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# Novel octahydro- and tetrahydro-fluorenyl containing $C_1$ symmetric zirconocenes for the stereoregular polymerization of propylene

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## Abstract

The synthesis and polymerization behavior of two new asymmetric metallocenes containing partially or fully hydrogenated fluorenyl moieties is reported. The zirconocenes, dimethylsilylene-[$\eta^5$-1-(2-methyl-4-phenyl)indenyl]-($\eta^5$-9-tetrahydrofluorenyl) zirconium dichloride (**9**) and dimethylsilylene-[$\eta^5$-1-(2-methyl-4-phenyl)indenyl]-($\eta^5$-9-octahydrofluorenyl) zirconium dichloride (**10**) were both found to be very stable complexes that were highly active catalyst precursors for the polymerization of ethylene and propylene. In the case of propylene, activities approaching $10^8$ g polymer ([mol Zr] [monomer] h)$^{-1}$ were obtained. Highly stereoregular polypropylene was produced at room temperature. The complexes **9** and **10** were significantly more stable and more active than the previously prepared fluorenyl analog. © 2001 Elsevier Science B.V. All rights reserved.

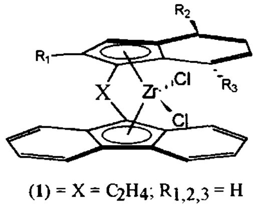
*Keywords:* Zirconocenes; Asymmetric metallocenes; Polymerization; Isotactic polypropylene; Octahydrofluorenyl; Tetrahydrofluorenyl

## 1. Introduction

The production of highly isotactic polypropylene (PP) using Ziegler–Natta type homogeneous metallocenes is an area of great interest industrially and academically. The discovery that chiral $C_2$ symmetric metallocenes could produce stereoregular polypropylenes [1] efficiently led to many studies in order to fully optimize the polymerization behavior of this class of metallocene [2,3]. In recent years, research has increased in the area of $C_1$ symmetric systems, which have been shown to polymerize propylene to PP with varying microstructures from aspecific [4] to stereoblock [5] to syndiotactic [6] to hemiisotactic [7] to isotactic [8], depending on the nature of the hapto ligands.

Rieger et al. [8b] published a study on the use of an asymmetric ethylene bridged indenyl-fluorenyl zirconocene: ethylene-1-[-9-fluorenyl]-2-[-1-indenyl] zirconium dichloride (**1**) that produced moderately isotactic PP (Chart 1).

We were interested to investigate the effects of placing substituents on the indenyl moiety of **1** on polymerization behavior and particularly PP microstructure. A series of substituted zirconocenes were prepared, which were all shown to be highly efficient catalyst precursors for both ethylene and propylene polymerization [9]. Depending on the substitution pattern on the indenyl ring and the polymerization conditions, polymers varying from aspecific to highly isotactic were obtained. We found that by placing substituents at both the 2- and 4-positions of the indenyl moiety, highly isotactic PP



(**1**) = X = $C_2H_4$; $R_{1,2,3}$ = H
(**2**) = X = $C_2H_4$; $R_{1,2,3}$ = Me
(**3**) = X = $SiMe_2$; $R_{1,2,3}$ = Me
(**4**) = X = $C_2H_4$; $R_1$ = Me; $R_2$ = Ph; $R_3$ = H
(**5**) = X = $SiMe_2$; $R_1$ = Me; $R_2$ = Ph; $R_3$ = H

Chart 1.

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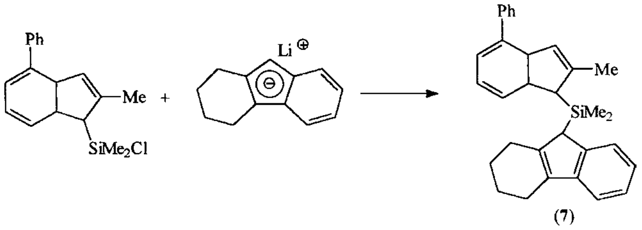
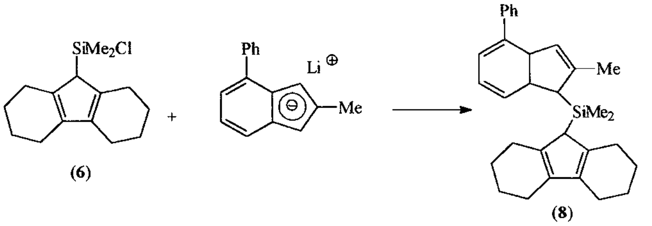


Scheme 1.



