Synthesis and catalytic applications of C_1 symmetric group 4 *ansa*-metallocene complexes

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Abstract

The group 4 *ansa*-metallocene complexes with chiral substituent bearing cyclopentadienyl ligands, $[M\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CHRR'\})\}Cl_2]$ (R = Pr^i, R′ = Me (**9**); R = Pr^i, R′ = Ph (**10**); R = Bu^t, R′ = Me (**11**); R = Bu^t, R′ = Ph (**12**); M = Zr (**a**), Hf (**b**)), were synthesized by the reaction of the dilithium compounds, $Li_2\{Me_2Si(C_5Me_4)(C_5H_3\{CHRR'\})\}$ (R = Pr^i, R′ = Me (**5**); R = Pr^i, R′ = Ph (**6**); R = Bu^t, R′ = Me (**7**); R = Bu^t, R′ = Ph (**8**)), with the tetrachloride salts of the transition metal. The molecular structures of **11a** and **12a** have been determined by single-crystal X-ray diffraction studies. The catalytic behaviour of **9–12** in the polymerization of ethylene and propylene has been studied. Isotactic polypropylene with [mmmm] pentads of the order of 60% were obtained with the C_1 symmetric *ansa*-zirconocene catalysts.
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1. Introduction

There is no doubt in the great interest in group 4 metallocene complexes due to their catalytic applications in the polymerization of olefins [1–3]. It is well established that the structural make-up of the catalyst directly influences the physical properties of the polymer [4]. Thus small variations in the metallocene complex should cause notable effects in the polymer produced. The design of new metallocene catalysts tailored to produce specific polymers is therefore of upmost importance [5].

Rigid *ansa*-metallocene systems have been widely used as olefin polymerization catalysts and generally offer better catalytic activity and selectivity than their non-*ansa* counterparts [6,7]. *ansa*-Catalysts with C_1 symmetry have shown to be isos-

elective (although to a lesser degree than their C_2 symmetric analogues) in the polymerization of propylene [8,9].

As part of our ongoing studies in the design of olefin polymerization catalysts [10–20] we present in this paper the synthesis and characterization of new *ansa*-metallocene complexes of zirconium and hafnium with C_1 symmetry and their catalytic activity and selectivity in the polymerization of ethylene and propylene.

2. Experimental

2.1. General procedures

All reactions were performed using standard Schlenk tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from the appropriate drying agents and degassed before use.

$Me_2Si(C_5Me_4H)Cl$, LiBu^n (1.6 M in hexane), MAO, ZrCl$_4$, and HfCl$_4$, were purchased from Aldrich and used directly.

Li{C_5H_4(CHRR′)} (R = Pr^i, Bu^t; R′ = Me, Ph) were prepared as previously reported [21].

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Mercury FT-400 spectrometer. Microanalyses were carried out with a Perkin-Elmer 2400 or LECO CHNS-932 microanalyzer. Mass spectroscopic analyses were preformed on a Hewlett-Packard 5988A (*m/z* 50–1000) instrument. Polymer molecular weights and distribution were determined by GPC (Waters 150C Plus) in 1,2,4-trichlorobenzene at 145 °C. Polymer isotacticity was calculated from ^{13}C NMR spectra of polymer samples dissolved in 1,2,4-trichlorobenzene and C_6D_6 (1:1).

2.2. Preparation of compounds

2.2.1. Me$_2$Si(C$_5$Me$_4$H)(C$_5$H$_4${CHPr^{i}Me}) (1)

Me$_2$Si(C$_5$Me$_4$H)Cl (3.03 g, 14.07 mmol) in THF (50 mL) was added to a solution of Li{C_5H_4(CHPr^{i}Me)} (2.00 g, 14.07 mmol) in THF (50 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 15 h. Solvent was removed in vacuo and hexane (150 mL) was added to the resulting dark orange oil. The mixture was filtered and solvent removed from the filtrate under reduced pressure to yield the title compound as an orange oil (3.94 g, 89%). ^{1}H NMR (400 MHz, CDCl$_3$; for the predominant isomer): δ −0.12 (s, 6H, Si*Me$_2$*), 0.87 (3H), 0.89 (3H) (d, CH*Me$_2$*), 1.11 (d, 3H, C*Me*), 1.75 (m, 1H, C*H*Pr^{i}Me), 1.87 (6H), 2.01 (6H) (s, C$_5$*Me$_4$*), 2.94 (1H), 3.22 (1H) (m, *H*C$_5$), 5.93 (1H), 6.16 (1H), 6.50 (1H) (m, C$_5$*H$_3$*). MS electron impact (*m/e* (relative intensity)): 314 (25) [M^+], 253 (11) [M^+ − Pr^i, −Me], 193 (80) [M^+ − C$_5$HMe$_4$], 179 (100) [M^+ − C$_5$H$_4$CHPr^{i}Me]. Anal. Calc. for C$_{21}$H$_{34}$Si: C, 80.18; H, 10.89. Found C, 79.97; H, 10.85%.

