MAO

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## 1. Introduction

Since the discovery of metallocene/methylaluminoxane (MAO) olefin polymerization catalysis by Kaminsky and Sinn [1], tremendous efforts have been made to search for novel transition metal catalysts through the use of appropriate ligand systems [2,3]. In general, the metallocene ligand geometry and central metal electronics allow for control of: (i) catalytic activity, (ii) olefin monomer and/or comonomer response, (iii) tacticity and (iv) polymer molecular weight [4,5]. To date, ethylene copolymerization by rationally designed *ansa*-metallocenes has been demonstrated for substrates including α-olefins, propene, hexene and various cycloolefins [6].

In particular, ethylene–norbornene (E–N) copolymers constitute a major commercial family of cyclic olefin copolymers (COCs), possessing applied mechanical and optical properties [7]. The novel properties of E–N copolymers may be used in place of polycarbonate (PC), acronitrile–butadiene–styrene (ABS) and glass substrates. E–N copolymers have also been of particular interest during last decade since they have been produced by metallocene catalysts [8]. Thus, the design of new ligands in metallocene catalysis has led to polymerization activity control studies, the acceptance of two different comonomers, and the stereoregularity of COCs to modulate the

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polymer's physical properties [9,10]. Recently, Lee et al. have reported the methylene-bridged *ansa*-zirconocene complex, [H$_2$C(Me$_2$C$_5$H$_2$)$_2$]ZrCl$_2$, bearing methyls adjacent to the bridge-head carbon. This derivative possesses exceptional E–N copolymerization activity [11] and the electronic effect can be tuned through substitution, and steric hindrance can be minimized to readily accept bulky substrates such as norbornene. Since the modification of ligands were limited to only Cp and four methyls on the carbons adjacent to the bridge-head carbon groups in the complex [H$_2$C(Me$_2$C$_5$H$_2$)$_2$]ZrCl$_2$, we are interested in expanding our scope toward designing heavier ligands, such as those involving indenyl or fluorenyl groups. Specifically, in the *ansa*-metallocene complexes bearing a Flu group, the bulkier substituents at the 2- and 7-position have shown to allow for higher olefin polymerization activity and higher molecular weight polymers, [12] which is less common and more challenging.

In this work, we report the syntheses of two novel methylene-bridged zirconocenes, methylene[9-(2,7-di-*tert*-butyl)fluorenyl(2-(1,3-dimethylcyclopentadienyl))] zirconium dichloride (**1a**) and methylene[(9-(2,7-di-*tert*-butyl)fluorenyl(2-(1-methyl-3-phenyl)cyclopentadienyl))] zirconium dichloride (**2a**). Their catalytic reactivity toward ethylene–norbornene copolymerization is also compared to the parent zirconocene **3a** [13].

## 2. Results and discussion

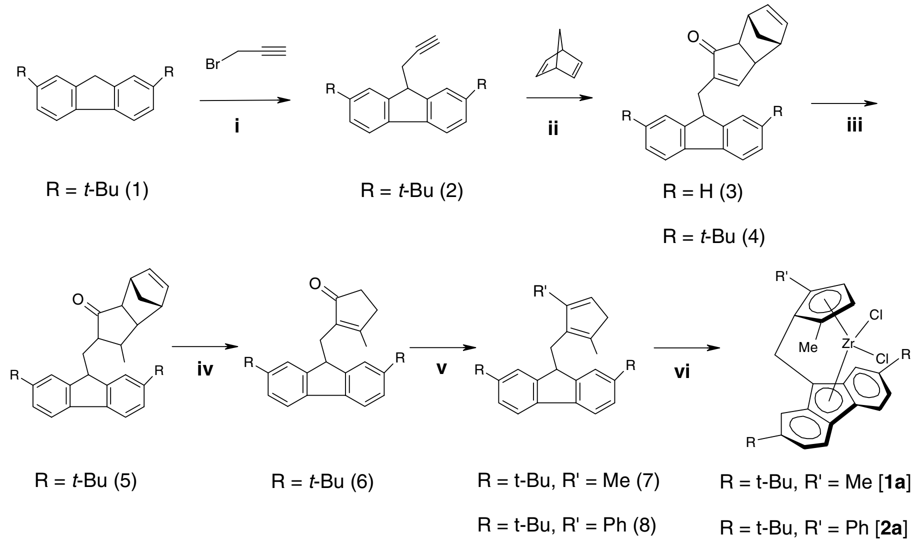
### 2.1. Preparation and characterization of complexes 1a and 2a

The new metallocene complexes for E–N copolymerization were synthesized according to the reactions illustrated in Scheme 1. While an *ansa* bridge carbon unit is commonly synthetically incorporated via a fulvene unit, here the methylene-bridge unit was brought about by an intermolecular Pauson–Khand reaction at the triple bond of substrate **2**, which later affords the accompanying substituted cyclopentadiene group.