Scheme 2.

was produced. Ethylene-1-[-9-fluorenyl]-2-[-1-(2,4,7-trimethyl)indenyl] zirconium dichloride (**2**) (Chart 1) polymerized propylene with a productivity of 1.3 × $10^8$ g polymer [(mol Zr) h]$^{-1}$ and the resulting polymer was 91% isotactic with a molecular weight of 27 000 [9,10].

In an effort to increase the molecular weight of the polymer, the silicon bridged analog of **2** was prepared [10]. Surprisingly however, dimethylsilylene-[9-fluorenyl]-[1-(2,4,7-trimethyl)indenyl] zirconium dichloride (**3**) (Chart 1) was found to be a highly unstable complex that showed lower activity and lower stereoselectivity towards propylene polymerization. The instability of **3** was attributed to a weak Zr-fluorenyl bond, and also to the presence of the 7-methyl group, which we believed interfered sterically with the methyl groups on the dimethylsilylene bridge [10]. We recently prepared several new asymmetric metallocenes including ethylene-1-(9-fluorenyl)-2-[1-(2-methyl-4-phenyl)indenyl]zirconium dichloride (**4**) and dimethylsilylene-(9-fluorenyl)-[1-(2-methyl-4-phenyl)indenyl]zirconium dichloride (**5**) (Chart 1) [11]. Both **4** and **5**, polymerized propylene in the presence of methylaluminoxane (MAO) to highly isotactic PP ([mmmm] ≥ 90%) with high Mw. However, it was found that the dimethylsilylene bridged analog was again lower in activity than the ethylene bridged complex.

To date, the focus of our investigations has been the effect of placing substituents on the indenyl moiety and also varying the bridging ligand. We were interested to extend this study to include changing the nature of the fluorenyl moiety. In particular, we were interested in trying to improve the polymerization behavior of the dimethylsilylene bridged metallocenes that we had prepared. The activities obtained with these complexes have been found to be lower by a factor of ten compared to the ethylene bridged complexes. We believe that this trend is a direct consequence of the nature of the Si–fluorenyl bond and the resulting Zr–fluorenyl bond. There are several reports of the instability of some fluorenyl containing metallocenes due to 'ring slippage' [12].

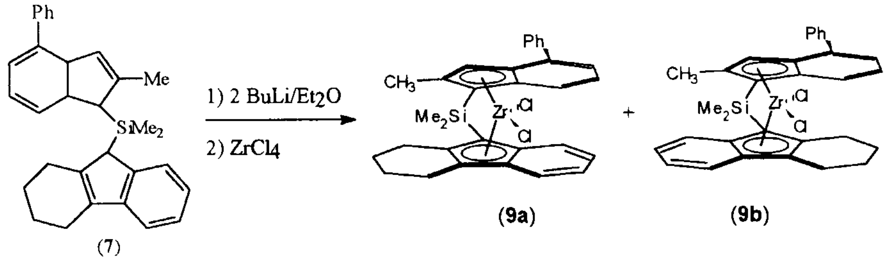
In 1997, Marks et al. published the results of a comparative study of the polymerization behavior of dimethylsilyl-[9-octahydrofluorenyl]-(−)-[menthylcyclopentadienyl] zirconium dichloride and the fluorenyl containing analog [13]. The former was shown to have similar or higher activities for propylene polymerization than the latter, and the polymers obtained were more isotactic [13]. Similar results are observed when indenyl is replaced by tetrahydroindenyl [14]. A second example of the use of octahydrofluorenyl in place of fluorenyl was reported by Näsman et al. in 1997 [15]. In that study, it was found that the use of the fully hydrogenated octahydrofluorenyl ligand led to higher Mw polyethylene (PE) than with the fluorenyl analog [15]. We were therefore interested in investigating the effect of changing the fluorenyl moiety to a partially or fully hydrogenated fluorenyl derivative, tetrahydrofluorenyl (THFlu) or octahydrofluorenyl (OHFlu), respectively, in asymmetric systems.