2.2.2. Me$_2$Si(C$_5$Me$_4$H)(C$_5$H$_4${CHPr^{i}Ph}) (2)

The synthesis of **2** was carried out in an identical manner to **1**. Me$_2$Si(C$_5$Me$_4$H)Cl (2.11 g, 9.79 mmol) and Li{C_5H_4(CHPr^{i}Ph)} (2.00 g, 9.79 mmol). Yield 3.54 g, 96%. ^{1}H NMR (400 MHz, CDCl$_3$; for the predominant isomer): δ 0.23 (s, 6H, Si*Me$_2$*), 0.92 (3H), 1.11 (3H) (d, CH*Me$_2$*), 1.98 (6H), 2.10 (6H) (s, C$_5$*Me$_4$*), 2.41 (m, 1H, C*H*Me$_2$), 3.05 (1H), 3.27 (1H) (m, *H*C$_5$), 3.45 (d, 1H, C*H*Pr^{i}Me), 6.17 (1H), 6.40 (1H), 6.63 (1H) (m, C$_5$*H$_3$*), 7.25 (2H), 7.32 (2H), 7.39 (1H) (m, *Ph*). MS electron impact (*m/e* (relative intensity)): 376 (10) [M^+], 253 (41) [M^+ − Pr^i, −Ph], 179 (58) [M^+ − C$_5$H$_4$CHPr^{i}Ph], 135 (100) [M^+ − Me$_2$Si(C$_5$HMe$_4$)(C$_5$H$_3$)]. Anal. Calc. for C$_{26}$H$_{36}$Si: C, 82.91; H, 9.63. Found C, 82.67; H, 9.55%.

2.2.3. Me$_2$Si(C$_5$Me$_4$H)(C$_5$H$_4${CHBu^{t}Me}) (3)

The synthesis of **3** was carried out in an identical manner to **1**. Me$_2$Si(C$_5$Me$_4$H)Cl (2.76 g, 12.80 mmol) and Li{C_5H_4(CHBu^{t}Me)} (2.00 g, 12.80 mmol). Yield 3.87 g, 93%. ^{1}H NMR (400 MHz, CDCl$_3$; for the predominant isomer): δ −0.14 (s, 6H, Si*Me$_2$*), 0.90 (s, 9H, *Bu^t*), 1.13 (d, 3H, C*Me*), 1.87 (6H), 2.01 (6H) (s, C$_5$*Me$_4$*), 2.42 (q, 1H, C*H*Bu^{t}Me), 2.92 (1H), 3.20 (1H) (m, *H*C$_5$), 5.97 (1H), 6.23 (1H), 6.47 (1H) (m, C$_5$*H$_3$*). MS electron impact (*m/e* (relative intensity)): 328 (24) [M^+], 253 (22) [M^+ − Bu^t, −Me], 207 (90) [M^+ − C$_5$HMe$_4$], 179 (79)

[M^+ − C$_5$H$_4$CHBu^{t}Me]. Anal. Calc. for C$_{22}$H$_{36}$Si: C, 80.41; H, 11.04. Found C, 80.14; H, 11.04%.

2.2.4. Me$_2$Si(C$_5$Me$_4$H)(C$_5$H$_4${CHBu^{t}Ph}) (4)

The synthesis of **4** was carried out in an identical manner to **1**. Me$_2$Si(C$_5$Me$_4$H)Cl (1.97 g, 9.16 mmol) and Li{C_5H_4(CHBu^{t}Ph)} (2.00 g, 9.16 mmol). Yield 3.11 g, 87%. ^{1}H NMR (400 MHz, CDCl$_3$; for the predominant isomer): δ −0.07 (s, 6H, Si*Me$_2$*), 1.03 (s, 9H, *Bu^t*), 1.90 (6H), 2.01 (6H) (s, C$_5$*Me$_4$*), 2.97 (1H), 3.25 (1H) (m, *H*C$_5$), 3.65 (s, 1H, C*H*Bu^{t}Ph), 6.17 (1H), 6.30 (1H), 6.69 (1H) (m, C$_5$*H$_3$*), 7.19 (2H), 7.28 (2H), 7.43 (1H) (m, *Ph*). MS electron impact (*m/e* (relative intensity)): 390 (10) [M^+], 269 (41) [M^+ − C$_5$HMe$_4$], 179 (77) [M^+ − C$_5$H$_4$CHBu^{t}Ph], 135 (100) [M^+ − Ph, −Me$_2$Si(C$_5$HMe$_4$)]. Anal. Calc. for C$_{21}$H$_{34}$Si: C, 83.01; H, 9.80. Found C, 82.78; H, 9.76%.

2.2.5. Li$_2${Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3${CHPr^{i}Me})} (5)

LiBu^n (1.6 M in hexane) (11.9 mL, 19.08 mmol) was added dropwise to a solution of **1** (3.00 g, 9.54 mmol) in Et$_2$O (100 mL) at −78 °C. The mixture was allowed to warm to 25 °C and stirred for 15 h. Solvent was removed in vacuo to give a white solid which was washed with hexane (2× 50 mL) and dried under vacuum to yield a white solid of the title complex (2.83 g, 91%). ^{1}H NMR (400 MHz, d_8-THF): δ 0.44 (s, 6H, Si*Me$_2$*), 0.82 (d, 6H, CH*Me$_2$*), 1.09 (d, 3H, C*Me*), 1.67 (m, 1H, C*H*Me$_2$), 1.87 (6H), 2.07 (6H) (s, C$_5$*Me$_4$*), 2.45 (m, 1H, C*H*Pr^{i}Me), 5.59 (1H), 5.76 (2H) (m, C$_5$*H$_3$*). ^{13}C{^{1}H} NMR (100 MHz, d_8-THF): δ 3.4, 3.7 (Si*Me$_2$*), 10.9, 11.1, 13.8, 14.1 (C$_5$*Me$_4$*), 18.9 (C*Me*), 19.7, 21.0, 35.4 (*Pr^i*), 41.1 (Cp*C*), 100.7, 101.0, 111.6, 113.1, 123.9 (*C$_5$*Me$_4$), 104.0, 108.9, 111.1, 115.4, 127.1 (*C$_5$H$_4$*). Anal. Calc. for C$_{21}$H$_{32}$Li$_2$Si: C, 77.26; H, 9.88. Found C, 76.92; H, 9.90%.