Deprotonation of 2,7-di-*tert*-butylfluorene (**1**) with *n*-BuLi gave the corresponding mono-anion compound which when treated with propargyl bromide gave **2** possessing a pendant alkyne group, in high yield (95%). The tricyclic compound **3** was then generated by an intermolecular Pauson–Khand reaction with norbornadiene requiring a catalytic amount of Co$_2$(CO)$_8$ [14]. Addition of Me$_2$CuLi to compound **4** produced the 1,4-addition product **5**. Interestingly, the addition of Me$_2$CuLi to the unsubstituted analog (**3**), did not give the 1,4-addition product. It is believed that compound **3** has poor solubility at −10 °C in diethyl ether and thus does not undergo reaction with the cuprate reagent [15], whereas; the presence of the *tert*-butyl groups in **4** improves its solubility, giving **5** in high yield (91%).

The retro-Diels–Alder reaction of **5** was performed at 300 °C to give compound **6**. This condition is milder than that for the retro-Diels–Alder synthesis of [H$_2$C(Me$_2$C$_5$H$_2$)$_2$]ZrCl$_2$ (420 °C), starting from 1,4-pentadiyne [11]. The 1,2-addition of MeLi and PhLi followed by dehydration during aqueous HCl workup, gave the desired cyclopentadiene compound **7** and **8**, respectively, in good yield.

The deprotonation of **7** and **8** with *n*-BuLi gave the corresponding dianions which were then treated with ZrCl$_4$ in hexane to cleanly afford the *ansa*-zirconocene complexes **1a** and **2a** as light red and bright red solids, respectively. The $^1$H NMR spectrum of **2a** indicated a molecular symmetry change from $C_S$ in complex **1a** to



Scheme 1. Synthesis of complexes **1a** and **2a**. (i) *n*-BuLi; (ii) CO/CO$_2$(CO)$_8$; (iii) Me$_2$CuL; (iv) 300 °C; (v) MeLi or PhLi, then aq. HCl; (vi) *n*-BuLi and ZrCl$_4$.

$C_1$ with the inclusion of a Cp ring phenyl substituent. Two doublets are present in the spectrum at $\delta$ 6.38 and 6.33 ($^3J_{\text{H-H}}=4$ Hz) in **2a**, compared to the singlet at $\delta$ 6.21 in **1a** assigned to the Cp-ring hydrogens. Also, two doublets at $\delta$ 5.36 and 5.08 ($^2J_{\text{H-H}}=15$ Hz) are present in **2a**, compared to a singlet at $\delta$ 4.89 for **1a**, assigned to the *ansa*-bridge hydrogens. Lastly two singlets at $\delta$ 1.37 and 0.90 are present for **2a**, compared to the singlet at $\delta$ 1.35 in **1a** assigned to the *tert*-butyl substituent on the Flu group.

### 2.2. Copolymerization of ethylene and norbornene with **1a** and **2a** and MAO

Catalysts **1a** and **2a** were used in combination with methylaluminoxane (MAO) for ethylene–norbornene copolymerization [16] and compared to isopropylene[9-fluorenylcyclopentadienyl]zirconium dichloride [**3a**] activity under identical conditions [17]. The results of E–N copolymerization are summarized in Table 1. A comparative reactivity of each catalyst is presented in Fig. 1, depending on ethylene pressure. The activity of catalysts increased as the ethylene pressure increases from 30 to 100 psi for all catalysts (**1a**–**3a**) [18]. The activity of catalyst **2a** was very poor compared to its derivative catalyst **1a**. The replacement of the α-methyl substituent with a phenyl group on the Cp ring in compound **2a** seems to give tremendous hindrance to introducing an olefin monomer into the active zirconium center although electronic stabilization of active cation–anion complex by phenyl group is expected during polymerization. Moreover the preactivation of catalyst **2a** for copolymerization did not increase the activity. It is probable that the phenyl group causes the inhibition of the activation of catalyst by MAO.