## 2. Results and discussion

### 2.1. Synthesis of the organic ligands

The synthesis of tetrahydrofluorene was reported by Colonge et al. in the 1950s [16]. Octahydrofluorene was prepared according to the method described by Marks et al. and further reacted as published to prepare the 9-(chlorodimethylsilyl)-octahydrofluorenyl (**6**) derivative [13]. Two new asymmetric dimethylsilylene bridged ligands were prepared containing the tetrahydrofluorenyl (**7**) (Scheme 1) and octahydrofluorenyl (Scheme 2) (**8**) moieties, respectively. Both compounds were isolated as oily solids in ca. 50% yields. It was difficult to purify the two compounds, as they would not crystallize fully in common solvent systems such as ethanol or toluene/hexane. The best results were obtained in 100% ethanol at −20 °C although the products became oily once isolated at room temperature. The new ligands were characterized by $^1$H-NMR and mass spectrometry.

Attempts to prepare the ethylene bridged analogs of **7** and **8** were unsuccessful due to a preference for acid–base chemistry over nucleophilic substitution, as a result of the more acidic nature of the protons in the hydrogenated fluorenyl compounds relative to fluorene



Scheme 3.

itself. Under various reaction conditions, either starting materials were recovered or spiro derivatives of the fluorenyl ligands were produced.

### *2.2. Synthesis of the zirconocenes*

The bridged ligands **7** and **8** were converted to their corresponding zirconocenes **9** (Scheme 3) and **10** (Scheme 4) by reaction of the appropriate dianion with one equivalent of $ZrCl_4$ in diethyl ether. The complexes could be isolated from either methylene chloride or toluene in good yields as highly stable solids. The tetrahydrofluorenyl complex **9** was isolated as a mixture of two isomers (**9a** and **9b** ca. 1:9) but as both isomers should lead to isospecific propylene polymerization, this was not thought to be a problem. The new zirconocenes **9** and **10** and were highly stable in solution and did not decompose upon exposure to air for short periods of time. Qualitatively, they appear much more stable than the dimethylsilylene-2,4,7-trimethylindenyl-fluorenyl zirconocene **3** [10]. The complexes were characterized by $^1$H-NMR and mass spectrometry.

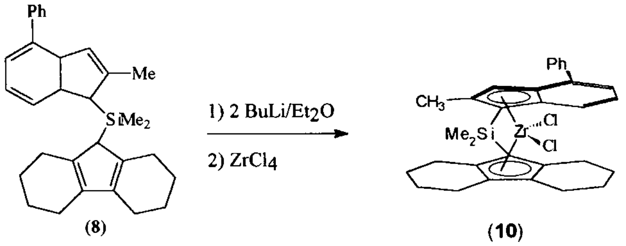
### *2.3. Polymerization results*

Polymerization studies were carried out in order to compare the behavior of the new zirconocenes **9** and **10** with the previously prepared fluorenyl analog **5** [11]. Table 1 summarizes the results obtained for the polymerization of ethylene. As can be seen, the two new catalyst precursors are highly efficient and the activities are comparable with the results for **5**/MAO as well as the other zirconocenes prepared in this series [9]. Complexes **9** and **10** were not preactivated due to their high stability in solution.

Table 2 summarizes the propylene polymerization results obtained in our laboratories at 30 psi propylene pressure, and at two different temperatures, 20 and 70 °C. It can be seen that the two new catalyst precursors are both highly efficient for the polymerization of propylene with activities of high $10^7$, approaching $10^8$ g polymer [(mol Zr) [$C_3$] h]$^{-1}$ for **9**/MAO at 70 °C. These activities are higher by a factor of at least 10 than those reported for **5**/MAO under the same conditions and are equal if not greater than those reported for the ethylene bridged systems such as **2**/MAO and **4**/MAO [9,11].

The polypropylenes produced at room temperature are highly isotactic for both **9** and **10**/MAO with [mmmm] = 84 and 87%, respectively. However, at higher $T_p$, the stereoregularity of the PP decreases and is only moderately isotactic with [mmmm] = ca. 50% for both systems. This is different to the results obtained for the fluorenyl analog **5**, which produced highly isotactic PP under all polymerization conditions [11]. The full pentad analysis for the polymers obtained is shown in Table 3.