2.2.6. Li$_2${Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3${CHPr^{i}Ph})} (6)

The preparation of **6** was carried out in an identical manner to **5**. **2** (3.00 g, 7.96 mmol) and LiBu^n (1.6 M in hexane) (10.0 mL, 15.92 mmol). Yield 2.97 g, 96%. ^{1}H NMR (400 MHz, d_8-THF): δ 0.40 (s, 6H, Si*Me$_2$*), 0.71 (3H), 0.90 (3H) (d, CH*Me$_2$*), 2.20 (m, 1H, C*H*Me$_2$), 1.89 (6H), 2.05 (6H) (s, C$_5$*Me$_4$*), 3.31 (d, 1H, C*H*Pr^{i}Ph), 5.74 (1H), 5.80 (1H), 5.83 (1H) (m, C$_5$*H$_3$*), 6.97 (1H), 7.10 (2H), 7.27 (2H) (m, *Ph*). ^{13}C{^{1}H} NMR (100 MHz, d_8-THF): δ 4.0, 4.3 (Si*Me$_2$*), 10.9, 11.0, 13.9, 14.2 (C$_5$*Me$_4$*), 22.0, 22.6, 34.9 (*Pr^i*), 56.8 (Cp*C*), 101.4, 102.2, 110.9, 111.6, 122.9 (*C$_5$*Me$_4$), 104.1, 110.3, 110.6, 115.6, 125.4 (*C$_5$H$_4$*), 124.4, 127.6, 128.3, 149.9 (*Ph*). Anal. Calc. for C$_{26}$H$_{34}$Li$_2$Si: C, 80.38; H, 8.82. Found C, 80.05; H, 8.90%.

2.2.7. Li$_2${Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3${CHBu^{t}Me})} (7)

The preparation of **7** was carried out in an identical manner to **5**. **3** (3.00 g, 9.13 mmol) and LiBu^n (1.6 M in hexane) (11.4 mL, 18.26 mmol). Yield 3.01 g, 97%. ^{1}H NMR (400 MHz, d_8-THF): δ 0.40 (3H), 0.41 (3H) (s, Si*Me$_2$*), 0.84 (s, 9H, *Bu^t*), 1.15 (d, 3H, C*Me*), 1.87 (6H), 2.05 (6H) (s, C$_5$*Me$_4$*), 2.42 (q, 1H, C*H*Bu^{t}Me), 5.60 (1H), 5.74 (2H) (m, C$_5$*H$_3$*). ^{13}C{^{1}H} NMR (100 MHz, d_8-THF): δ 3.7, 4.3 (Si*Me$_2$*), 10.9, 11.0, 13.8, 14.1 (C$_5$*Me$_4$*), 18.1

(C*Me*), 28.3, 33.9 (*Bu^t*), 45.5 (Cp*C*), 100.3, 102.6, 111.6, 115.6, 122.6 (*C*$_5$Me$_4$), 105.4, 108.9, 110.9, 116.1, 125.3 (*C*$_5$H$_4$). Anal. Calc. for C$_{22}$H$_{34}$Li$_2$Si: C, 77.61; H, 10.07. Found C, 77.32; H, 10.15%.

2.2.8. *Li$_2$*{*Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3$*{*CHBu^tPh*})} (*8*)

The preparation of **8** was carried out in an identical manner to **5**. **4** (3.00 g, 7.68 mmol) and LiBu^n (1.6 M in hexane) (9.6 mL, 15.36 mmol). Yield 2.87 g, 93%. ^{1}H NMR (400 MHz, d_8-THF): δ 0.38 (3H), 0.40 (3H) (s, Si*Me$_2$*), 0.91 (s, 9H, *Bu^t*), 1.89 (6H), 2.04 (6H) (s, C$_5$*Me$_4$*), 3.64 (m, 1H, C*H*Bu^{t}Ph), 5.83 (1H), 5.88 (1H), 5.94 (1H) (m, C$_5$*H$_3$*), 7.00 (1H), 7.12 (2H), 7.47 (2H) (m, *Ph*). ^{13}C{^{1}H} NMR (100 MHz, d_8-THF): δ 3.9, 4.7 (Si*Me$_2$*), 11.0, 11.1, 13.9, 14.2 (C$_5$*Me$_4$*), 27.4, 29.2 (*Bu^t*), 35.2 (Cp*C*), 101.2, 104.5, 111.6, 115.8, 124.4 (*C$_5$*Me$_4$), 106.0, 110.8, 113.7, 123.7, 124.5 (*C$_5$*H$_4$), 120.4, 126.9, 130.2, 147.9 (*Ph*). Anal. Calc. for C$_{27}$H$_{36}$Li$_2$Si: C, 80.56; H, 9.01. Found C, 81.00; H, 9.04%.