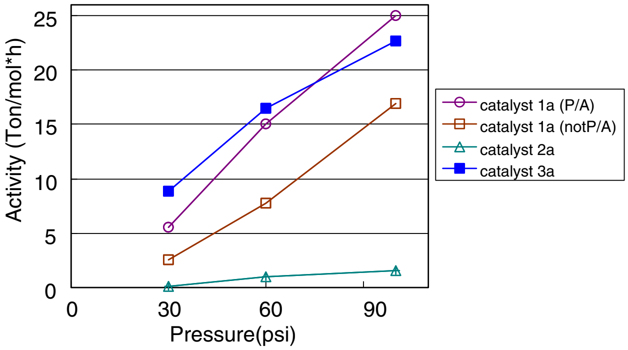


Fig. 1. Catalyst activity for the E–N copolymerization at different ethylene pressures (70 °C).

It is noted that all catalysts show much higher increasing activities as increasing ethylene pressure, whether the catalyst was preactivated or not. Specifically, when the copolymerization was carried out after adding active species by MAO preactivation of catalyst **1a**, resulted in nearly twice as high an activity as that without preactivation (Table 1, entries 1–6). E–N copolymerization activity of catalyst **3a**, however, was not affected by the preactivation of the catalyst at all. Thus, somehow longer time is needed for catalyst **1a** to become an activated cation–anion complex to initiate polymerization, compared to catalyst **3a**. Apparently, the steric hindrance imparted by the Cp and Flu ring substituents affects the accessibility of the approaching cocatalyst MAO; thus it is believed that the preactivation of catalyst *before* starting copolymerization is what resulted in the different activities.

The glass transition temperatures ($T_g$s) of the resulting copolymers as a function of ethylene pressure are presented for each catalyst in Fig. 2. The copolymer

Table 1
Ethylene–norbornene copolymerization[a] results

| Entry | Catalyst | Pressure (psi) | Time (min) | Yield (g)[b] | Activity[c] | $T_g$ (°C) | $M_w$ | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|---|
| 1 | **1a** | 30 | 20 | 5.5 | 8.33 | 185 | 138,000 | 1.8 |
| 2 | **1a** | 60 | 20 | 15.0 | 22.73 | 171 | 124,000 | 1.8 |
| 3 | **1a** | 100 | 20 | 25.0 | 37.88 | 158 | 98,000 | 1.5 |
| 4[d] | **1a** | 30 | 20 | 2.5 | 3.78 | 186 | 139,000 | 2.1 |
| 5[d] | **1a** | 60 | 20 | 7.7 | 11.67 | 164 | 117,000 | 1.6 |
| 6[d] | **1a** | 100 | 20 | 16.9 | 25.6 | 145 | 84,000 | 1.8 |
| 7[d] | **1a** | 60 | 40 | 16 | 12.1 | 157 | 116,000 | 2.0 |
| 8[d] | **1a** | 60 | 60 | 25 | 12.5 | 170 | 114,000 | 2.0 |
| 9 | **2a** | 30 | 20 | 0.1 | 0.15 | – | – | – |
| 10 | **2a** | 60 | 20 | 1.0 | 1.52 | 142 | 249,000 | 1.9 |
| 11 | **2a** | 100 | 20 | 1.5 | 2.27 | 122 | 270,000 | 2.1 |
| 12 | **3a** | 30 | 20 | 8.9 | 13.5 | 204 | 312,000 | 2.3 |
| 13 | **3a** | 60 | 20 | 16.5 | 25 | 189 | 224,000 | 2.1 |
| 14 | **3a** | 100 | 20 | 22.7 | 34.4 | 188 | 256 | 1.9 |

[a] Polymerization conditions: zirconocene 2 μmol, Al/Zr = 2000, toluene 150 mL (56 wt% norbornene), $T_p = 70$ °C.

[b] Yield is defined as the weight of copolymer obtained.

[c] Activity in $10^3$ kg COC/mol of Zr h.

[d] Preactivation of catalyst with MAO was not conducted.

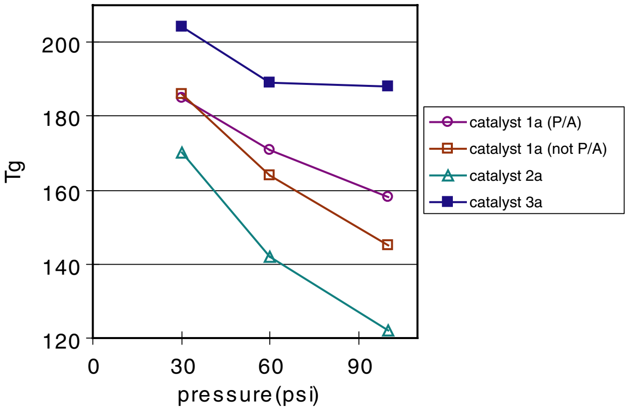


Fig. 2. Glass transition temperature ($T_g$) of E–N copolymers produced at different ethylene pressure (70 °C).