The pentad distribution patterns for the polymer samples obtained at $T_p = 20$ °C with **9** and **10** are very similar for the polymer samples obtained with **5** at both $T_p$. This suggests that changing the nature of the fluorenyl moiety to a hydrogenated analog has no effect on stereoregularity at $T_p = 20$ °C and leads to a much more active precursor. At $T_p = 70$ °C for the new precursors **9** and **10**, the stereoerrors become more significant and [mmmm] is much lower indicating that under



Scheme 4.

Table 1
Polymerization of ethylene with asymmetric zirconocenes **9** and **10**/MAO: comparison with **5**/MAO [a]

| Catalyst precursor | Yield (g) | *A* [b] |
|---|---|---|
| 9 | 0.59 | $8.6 \times 10^7$ |
| 10 | 0.65 | $9.5 \times 10^7$ |
| 5 [c] | 0.54 | $7.9 \times 10^7$ |

[a] Polymerization conditions: [Zr] = 5 μM; Al/Zr = 4000:1; time of polymerization = 6 min; $T_p = 50$ °C; monomer pressure = 15 psi.

[b] *A* (activity) = g polymer [(mol Zr)[$C_2$] h]$^{-1}$.

[c] Preactivated for 10 min with 1 ml of MAO.

Table 2
Propylene polymerization results for catalyst precursors **9** and **10**/MAO at 30 psi: comparison with **5**/MAO [a]

| Catalyst precursor | Temperature (°C) | Yield (g) | A [b] | $T_m$ (°C) | [mmmm] [c] |
|---|---|---|---|---|---|
| 9 | 20 | 17.90 | $1.40 \times 10^7$ | 118 | 84 |
| 9 | 70 | 15.94 | $9.00 \times 10^7$ | No m.p. | 49 |
| 10 | 20 | 6.49 | $0.52 \times 10^7$ | 138 | 87 |
| 10 | 70 | 11.30 | $6.40 \times 10^7$ | 81 | 56 |
| 5 [d] | 20 | 0.7 | $0.06 \times 10^7$ | 137 | 91 |
| 5 [d] | 70 | 0.8 | $0.43 \times 10^7$ | 135 | 89 |

[a] Conditions: Toluene solution, polymerization pressure = 30 psi; time of polymerization = 1 h; [Zr] = 25 μM; Al:Zr = 4000:1.
[b] Activity expressed as g polymer [(mol Zr) [$C_3$] h]$^{-1}$.
[c] [mmmm] pentad analysis by $^{13}$C-NMR.
[d] Preactivated for 10 min with 1 ml of MAO.

Table 3
Pentad distributions for polypropylenes produced in Table 2 for **9** and **10**/MAO: comparison with **5**/MAO [a]

| Catalyst | Temperature [b] | mmmm | mmmr | rmmr | mmrr | mmrm + rmrr | mrmr | rrrr | mrrr | mrrm |
|---|---|---|---|---|---|---|---|---|---|---|
| 9 | 20 | 83.7 | 6.99 | 0 | 6.89 | 0 | 0 | 0 | 0 | 2.40 |
| 9 | 70 | 49.1 | 19.4 | 0 | 20.8 | 4.48 | 0 | 0 | 1.20 | 5.02 |
| 10 | 20 | 87.0 | 5.6 | 0 | 5.61 | 0 | 0 | 0 | 0 | 1.81 |
| 10 | 70 | 56.1 | 16.8 | 0 | 19.3 | 1.69 | 0 | 0 | 0.95 | 5.21 |
| 5 | 20 | 90.5 | 5.60 | 0 | 3.94 | 0 | 0 | 0 | 0 | 0 |
| 5 | 70 | 88.9 | 3.91 | 0 | 6.14 | 0 | 0 | 0 | 0 | 1.0 |

[a] Pentad distributions expressed as %.
[b] $T_p$ (°C).