2.2.9. *[Zr*{*Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$*{*CHPr^iMe*})}*Cl$_2$] (*9a*)

THF (50 mL) was added to a solid mixture of ZrCl$_4$ (0.71 g, 3.06 mmol) and Li$_2${Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3${CHPr^{i}Me})} (**5**) (1.00 g, 3.06 mmol). The resulting solution was stirred for 15 h. Solvent was removed in vacuo and toluene (75 mL) added to the resulting solid. The mixture was filtered and the filtrate concentrated (10 mL) and cooled to −30 °C to yield crystals of the title complex (0.72 g, 50%). MS electron impact (*m/e* (relative intensity)): 475 (100) [M^+], 407 (19) [M^+ − Cl, −2× Me], 389 (55) [M^+ − Me, −2× Cl]. Anal. Calc. for C$_{21}$H$_{32}$Cl$_2$SiZr: C, 53.13; H, 6.79. Found C, 53.45; H, 6.81%.

Isolated isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.82 (3H), 0.89 (3H) (s, Si*Me$_2$*), 0.99 (3H), 1.06 (3H) (d, CH*Me$_2$*), 1.28 (d, 3H, C*Me*), 1.80 (m, 1H, C*H*Me$_2$), 1.92 (3H), 1.96 (3H), 2.06 (3H), 2.08 (3H) (s, C$_5$*Me$_4$*), 2.99 (d, 1H, C*H*Pr^{i}Me), 5.37 (1H), 5.72 (1H), 6.70 (1H) (m, C$_5$*H$_3$*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −0.4, 0.2 (Si*Me$_2$*), 12.2, 12.4, 14.9, 15.1 (C$_5$*Me$_4$*), 12.6 (C*Me*), 17.1, 21.0, 33.6 (*Pr^i*), 39.6 (Cp*C*), 96.9, 104.5 (*C^1*–Cp), 110.8, 115.0, 123.0, 149.0 (*C$_5$H$_3$*), 126.4, 127.0, 134.0, 136.5 (*C$_5$Me$_4$*).

Second isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.82 (3H), 0.87 (3H) (s, Si*Me$_2$*), 0.72 (3H), 0.79 (3H) (d, CH*Me$_2$*), 0.91 (d, 3H, C*Me*), 1.82 (m, 1H, C*H*Me$_2$), 1.91 (3H), 1.94 (3H), 2.04 (3H), 2.06 (3H) (s, C$_5$*Me$_4$*), 3.09 (d, 1H, C*H*Pr^{i}Me), 5.39 (1H), 5.75 (1H), 6.67 (1H) (m, C$_5$*H$_3$*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −0.4, 0.1 (Si*Me$_2$*), 12.0, 12.1, 14.8, 15.0 (C$_5$*Me$_4$*), 12.3 (C*Me*), 18.7, 21.0, 34.5 (*Pr^i*), 38.7 (Cp*C*), 96.7, 104.4 (*C^1*–Cp), 111.7, 114.9, 123.8, 136.4 (*C$_5$H$_3$*), 123.0, 126.3, 126.9, 134.0 (*C$_5$Me$_4$*).

2.2.10. *[Hf*{*Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$*{*CHPr^iMe*})}*Cl$_2$] (*9b*)

The synthesis of **9b** was carried out in an identical manner to **9a**. HfCl$_4$ (0.98 g, 3.06 mmol) and Li$_2${Me$_2$-Si(C$_5$Me$_4$)(C$_5$H$_3${CHPr^{i}Me})} (**5**) (1.00 g, 3.06 mmol). Yield 0.68 g, 38%. MS electron impact (*m/e* (relative intensity)): 562

(8) [M^+], 519 (18) [M^+ − Pr^i], 483 (100) [M^+ − Pr^i, –Cl]. Anal. Calc. for C$_{21}$H$_{32}$Cl$_2$SiHf: C, 44.48; H, 5.74. Found C, 44.60; H, 5.70%.

Isolated isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.84 (3H), 0.87 (3H) (s, Si*Me$_2$*), 0.98 (3H), 1.05 (3H) (d, CH*Me$_2$*), 1.24 (d, 3H, C*Me*), 1.80 (m, 1H, C*H*Me$_2$), 2.00 (3H), 2.03 (3H), 2.08 (3H), 2.11 (3H) (s, C$_5$*Me$_4$*), 3.12 (d, 1H, C*H*Pr^{i}Me), 5.34 (1H), 5.67 (1H), 6.60 (1H) (m, C$_5$*H$_3$*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −0.3, 0.2 (Si*Me$_2$*), 12.0, 12.4, 14.0, 14.6 (C$_5$*Me$_4$*), 12.6 (C*Me*), 17.3, 21.1, 33.8 (*Pr^i*), 38.7 (Cp*C*), 98.5, 106.2 (*C^1*–Cp), 108.3, 112.7, 121.7, 147.6 (*C$_5$H$_3$*), 124.1, 125.6, 132.0, 134.9 (*C$_5$Me$_4$*).

Second isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.81 (3H), 0.88 (3H) (s, Si*Me$_2$*), 0.75 (3H), 0.89 (3H) (d, CH*Me$_2$*), 0.70 (d, 3H, C*Me*), 1.81 (m, 1H, C*H*Me$_2$), 1.96 (3H), 2.06 (3H), 2.07 (3H), 2.12 (3H) (s, C$_5$*Me$_4$*), 3.00 (d, 1H, C*H*Pr^{i}Me), 5.28 (1H), 5.60 (1H), 6.68 (1H) (m, C$_5$*H$_3$*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −0.2, 0.3 (Si*Me$_2$*), 12.2, 13.9, 14.9, 15.0 (C$_5$*Me$_4$*), 12.4 (C*Me*), 20.3, 25.0, 34.7 (*Pr^i*), 39.6 (Cp*C*), 98.3, 106.9 (*C^1*–Cp), 108.2, 108.9, 110.5, 143.3 (*C$_5$H$_3$*), 120.6, 123.1, 132.7, 134.4 (*C$_5$Me$_4$*).