$T_g$ appears to have a linear dependence on the mole ratio of the fed norbornene over ethylene in the copolymerization media. These data suggest that as the ethylene pressure in reaction media increases and the norbornene content in the copolymer decreases, $T_g$ of the resulting copolymer decreases [19]. For **1a**, the $T_g$ of copolymer obtained at the same reaction conditions was lower by 18–36 °C than that for **3a**. The $T_g$ of copolymer by the catalyst **2a** shows a significantly lower $T_g$ by 15–30 °C than that for complex **1a**. It is possible that catalyst **3a** has a higher ability for norbornene incorporation, on steric grounds, owing to the absence of ring substituents. It follows that complex **2a**, possessing a Cp-phenyl substituent shows a much larger steric influence on the incoming bulky norbornene; thus, the final percentage of polymeric norbornene would be low. Also, the molecular weight of copolymers ($M_w$) for the each catalyst decreases with increasing ethylene pressure. This suggests that the higher ethylene concentration provides more of a chance for chain transfer by β-hydride elimination compared to the propagation reaction [20]. In the E–N copolymer, only bound ethylene undergoes β-hydride elimination to be chain transferred (or by extra MAO) which dictates the $M_w$ value. If propagation is fast or dominates over chain transfer then a higher $M_w$ polymer is obtained. Interestingly, the molecular weight of copolymers by catalyst **1a** was much lower than those for catalyst **2a** and **3a**, indicating that Cp-methyl substitution may facilitate chain transfer better than Flu-*tert*-butyl substitution.

## 3. Conclusion

In summary, we have synthesized two new *ansa*-zirconocene dichlorides with substituents α- to the *ansa*-bridge to investigate their E–N copolymerization in the presence of excess MAO. The precatalyst **1a** bearing methyl substituents showed higher copolymerization activity than for precatalyst **3a**. However, owing primarily to substituents effects in norbornene, monomer acceptance is believed to decrease in the order **2a** < **1a** < **3a**, judging from the $T_g$ of the resulting polymers. In addition, it was found that the preactivation of catalysts beforehand was crucial to maximize the catalytic activity for E–N copolymerization, depending on electronics and sterics imparted to the central metal by the *ansa*-metallocene ligand.

## 4. Experimental

### 4.1. General techniques and reagents

All manipulations were performed under an inert atmosphere using a combination of glove box, high vacuum, and Schlenk techniques. All solvents were purchased from Aldrich and purified by distillation over Na/K alloys with benzophenone ketyl. All available reagents, including fluorene and 2,7-di-*tert*-butylfluorene, were purchased commercially and used as received unless otherwise noted in the experimental procedure. Compound **3a** which can be prepared by a literature method [13] was purchased here for polymerization testing from the Boulder Scientific Company. The cocatalyst, 10 wt% methylaluminoxane (MAO) in toluene, purchased from Akzo. The comonomer, norbornene (bicyclo[2,2,1]hept-2-ene), was obtained from Aldrich with a purity of 99% and was further purified prior to use. Ethylene (99.9%) was purified in columns containing molecular sieves, CuO, and $Al_2O_3$. $^1H$ and $^{13}C$ NMR spectra were obtained on a Bruker ARX-300 spectrometer. $^1H$ and $^{13}C$ NMR chemical shifts are reported in ppm, relative to $SiMe_4$ ($\delta = 0$) and referenced internally relative to the protio solvent impurity ($\delta = 7.26$ and $\delta = 77.0$, respectively for $CDCl_3$). All coupling constants are reported in hertz. Elemental analyses were carried out on a Perkin–Elmer 2400 CHN microanalyzer. IR spectra were obtained on a Bio-Rad FTA-60A instrument. Values for the glass transition temperature ($T_g$) were measured using a TA instrument DSC2010. The sample was first heated to 300 °C, then cooled to 30 °C (20 °C/min), and then reheated to 250 °C or 300 °C (20 °C/min). The data used in this work was taken from the second heating. The average molecular weight ($M_w$) and the molecular weight distribution (MWD) of E–N copolymers were measured by gel permeation chromatography (GPC), waters 150 CV equipped with three Waters chromatographic columns. Chloroform solvent was used with a flow rate 1 mL/min at 25 °C. Polystyrene (PS) standards with a narrow molecular weight distribution were used for the calibration of molecular weights versus retention time of the column set.