Table 4
Propylene polymerization results for asymmetric catalyst precursors **9** and **10/**MAO in liquid propylene: comparison with **5**/MAO [a]

| Catalyst precursor | Productivity [b] | Isotacticity (mm, mol%) | $T_m$ (°C) | Mw $10^{-5}$g mol$^{-1}$ [c] |
|---|---|---|---|---|
| 9 | $0.62 \times 10^8$ | 85 | 125 | 0.2 |
| 10 | $1.06 \times 10^8$ | 91 | 140 | 0.3 |
| 5 | $0.10 \times 10^8$ | 91 | 138 | 0.5 |

[a] Conditions; liquid pool, pressure = 30 bar, temperature = 70 °C, time of polymerization = 1 h.
[b] Productivity expressed as g polymer [(mol Zr) h]$^{-1}$.
[c] Molecular weights determined by GPC.

these conditions, the use of a hydrogenated fluorenyl moiety negatively effects the stereoregularity of the propylene polymeriation. We believe this may be due to the hydrogenated rings of the fluorenyl moieties that can 'ring flip' and are therefore less stereorigid than fluorenyl itself. At higher $T_p$, ring flip can occur more rapidly, therefore reducing the steric directing effect on both the polymer configuration and the incoming monomer leading to more random chain propagation.

Polymerizations were also carried out in liquid pool propylene. The results are shown in Table 4. Under these conditions, it can be seen that the isotacticity of the polypropylene remains high at $T_p = 70$ °C with [mm] = 85 and 91% for **9** and **10**, respectively (Table 4). This may be explained by the fact that the tendency of the hydrogenated rings to flip at higher temperature may be overcome by the higher propylene concentration.

The molecular weights of the polymers obtained under liquid pool conditions with **9** and **10** are lower than for **5**. This may be due to the more indenyl like character of the hapto ligand. It is known that bisfluorenyl metallocenes produce very high molecular weight polymers. A further explanation may be that the less stereorigid geometry of the partially and fully hydrogenated analogs allows for easier β-hydride elimination and therefore lower molecular weight polymer.

We have discussed the mechanisms of polymerization for the asymmetric catalyst precursors [10]. A related discussion for a different series of asymmetric metallocenes was also published by Rieger et al. [17]. In the case of **5** a chain stationary mechanism similar to that proposed by Razavi et al. was proposed due to the steric bulk of the phenyl group prohibiting chain migration [11]. Due to the less stereorigid geometry of **9** and **10**, however, any restriction placed on the polymer chain by the steric nature of the phenyl group and the fluorenyl moiety in **5** may be relieved, allowing for a chain migratory insertion mechanism instead of the chain stationary mechanism proposed for **5** [18]. The only other report of octahydrofluorenyl containing metallocenes as propylene polymerization catalysts was by Marks et al. and in this case, polymerizations were carried out at 25 °C and below [13].

The high stability of the complexes compared to Si–fluorenyl analogs can be explained by the fact that the ligand actually behaves more like a substituted indenyl (Ind) in the case of tetrahydrofluorenyl, and more like a cyclopentadienyl (Cp) ligand in the case of octahydrofluorenyl. Zirconium complexes of Cp and Ind are generally more stable and less susceptible to fluctuating hapticity [12]. Our findings support the theory that the instability of complexes such as **5** was a consequence of the nature of the weak Si–fluorenyl bond and the resulting Zr–fluorenyl bond.

## 3. Conclusion

In summary, we have shown that by replacing the fluorenyl moiety of mixed ring indenyl-fluorenyl dimethylsilylene bridged metallocenes with a partially or fully hydrogenated fluorenyl derivative, highly stable complexes can be prepared. The new zirconocenes were found to be highly efficient catalyst precursors for the polymerization of propylene and ethylene. In the case of propylene, the activities were at least tenfold higher than those obtained with fluorenyl analogs. In addition, polymerization of propylene at room temperature or under liquid pool conditions leads to highly isotactic PP.

## 4. Experimental

Reactions were carried out under an argon atmosphere using standard Schlenk techniques. MAO was purchased as a solution in toluene from Akzo Nobel and used as received. All other reagents were purchased from Aldrich and used without further purification. Diethyl ether, THF, and pentane were distilled from Na/K alloy under argon. Dichloromethane was distilled from $CaH_2$ under argon. Tetrahydrofluorene [16], octahydrofluorene [13], 2-methyl-7-phenylindene [3a] and chlorodimethylsilyloctahydrofluorene (**6**) [13] were synthesized according to literature procedures. $^1$H-NMR spectra were recorded on an AC-200 spectrometer. $^{13}$C-NMR spectra were recorded on an AMX500 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA. Mass spectra were recorded at the University of Massachusetts, Amherst, MA.