2.2.11. *[Zr*{*Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$*{*CHPr^iPh*})}*Cl$_2$] (*10a*)

The preparation of **10a** was carried out in an identical manner to **9a**. ZrCl$_4$ (0.60 g, 2.57 mmol) and Li$_2${Me$_2$-Si(C$_5$Me$_4$)(C$_5$H$_3${CHPr^{i}Ph})} (**6**) (1.00 g, 2.57 mmol). Yield 0.73 g, 53%. MS electron impact (*m/e* (relative intensity)): 536 (7) [M^+], 493 (100) [M^+ − Pr^i], 455 (13) [M^+ − Pr^i, –Cl], 365 (7) [M^+ − CHPr^{i}Ph]. Anal. Calc. for C$_{26}$H$_{34}$Cl$_2$SiZr: C, 58.18; H, 6.38. Found C, 58.01; H, 6.41%.

Isolated isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.70 (3H), 0.86 (3H) (s, Si*Me$_2$*), 0.80 (3H), 1.13 (3H) (d, CH*Me$_2$*), 2.49 (m, 1H, C*H*Me$_2$), 1.80 (3H), 2.00 (3H), 2.09 (3H), 2.12 (3H) (s, C$_5$*Me$_4$*), 4.29 (d, 1H, C*H*Pr^{i}Ph), 5.04 (1H), 5.72 (1H), 6.99 (1H) (m, C$_5$*H$_3$*), 7.19 (2H), 7.24 (2H), 7.28 (1H) (m, *Ph*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −0.2, 0.0 (Si*Me$_2$*), 12.4, 12.5, 22.7, 22.8 (C$_5$*Me$_4$*), 15.1, 19.6, 31.3 (*Pr^i*), 51.7 (Cp*C*), 96.7, 105.7 (*C^1*–Cp), 112.0, 113.5, 124.8, 128.1 (*C$_5$H$_3$*), 135.4, 135.7, 142.7, 144.9 (*C$_5$Me$_4$*), 125.9, 127.6, 129.8, 140.9 (*Ph*).

Second isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.88 (3H), 0.89 (3H) (s, Si*Me$_2$*), 0.83 (3H), 0.97 (3H) (d, CH*Me$_2$*), 2.31 (m, 1H, C*H*Me$_2$), 1.95 (3H), 1.96 (3H), 2.02 (3H), 2.11 (3H) (s, C$_5$*Me$_4$*), 4.25 (d, 1H, C*H*Pr^{i}Ph), 5.55 (1H), 5.61 (1H), 6.48 (1H) (m, C$_5$*H$_3$*), 7.00 (2H), 7.22 (2H), 7.26 (1H) (m, *Ph*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −0.3, 0.1 (Si*Me$_2$*), 14.4, 14.5, 19.6, 19.7 (C$_5$*Me$_4$*), 15.0, 19.7, 32.4 (*Pr^i*), 52.0 (Cp*C*), 96.8, 104.6 (*C^1*–Cp), 112.1, 113.4, 124.7, 126.0 (*C$_5$H$_3$*), 135.1, 135.6, 141.0, 144.2 (*C$_5$Me$_4$*), 125.8, 127.4, 130.3, 140.9 (*Ph*).

2.2.12. *[Hf*{*Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$*{*CHPr^iPh*})}*Cl$_2$] (*10b*)

The preparation of **10b** was carried out in an identical manner to **9a**. HfCl$_4$ (0.82 g, 2.57 mmol) and Li$_2${Me$_2$-Si(C$_5$Me$_4$)(C$_5$H$_3${CHPr^{i}Ph})} (**6**) (1.00 g, 2.57 mmol). Yield 0.69 g, 44%. MS electron impact (*m/e* (relative intensity)):

624 (3) [M^+], 581 (17) [$M^+ − Pr^i$], 547 (4) [$M^+ − Ph$], 155 (60) [$M^+ − Pr^i$, $−Me_2Si(C_5Me_4)HfCl_2$]. Anal. Calc. for $C_{26}H_{34}Cl_2SiHf$: C, 50.04; H, 5.49. Found C, 49.84; H, 5.45%.

Isolated isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.70 (3H), 0.86 (3H) (s, Si*Me$_2$*), 0.80 (3H), 1.12 (3H) (d, CH*Me$_2$*), 2.47 (m, 1H, C*H*Me$_2$), 1.87 (3H), 2.08 (3H), 2.12 (3H), 2.15 (3H) (s, C$_5$*Me$_4$*), 4.34 (d, 1H, C*H*Pr^{i}Ph), 5.00 (1H), 5.68 (1H), 7.01 (1H) (m, C$_5$*H$_3$*), 7.19 (2H), 7.24 (2H), 7.26 (1H) (m, *Ph*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −0.3, −0.1 (Si*Me$_2$*), 12.2, 12.3, 22.0, 22.8 (C$_5$*Me$_4$*), 14.8, 19.5, 31.3 (*Pr^i*), 51.6 (Cp*C*), 98.3, 107.8 (*C^1*–Cp), 109.4, 111.1, 121.8, 122.3 (*C$_5$H$_3$*), 133.6, 133.7, 142.6, 143.3 (*C$_5$Me$_4$*), 125.8, 127.5, 129.8, 141.0 (*Ph*).