### *4.2. 2,7-Di-tert-butyl-9-prop-2-ynyl-9H-fluorene (**1**)*

To a Schlenk flask containing 2,7-di-*tert*-butylfluorene (**1**) (21.2 g, 76.13 mmol) in THF (90.0 mL) *n*-BuLi (2.5 M in hexane solution, 36.54 mL, 91.36 mmol) was slowly added at −78 °C. The solution was warmed to room temperature and stirred for 4 h, before being cooled again to −78 °C. Propargyl bromide (8.48 ml, 76.13 mmol, 80% in toluene solution) was added dropwise to the solution. The resulting solution was allowed to warm to room temperature and stirred at room temperature for 5 h before it was poured into cold water (200 mL). Diethylether (300 mL) was then added and the mixture was poured into a separatory funnel. The aqueous layer was removed and the organic portions were combined and dried over anhydrous $MgSO_4$. After removal of the solvent by rotary evaporation, the residue was purified by silica gel column chromatography using hexane and ethyl acetate as the eluents (20:1 v/v), giving 23 g of product **2** (95%). $^1$H NMR ($CDCl_3$): $\delta$ 7.78 (s, 2H, Ph), 7.64 (d, 2H, Ph, $J=8$ Hz), 7.42 (d, 2H, Ph, $J=8$ Hz), 4.02 (t, 1H, $J=7$ Hz), 2.68 (dod, 2H, $CH_2$, $J=7$, 3 Hz), 2.17 (s, 1H, CH) 1.40 (s, 18H, *t*-Bu). $^{13}$C NMR ($CDCl_3$): $\delta$ 149.8, 146.1, 138.1, 124.5, 121.6, 119.0, 83.4, 69.5, 45.8, 34.9, 31.6, 23.7. Anal. Calc. for $C_{24}H_{28}$: C, 91.08; H, 8.92. Found: C, 91.14; H, 8.86%.

### *4.3. 2-(9H-Fluoren-9-ylmethyl)-3a,4,7,7a-tetrahydro-4,7-methano-inden-1-one (**3**)*

Compound **3** was synthesized from 9-prop-2-ynyl-9H-fluorene according to a literature preparation [c]. The crude product was purified by silica gel column chromatography with hexane and ethyl acetate as the eluents (10:1 v/v). After rotatory evaporation, the yield was 73%. $^1$H NMR ($CDCl_3$): $\delta$ 7.75–7.60 (m, 2H, Ph), 7.40–7.50 (m, 2H, Ph), 7.40–7.15 (m, 4H, Ph), 7.32 (d, 1H, Ph, $J=8$ Hz), 6.45–6.38 (m, 1H), 6.15–5.95 (m, 2H), 4.21 (t, 1H, $J=5$ Hz), 3.00–2.80 (m, 2H), 2.68 (s, 1H), 2.41 (s, 1H), 2.26 (s, 1H), 2.07 (d, 1H, $J=5$ Hz), 1.01 (d, 1H, $J=9$ Hz), 0.39 (d, 1H, $J=9$ Hz).

### *4.4. 2-(2,7-Di-tert-butyl-9H-fluoren-9-ylmethyl)-3a,4,7,7a-tetrahydro-4,7-methano-inden-1-one (**4**)*

Compound **4** was synthesized from 9-propynyl-(2,7-di-*tert*-butyl)fluorene (**2**) according to a literature procedure [c]. The crude product was purified by silica gel column chromatography with hexane and ethyl acetate as the eluents (10:1 v/v). After rotatory evaporation, the yield was 78%. $^1$H NMR ($CDCl_3$): $\delta$ 7.61 (d, 1H, Ph, $J=8$ Hz), 7.56 (d, 1H, Ph, $J=8$ Hz), 7.55 (s, 1H, Ph), 7.53 (s, 1H, Ph), 7.40 (d, 1H, Ph, $J=8$ Hz), 7.32 (d, 1H, Ph, $J=8$ Hz), 6.45–6.38 (m, 1H), 6.15–6.03 (m, 2H), 4.16 (t, 1H, $J=6$ Hz), 3.06 (dd, 1H, $J=15$, 6 Hz), 2.89 (dd, 1H, $J=15$, 5 Hz), 2.68 (s, 1H), 2.44 (s, 1H), 2.27 (s, 1H), 2.12 (d, 1H, $J=5$ Hz), 1.39 (s, 9H, *t*-Bu), 1.36 (s, 9H, *t*-Bu), 0.96 (d, 1H, $J=9$ Hz), 0.25 (d, 1H, $J=9$ Hz). Anal. Calc. for $C_{32}H_{36}O$: C, 88.03; H, 8.31. Found: C, 88.37; H, 8.41%.