### 4.1. *[1-(2-Methyl-4-phenyl)indenyl]-[-9-tetrahydrofluorenyl] dimethylsilane (**7**)*

To a solution of 2.00 g (9.70 mmol) of 2-methyl-7-phenylindene in 40 ml of dry diethyl ether at 0 °C was added dropwise a 1.6 M solution of butyllithium in hexane (6.06 ml, 9.70 mmol). The solution was stirred at room temperature (r.t.) for 5 h. The solvent was removed under vacuum and the residue was washed with 2 × 20 ml of dry pentane. The anion was dried under vacuum, dissolved in 40 ml of dry diethyl ether and 5 ml of dry THF, and then added dropwise via cannula to 2.36 ml (19.4 mmol) of dichlorodimethylsilane in 20 ml of dry diethyl ether at 20 °C. The addition was carried out over a 1 h period and the suspension was then stirred for 1 h at r.t. The solvents and excess dichlorodimethylsilane were then removed under vacuum and the resulting oil was suspended in 30 ml of dry diethyl ether at 0 °C. To this was added dropwise by cannula one equivalent of 5,6,7,8-tetrahydrofluorenyllithium, prepared from 1.65 g (9.70 mmol) of 5,6,7,8-tetrahydrofluorene and 6.06 ml (9.70 mmol) of butyllithium in 30 ml of dry ether and 10 ml of dry tetrahydrofuran. The suspension was allowed to stir overnight at r.t. and hydrolyzed with aqueous $NH_4Cl$. The organic phase was separated and the aqueous layer was extracted with ether. The combined organic phases were dried ($MgSO_4$), filtered and the solvent was removed. The oily residue was crystallized from 100% ethanol to give 2.10 g of **7** (50%). The compound was an oily solid that did not display a true m.p. $^1$H-NMR ($CDCl_3$): $\delta$ 7.57–7.11 (m, 12 H, arom), 6.78 (bs, 1 H Ind-$C_5$-sp$^2$), 3.77 (bs, 1 H, Ind-$C_5$-sp$^3$), 3.63 (bs, 1 H, THFlu-$C_5$-sp$^3$), 2.54–2.42 (m, 4 H, $CH_2$), 2.20–2.17 (d, 3 H, $CH_3$), 1.95–1.55 (m, 4 H, $CH_2$), −0.26 (s, 3 H, Si–$CH_3$), −0.27 (s, 3 H, Si–$CH_3$). HRMS (EI) *m/z* for $C_{31}H_{32}Si$: Anal. Calc.: 432.2273; Found: 432.2253.

### 4.2. *[1-(2-Methyl-4-phenyl)indenyl]-[-9-octahydrofluorenyl] dimethylsilane (**8**)*

To a solution of 1.55 g (7.51 mmol) of 2-methyl-7-phenylindene in 30 ml of dry diethyl ether at 0 °C was added dropwise a 1.6 M solution of butyllithium in hexane (4.68 ml, 7.51 mmol). The solution was stirred at r.t. for 5 h. The solvent was removed under vacuum and the residue was washed with 2 × 20 ml of dry pentane. The anion was dried under vacuum, dissolved in 30 ml of dry diethyl ether and 5 ml of dry THF and then added dropwise to 2.00 g (7.51 mmol) of 9-(chlorodimethylsilyl)-octahdrofluorene (**6**) in 20 ml of dry diethyl ether at −78 °C. The mixture was allowed to warm to r.t. and stirred overnight to give a yellow suspension which was hydrolyzed with aqueous $NH_4Cl$.