Second isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.89 (3H), 0.93 (3H) (s, Si*Me$_2$*), 0.83 (3H), 0.97 (3H) (d, CH*Me$_2$*), 2.31 (m, 1H, C*H*Me$_2$), 2.03 (3H), 2.04 (3H), 2.14 (3H), 2.16 (3H) (s, C$_5$*Me$_4$*), 4.32 (d, 1H, C*H*Pr^{i}Ph), 5.57 (1H), 5.60 (1H), 6.40 (1H) (m, C$_5$*H$_3$*), 6.99 (2H), 7.23 (2H), 7.28 (1H) (m, *Ph*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −0.2, 0.0 (Si*Me$_2$*), 14.6, 14.8, 21.7, 21.9 (C$_5$*Me$_4$*), 14.7, 19.0, 32.5 (*Pr^i*), 52.0 (Cp*C*), 98.5, 106.4 (*C^1*–Cp), 110.0, 111.2, 121.7, 122.7 (*C$_5$H$_3$*), 128.0, 133.3, 133.8, 142.5 (*C$_5$Me$_4$*), 126.0, 127.4, 130.3, 141.0 (*Ph*).

2.2.13. [Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3${CHBu^{t}Me})}Cl$_2$] (11a)

The synthesis of **11a** was carried out in an identical manner to **9a**. ZrCl$_4$ (0.68 g, 2.94 mmol) and Li$_2${Me$_2$-Si(C$_5$Me$_4$)(C$_5$H$_3${CHBu^{t}Me})} (**7**) (1.00 g, 2.94 mmol). Yield 0.80 g, 55%. MS electron impact (*m/e* (relative intensity)): 488 (6) [M^+], 429 (27) [$M^+ − Bu^t$], 393 (100) [$M^+ − Bu^t$, $−Cl$]. Anal. Calc. for $C_{22}H_{34}Cl_2SiZr$: C, 54.07; H, 7.01. Found C, 54.33; H, 7.06%.

Isolated isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.81 (3H), 0.91 (3H) (s, Si*Me$_2$*), 0.87 (s, 9H, *Bu^t*), 1.14 (d, 3H, C*Me*), 1.96 (3H), 2.00 (3H), 2.07 (6H) (s, C$_5$*Me$_4$*), 2.80 (q, 1H, C*H*Bu^{t}Me), 5.47 (1H), 5.79 (1H), 6.64 (1H) (m, C$_5$*H$_3$*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −0.8, 0.7 (Si*Me$_2$*), 11.8, 12.7, 14.8, 15.7 (C$_5$*Me$_4$*), 14.0 (C*Me*), 28.2, 34.4 (*Bu^t*), 43.5 (Cp*C*), 97.3, 104.6 (*C^1*–Cp), 111.1, 117.0, 121.7, 149.1 (*C$_5$H$_3$*), 122.7, 130.2, 132.4, 138.0 (*C$_5$Me$_4$*).

Second isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.82 (3H), 0.92 (3H) (s, Si*Me$_2$*), 0.88 (s, 9H, *Bu^t*), 1.33 (d, 3H, C*Me*), 1.89 (3H), 2.05 (3H), 2.10 (6H) (s, C$_5$*Me$_4$*), 2.80 (q, 1H, C*H*Bu^{t}Me), 5.34 (1H), 5.64 (1H), 6.76 (1H) (m, C$_5$*H$_3$*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −0.4, 0.3 (Si*Me$_2$*), 12.2, 12.6, 15.0, 15.3 (C$_5$*Me$_4$*), 13.9 (C*Me*), 28.0, 33.8 (*Bu^t*), 44.2 (Cp*C*), 103.3, 109.7 (*C^1*–Cp), 115.0, 125.1, 128.0, 143.2 (*C$_5$H$_3$*), 127.0, 127.9, 128.9, 134.2 (*C$_5$Me$_4$*).

2.2.14. [Hf{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3${CHBu^{t}Me})}Cl$_2$] (11b)

The synthesis of **11b** was carried out in an identical manner to **9a**. HfCl$_4$ (0.94 g, 2.94 mmol) and Li$_2${Me$_2$-Si(C$_5$Me$_4$)(C$_5$H$_3${CHBu^{t}Me})} (**7**) (1.00 g, 2.94 mmol). Yield 0.71 g, 42%. MS electron impact (*m/e* (relative intensity)): 576 (1) [M^+], 519 (13) [$M^+ − Bu^t$], 483 (23) [$M^+ − Bu^t$, $−Cl$], 207 (51) [$M^+ − Hf(C_5Me_4)Cl_2$]. Anal. Calc. for $C_{22}H_{34}Cl_2SiHf$: C, 45.88; H, 5.95. Found C, 45.52; H, 5.92%.

Isolated isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.80 (3H), 0.90 (3H) (s, Si*Me$_2$*), 0.87 (s, 9H, *Bu^t*), 1.12 (d, 3H, C*Me*), 2.03 (3H), 2.08 (3H), 2.09 (3H), 2.10 (3H) (s, C$_5$*Me$_4$*), 2.79 (q, 1H, C*H*Bu^{t}Me), 5.43 (1H), 5.72 (1H), 6.52 (1H) (m, C$_5$*H$_3$*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −0.8, −0.6 (Si*Me$_2$*), 12.2, 14.0, 16.2, 17.4 (C$_5$*Me$_4$*), 13.3 (C*Me*), 33.4, 34.5 (*Bu^t*), 39.7 (Cp*C*), 96.4, 102.6 (*C^1*–Cp), 113.9, 120.1, 128.2, 154.7 (*C$_5$H$_3$*), 133.8, 133.9, 140.3, 144.8 (*C$_5$Me$_4$*).