### *4.5. 2-(2,7-Di-tert-butyl-9H-fluoren-9-ylmethyl)-3-methyl-2,3,3a,4,7,7a-hexahydro-4,7-methano-inden-1-one (**5**)*

To a Schlenk flask containing a slurry of CuI (11.4 g, 60 mmol) in $Et_2O$ (150 mL), a portion of MeLi (1.4 M in $Et_2O$ solution, 85.7 mL, 90 mmol) was added at −20 °C. The solution was stirred at −20 °C for 30 min and cooled to −78 °C. The solid compound **4** (9.5 g, 21.8 mmol) was added to the solution in one portion. The resulting solution was allowed to warm to room temperature. The solution was stirred at room temperature for 12 h and was then poured into a large volume of cold water (200 mL). The mixture was filtered over celite and the organic layer was separated. The aqueous solution was re-extracted with $Et_2O$ (50 mL). The organic solutions were then combined, dried over anhydrous $MgSO_4$, filtered and dried in vacuo. Purification of the crude product was performed with silica gel column chromatography with hexane and ethyl acetate as eluents (10:1 v/v) to give 9.0 g of pure white solid (91%). $^1$H NMR ($CDCl_3$): $\delta$ 7.65–7.55 (m, 4H, Ph), 7.45–7.35 (m, 2H, Ph), 6.10–6.20 (m, 2H), 4.21 (t, 1H, $J=6$ Hz), 3.15 (s, 1H), 2.66 (s, 1H), 2.65–2.55 (m, 1H), 2.26 (d, 1H, $J=9$ Hz), 2.12–2.03 (m, 1H), 1.85–1.65 (m, 2H), 1.41 (s, 18H, *t*-Bu), 1.35–1.20 (m, 2H), 1.06 (d, 1H, $J=9$ Hz), 0.92 (d, 3H, $CH_3$, $J=6$ Hz). $^{13}$C NMR ($CDCl_3$): 217.3 (carbonyl), 149.5, 149.4, 147.3, 146.9, 138.4, 138.2, 137.3, 124.1, 123.9, 122.1, 121.8, 118.9, 118.8, 57.9, 53.9, 48.5, 46.4, 45.8, 44.8, 44.2, 41.4, 34.8, 31.6, 26.9, 20.5. Anal. Calc. for $C_{33}H_{40}O$: C, 87.56; H, 8.91. Found: C, 87.67; H, 8.63%. IR (cm$^{-1}$): 3058, 2959, 1733(CO), 1490, 1483, 1380, 1325, 1260, 797, 710, 619.

### *4.6. 2-(2,7-Di-tert-butyl-9H-fluoren-9-ylmethyl)-3-methyl-cyclopent-2-enone (**6**)*

A sample of compound **5** (3.5 g, 7.7 mmol) was placed in a quartz tube that was connected via a flexible tube to a Schlenk flask. After the system was purged with nitrogen, the quartz tube was placed in a furnace whose temperature had been set at 300 °C and the Schlenk flask was immersed in a liquid nitrogen bath. After 10 min, the quartz tube was removed from the furnace and was allowed to cool to room temperature. Purification of the crude product was carried out by silica gel column chromatography, eluting with hexane and ethyl acetate (4:1 v/v) to give 1.8 g of product (60%). $^1$H NMR ($CDCl_3$): $\delta$ 7.63 (d, 2H, Ph, $J=8$ Hz), 7.41–7.35 (m, 4H, Ph), 4.22 (t, 1H, $J=8$ Hz), 2.5–2.6 (m, 4H), 2.63 (d, 2H, $J=8$ Hz), 1.68 (s, 3H, $CH_3$), 1.36 (s, 18H, *t*-Bu). $^{13}$C NMR ($CDCl_3$): $\delta$ 209.5 (carbonyl), 172.2, 149.6, 147.2, 138.9, 138.1, 124.0, 121.6, 119.0, 44.9, 34.8, 34.5, 31.9, 31.6, 28.8, 17.5. Anal. Calc. for $C_{28}H_{34}O$: C, 87.00; H, 8.87. Found: C, 87.08; H, 9.06%. IR ($cm^{-1}$): 2957, 1695 (CO), 1647, 1476, 1398, 1375, 1258, 1171, 911, 820, 731, 621.