The organic phase was separated and the aqueous layer was extracted with ether. The combined organic phases were dried ($MgSO_4$), filtered and the solvent was removed. The oily residue was crystallized from 100% ethanol to give 1.85 g of **8** (56%). The compound was an oily solid that did not display a true m.p. $^1$H-NMR ($CDCl_3$): $\delta$ 7.52–7.15 (m, 8 H, arom), 6.79 (s, 1 H Ind-$C_5$-sp$^2$), 3.74 (s, 1 H, Ind-$C_5$-sp$^3$), 3.18 (bs, 1 H, OHFlu-$C_5$-sp$^3$), 2.44–1.59 (m, 16 H, $CH_2$), 2.22 (s, 3 H, $CH_3$), −0.21 (s, 3 H, Si–$CH_3$), −0.25 (s, 3 H, S–$CH_3$) HRMS (EI) $m/z$ for $C_{31}H_{36}Si$: Anal. Calc.: 436.2586; Found: 436.2608.

### *4.3. Dimethylsilylene-[$\eta^5$-1-(2-methyl-4-phenyl)indenyl]-($\eta^5$-9-tetrahydrofluorenyl) zirconium dichloride (**9**)*

To a solution of **7**(0.50 g, 1.16 mmol), in 20 ml of dry diethyl ether at 0 °C was added dropwise two equivalents of 1.6 M butyllithium in hexane (1.45 ml, 2.32 mmol). The resulting suspension was stirred for 6 h at r.t. The solvent was removed under vacuum and the residue was washed with $2 \times 10$ ml portions of dry pentane. The yellow solid was suspended in 20 ml of dry diethyl ether and cooled to 0 °C. $ZrCl_4$ (0.27 g, 1.16 mmol) was added as a solid. The orange suspension was stirred overnight at r.t. and the solvent was removed by filtration. The residue was extracted in dry methylene chloride, concentrated and stored at −20 °C to give **9** (290 mg, 42.2%), an orange solid, as a mixture of isomers (ca. 9:1). $^1$H-NMR ($CDCl_3$): $\delta$ 7.65–6.90 (m, 12 H, arom), 6.89 (s, 1 H, Ind-$C_5$-sp$^2$), 3.04–2.55 (m, 4 H, $CH_2$), 2.34 minor, 2.23 major (s, 3 H, $CH_3$), 1.90–1.35 (m, 4 H, $CH_2$), 1.46 minor, 1.31–1.29 major, 1.19 minor (s, 6 H, Si–$CH_3$). HRMS (EI) $m/z$ for $C_{31}H_{30}Cl_2SiZr$: Anal. Calc.: 590.0541; Found: 590.0535.

### *4.4. Dimethylsilylene-[$\eta^5$-1-(2-methyl-4-phenyl)indenyl]-($\eta^5$-9-octahydrofluorenyl) zirconium dichloride (**10**)*

Following the procedure described for **9**, **8** (0.50 g, 1.14 mmol), 1.6 M butyllithium in hexane (1.43 ml, 2.28 mmol and $ZrCl_4$ (0.27 g, 1.14 mmol) gave **10** (310 mg, 45.6%) as a yellow solid. $^1$H-NMR ($CDCl_3$): $\delta$ 7.74–7.02 (m, 8 H, arom and 1 H, Ind-$C_5$-sp$^2$), 2.76–1.20 (m, 16 H, $CH_2$), 2.30 (s, 3 H, $CH_3$), 1.17 (s, 3 H, Si–$CH_3$), 1.05 (s, 3 H, Si–$CH_3$). HRMS (EI) $m/z$ for $C_{31}H_{34}Cl_2SiZr$: Anal. Calc.: 594.0854; Found: 594.0829.

### *4.5. Polymerization procedures*

A 250-ml crown capped glass pressure reactor containing 50 ml of toluene was equilibrated with the appropriate monomer at the desired temperature and pressure. The desired amount of MAO was added as a solution in toluene via syringe, and the solution was stirred for 5 min. One milliliter of the appropriate catalyst solution in toluene was added and the mixture was stirred until the desired reaction time was reached. The mixture was quenched with 2% HCl in methanol, filtered (or extracted in hexane in the case of *a*-PP), and dried in a vacuum oven at an appropriate temperature for the polymer sample.

### *4.6. Polymer analyses*

M.p.s were determined by DSC with a Perkin–Elmer DSC-4 system. $^{13}$C-NMR spectra were determined at 90 °C in $C_6H_3Cl_3$ with $C_6D_6$ on an AMX 500 spectrometer. Molecular weights were determined by gel permeation chromatography using a Waters 150C instrument (solution in 1,2,4-trichlorobenzene at 135 °C and PS standards for calibration.

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