Second isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.88 (3H), 0.92 (3H) (s, Si*Me$_2$*), 0.84 (s, 9H, *Bu^t*), 1.20 (d, 3H, C*Me*), 2.03 (3H), 2.06 (3H), 2.07 (3H), 2.12 (3H) (s, C$_5$*Me$_4$*), 2.78 (q, 1H, C*H*Bu^{t}Me), 5.27 (1H), 5.59 (1H), 6.68 (1H) (m, C$_5$*H$_3$*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −0.7, 0.2 (Si*Me$_2$*), 11.5, 14.2, 16.4, 17.8 (C$_5$*Me$_4$*), 13.6 (C*Me*), 33.3, 34.3 (*Bu^t*), 40.5 (Cp*C*), 99.8, 110.1 (*C^1*–Cp), 115.1, 116.5, 128.4, 149.3 (*C$_5$H$_3$*), 131.8, 135.8, 141.6, 144.3 (*C$_5$Me$_4$*).

2.2.15. [Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3${CHBu^{t}Ph})}Cl$_2$] (12a)

The preparation of **12a** was carried out in an identical manner to **9a**. ZrCl$_4$ (0.57 g, 2.44 mmol) and Li$_2${Me$_2$-Si(C$_5$Me$_4$)(C$_5$H$_3${CHBu^{t}Ph})} (**8**) (1.00 g, 2.44 mmol). Yield 0.52 g, 39%. MS electron impact (*m/e* (relative intensity)): 550 (4) [M^+], 493 (100) [$M^+ − Bu^t$], 455 (20) [$M^+ − Bu^t$, $−Ph$]. Anal. Calc. for $C_{27}H_{36}Cl_2SiZr$: C, 58.88; H, 6.59. Found C, 58.21; H, 6.51%.

Isolated isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.67 (3H), 0.84 (3H) (s, Si*Me$_2$*), 1.12 (s, 9H, *Bu^t*), 1.72 (3H), 1.99 (3H), 2.08 (3H), 2.09 (3H) (s, C$_5$*Me$_4$*), 4.36 (s, 1H, C*H*Bu^{t}Ph), 4.89 (1H), 5.71 (1H), 7.13 (1H) (m, C$_5$*H$_3$*), 7.18 (2H), 7.21 (2H), 7.26 (1H) (m, *Ph*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −0.2, 0.0 (Si*Me$_2$*), 12.4, 12.5, 14.9, 15.1 (C$_5$*Me$_4$*), 29.3, 34.6 (*Bu^t*), 56.3 (Cp*C*), 96.4, 104.8 (*C^1*–Cp), 111.8, 115.1, 125.7, 127.2 (*C$_5$H$_3$*), 135.8, 135.9, 144.3, 144.4 (*C$_5$Me$_4$*), 124.7, 125.4, 125.6, 137.9 (*Ph*).

Second isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.82 (3H), 0.88 (3H) (s, Si*Me$_2$*), 0.94 (s, 9H, *Bu^t*), 1.90 (3H), 1.94 (3H), 1.96 (3H), 2.01 (3H) (s, C$_5$*Me$_4$*), 4.05 (s, 1H, C*H*Bu^{t}Ph), 5.55 (1H), 5.63 (1H), 6.99 (1H) (m, C$_5$*H$_3$*), 7.22 (2H), 7.28 (2H), 7.46 (1H) (m, *Ph*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −0.1, 0.1 (Si*Me$_2$*), 12.0, 12.7, 15.2, 15.9 (C$_5$*Me$_4$*), 29.4, 36.0 (*Bu^t*), 57.8 (Cp*C*), 96.7, 104.1 (*C^1*–Cp), 111.0, 115.7, 125.9, 127.8 (*C$_5$H$_3$*), 129.8, 136.4, 139.9, 140.3 (*C$_5$Me$_4$*), 122.4, 124.5, 125.7, 134.8 (*Ph*).

2.2.16. [Hf{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3${CHBu^{t}Ph})}Cl$_2$] (12b)

The preparation of **12b** was carried out in an identical manner to **9a**. HfCl$_4$ (0.78 g, 2.44 mmol) and Li$_2${Me$_2$-Si(C$_5$Me$_4$)(C$_5$H$_3${CHBu^{t}Ph})} (**8**) (1.00 g, 2.44 mmol). Yield 0.48 g, 31%. MS electron impact (*m/e* (relative intensity)): 638 (2) [M^+], 581 (28) [$M^+ − Bu^t$], 505 (2) [$M^+ − Bu^t$, $−Ph$], 461 (23) [$M^+ − Bu^t$, $−Ph$, $−Cl$], 211 (49) [$M^+ − Me_2Si(C_5Me_4)HfCl_2$]. Anal. Calc. for $C_{27}H_{36}Cl_2SiHf$: C, 50.82; H, 5.69. Found C, 50.71; H, 5.64%.

Isolated isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.88 (3H), 0.93 (3H) (s, Si*Me$_2$*), 1.10 (s, 9H, *Bu^t*), 1.76 (3H), 2.06 (3H),

2.09 (3H), 2.10 (3H) (s, C$_5$*Me*$_4$), 4.38 (s, 1H, C*H*Bu^{t}Ph), 4.86 (1H), 5.66 (1H), 7.03 (1H) (m, C$_5$*H*$_3$), 7.18 (2H), 7.24 (2H), 7.33 (1H) (m, *Ph*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −0.2, −0.1 (Si*Me*$_2$), 12.2, 14.3, 14.6, 14.8 (C$_5$*Me*$_4$), 29.3, 34.7 (*Bu^t*), 56.2 (Cp*C*), 98.0, 103.1 (*C*^{1}–Cp), 109.5, 112.5, 122.0, 126.1 (*C*$_5$*H*$_3$), 133.5, 133.7, 142.0, 144.3 (*C*$_5$*Me*$_4$), 125.0, 125.7, 127.1, 135.1 (*Ph*).