### *4.7. 2,7-Di-tert-butyl-9-(2,5-dimethyl-cyclopentadienyl-methyl)-9H- fluorene (7)*

To a Schlenk flask containing complex **6** (5 g, 12.9 mmol) in $Et_2O$ (50 mL) was added MeLi (1.5 M in $Et_2O$, 13.86 mL, 19.4 mmol) at −78 °C. The solution was allowed to warm to room temperature. After the solution was stirred for 20 h, water (20 mL) was slowly added. The reaction solvent was removed by way of rotary evaporation. Ethyl acetate (150 mL) was then added to the residue and the mixture was poured into a separatory funnel. The aqueous layer was removed and a 2 N HCl solution (150 mL) was added. The contents of the separatory funnel were vigorously shaken for 2 min, the aqueous layer was removed, and the organic layer was washed with concentrated $NaHCO_3$ (30 mL). The organic layer was collected and dried over anhydrous $MgSO_4$. After removal of the solvent by rotary evaporation, the residue was purified by silica gel column chromatography, eluting with hexane to give **7** (3.57 g, 72%). $^1H$ NMR ($CDCl_3$): $\delta$ 7.71 (d, 2H, Ph, $J=8$ Hz), 7.45 (d, 2H, Ph, $J=8$ Hz), 7.40 (s, 2H, Ph), 6.05 (s, 1H), 4.08 (t, 1H, $J=9$ Hz), 3.05–2.95 (m, 2H), 2.76 (d, 2H, $J=9$ Hz), 2.01 (s, 3H, $CH_3$), 1.91 (s, 3H, $CH_3$), 1.44 (s, 18 H, *t*-Bu). $^{13}C$ NMR ($CDCl_3$): $\delta$ 149.3, 147.3, 144.0, 139.2, 138.7, 138.1, 124.0, 121.6, 118.9, 46.7, 44.0, 34.8, 34.5, 31.6, 30.8, 14.8, 14.2. Anal. Calc. for $C_{29}H_{36}$: C, 90.57; H, 9.43. Found: C, 90.86; H, 9.14%. IR ($cm^{-1}$): 2957, 1695 (CO), 1647, 1476, 1398, 1375, 1258, 1171, 911, 820, 731, 621.

### *4.8. 2,7-Di-tert-butyl-9-(2-methyl-5-phenyl-cyclopentadienylmethyl)-9H-fluorene (8)*

The general procedure in Section 4.7 for preparing **7** was followed in preparing compound **8** here. Product **8** was obtained purely by way of silica gel column chromatography, eluting with hexane to give 3.72 g of product (68%). $^1H$ NMR ($CDCl_3$): $\delta$ 7.64 (d, 2H, Ph, $J=8$ Hz), 7.37 (d, 2H, Ph, $J=8$ Hz), 7.32 (s, 2H, Ph), 7.25–7.15 (m, 5H, Ph), 6.21 (s, 1H), 4.15 (t, 1H, $J=8$ Hz), 3.45–3.35 (m, 2H), 2.94 (d, 2H, $J=8$ Hz), 1.97 (s, 3H, $CH_3$), 1.3 (s, 18H, *t*-Bu). $^{13}C$ NMR ($CDCl_3$): $\delta$ 149.4, 147.1, 145.0, 142.1, 141.2, 138.1, 128.2, 127.8, 127.5, 126.6, 126.0, 124.0, 121.6, 118.9, 46.1, 43.0, 34.8, 31.5, 15.1.

### *4.9. Methylene[(9-(2,7-di-tert-butyl)fluorenyl-2-(1,3-dimethyl)cyclopentadienyl)] zirconium dichloride (1a)*

To a stirred solution of **7** (0.8 g, 2.08 mmol) in cold THF (15 mL, −30 °C), *n*-BuLi (2.5 M in hexane, 1.83 mL, 4.58 mmol) was added in a dropwise fashion. After the solution was stirred at room temperature for 12 hours, the solvent was removed in vacuo and the residue was washed with pentane (2×30 mL) and dried. The dilithium salt solution was added to $ZrCl_4$ (0.485 g, 2.08 mmol) in *n*-hexane (30 mL) and the mixture was stirred for 12 h. The solvent was decanted and the product was extracted with cyclohexane (ca. 40 mL) to give 0.6 g of pure product (**1a**) (47%). $^1H$ NMR ($CDCl_3$): $\delta$ 7.88 (d, 2H, Ph, $J=8$ Hz), 7.59 (d, 2H, Ph, $J=8$ Hz) 7.55 (s, 2H, Ph), 6.21 (s, 2H), 4.89 (s, 2H, $CH_2$), 2.21 (s, 6H, $CH_3$), 1.35 (s, 18H, *t*-Bu). $^{13}C$ NMR ($CDCl_3$): $\delta$ 125.4, 124.3, 124.1, 122.1, 121.8, 120.6, 118.7, 107.3, 95.7, 69.6, 34.8, 30.9, 21.0, 17.5. Anal. Calc. for $C_{29}H_{34}ZrCl_2$: C, 63.95; H, 6.29. Found: C, 64.41; H, 6.77%.

### *4.10. Methylene[(9-(2,7-di-tert-butyl)fluorenyl)(2-(1-methyl)(3-phenyl)cyclopentadienyl)]zirconium dichloride (2a)*

The general procedure for preparing **2a** is the same as preparing complex **1a** in Section 4.9, with a corresponding yield of 68%. $^1H$ NMR ($CDCl_3$): $\delta$ 7.86 (d, 2H, Flu, $J=9$ Hz), 7.6–7.55 (m, 4H, Flu 2H and Ph 2H), 7.43 (d, 2H, Flu, $J=9$ Hz), 7.40–7.28 (m, 2H, Ph), 6.49 (s, 1H, Ph), 6.38 (d, 1H, Cp, $J=4$ Hz), 6.33 (d, 1H, Cp, $J=4$ Hz), 5.36 (d, 1H, $CH_2$, $J=15$ Hz), 5.08 (d, 1H, $CH_2$, $J=15$ Hz), 2.32 (s, 3H, $CH_3$), 1.37 (s, 9H, *t*-Bu), 0.9 (s, 9H, *t*-Bu). $^{13}C$ NMR ($CDCl_3$): $\delta$ 150.1, 136.4, 129.5, 128.5, 127.9, 127.5, 125.7, 125.4, 124.9, 124.8, 124.7, 124.4, 124.0, 123.6, 122.2, 121.0, 120.8, 120.7, 119.1, 118.6, 93.7, 71.4, 35.3, 31.6, 30.9, 30.0, 22.1, 17.9. Anal. Calc. for $C_{34}H_{36}ZrCl_2$: C, 67.30; H, 5.98. Found: C, 67.71; H, 6.18%.

### *4.11. General procedure for the copolymerization of ethylene–norbornene*

Ethylene–norbornene copolymerization was carried out using a 500 mL jacketed stainless steel reactor, equipped with a mechanical stirrer. All manipulations were carried out in an inert atmosphere using a standard Schlenk technique or a VAC drybox. The norbornene was dissolved in toluene to obtain 150 mL of a 56% (by weight) solution. The solution was passed through the purification column and injected into the reactor. After the reactor temperature was stabilized, the MAO-toluene solution (Al/Zr = 2000, 2.0 mL, 2.0 mmol, 8.2 wt% in toluene) was injected into the reactor and the reaction mixture was stirred for 15 min. The catalyst ($2\times10^{-6}$ mol/L) was added to the reactor and ethylene was fed at a constant pressure. The polymerization time was measured from the moment reaction mixture stirring started. After polymerization occurred, the reactor was vented and the reaction mixture was poured into 2 L of acetone. The precipitated white polymer was filtered, washed with acetone and dried in a vacuum oven at 80 °C. In case of preactivation of catalyst, half of the MAO-toluene (Al/Zr = 1000, 1.0 mL, 1.0 mmol, 8.2 wt% in toluene) solution was used as a scavenger in the polymerization reactor, and the other MAO toluene solution (Al/Zr = 1000, 1.0 mL, 1.0 mmol, 8.2 wt% in toluene) was added to the catalyst toluene solution and stirred at room temperature for 15 min. After the addition of preactivated catalyst ($2 \times 10^{-6}$ mol/L), polymerization was allowed to start by supplying a constant ethylene pressure to the reactor.

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