Second isomer. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.81 (3H), 0.88 (3H) (s, Si*Me*$_2$), 0.93 (s, 9H, *Bu^t*), 1.96 (3H), 1.98 (3H), 2.03 (3H), 2.04 (3H) (s, C$_5$*Me*$_4$), 4.06 (s, 1H, C*H*Bu^{t}Ph), 5.49 (1H), 5.52 (1H), 6.92 (1H) (m, C$_5$*H*$_3$), 7.20 (2H), 7.28 (2H), 7.47 (1H) (m, *Ph*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ −0.1, 0.3 (Si*Me*$_2$), 12.0, 12.2, 14.7, 15.0 (C$_5$*Me*$_4$), 29.2, 36.1 (*Bu^t*), 57.6 (Cp*C*), 98.3, 105.1 (*C*^{1}–Cp), 111.2, 113.3, 117.0, 117.8 (*C*$_5$*H*$_3$), 132.9, 134.0, 141.3, 142.3 (*C*$_5$*Me*$_4$), 124.8, 125.9, 126.8, 140.9 (*Ph*).

2.3. Polymerization reactions

2.3.1. Polymerization of ethylene

The zirconocene catalyst (6 μmol), MAO (10% in toluene) (6000 μmol) and toluene (200 mL) were mixed together for 15 min in a 1 L glass autoclave. The N$_2$ pressure inside the autoclave was reduced by applying vacuum. Ethylene pressure of 2 bar was then applied and maintained to the autoclave and stirring of the mixture commenced (1000 rpm). After exactly 15 min, stirring was halted and the ethylene pressure released. Excess MAO was then destroyed by adding cautiously a mixture of methanol/HCl (90:10). The polymer was isolated by filtration and washed with ethanol and dried under vacuum at 90 °C for 16 h.

2.3.2. Polymerization of propylene

The zirconocene catalyst (6 μmol), MAO (10% in toluene) (12,000 μmol) and toluene (200 mL) were mixed together for 15 min in a 1 L glass autoclave. The N$_2$ pressure inside the autoclave was reduced by applying vacuum. Propylene pressure of 2.5 bar was then applied and maintained to the autoclave and stirring of the mixture commenced (1000 rpm). After exactly 30 min, stirring was halted and the propylene pressure released. Solvent was then removed under reduced pressure and methanol (200 mL) added. The mixture was stirred for 16 h and then filtered to isolate the polymer which was washed with ethanol and dried under vacuum at 25 °C for 16 h.

2.4. X-ray data collection

2.4.1. [Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3${CHBu^{t}Me})}Cl$_2$] (11a)

Data were collected on a Bruker SMART CCD-based diffractometer operating at 50 kV and 30 mA, using ω/2θ scan-technique. Absorption corrections were applied using the SAD-ABS program (maximum and minimum transmission coefficients 0.8122 and 0.7539) [22]. The structure was solved using the Bruker SHELXTL Structure Determination Package [23] by direct methods and refined by full-matrix least-squares methods on F^2. All non-hydrogen atoms were refined anisotropically.

Table 1
Crystal data and structure refinement details for **11a** and **12a**

	11a	**12a**
Formula	C$_{22}$H$_{34}$Cl$_2$SiZr	C$_{34}$H$_{44}$Cl$_2$SiZr
fw	488.70	642.90
T (K)	298(2)	100(2)
Cryst. syst.	Monoclinic	Triclinic
Space group	P2(1)/c	P-1
a (Å)	11.4152(4)	9.3673(2)
b (Å)	9.9214(3)	13.3628(3)
c (Å)	21.1226(7)	14.2358(3)
$α$ (°)		116.5720(10)
$β$ (°)	99.9110(10)	96.0100(10)
$γ$ (°)		95.6690(10)
V (Å^3)	2356.53(13)	1563.58(6)
Z	4	2
Dc (g cm^{-3})	1.377	1.366
$μ$ (mm^{-1})	0.749	4.968
$F(0\,0\,0)$	1016	672
Cryst. dimens. (mm)	0.40 × 0.38 × 0.29	0.10 × 0.08 × 0.04
$θ$ range (°)	1.81–26.37	3.52–70.57
$h\,k\,l$ ranges	−14 ≤ h ≤ 6, −11 ≤ k ≤ 12, −254 ≤ l ≤ 26	−11 ≤ h ≤ 10, −16 ≤ k ≤ 16, −16 ≤ l ≤ 17
Data/parameters	4805/235	5664/353
Goodness-of-fit on F^2	1.018	0.993
Final R indices [$I > 2σ(I)$]	$R_1 = 0.0465$, $wR_2 = 0.1026$	$R_1 = 0.0386$, $wR_2 = 0.0914$
R indices (all data)	$R_1 = 0.0303$, $wR_2 = 0.0686$	$R_1 = 0.0487$, $wR_2 = 0.0965$
Largest diff. peak and hole (e Å^{-3})	0.334/−0.340	1.035/−0.552

$R_1 = \Sigma \|F_0| - |F_c\|/\Sigma|F_0|$; $wR_2 = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{0.5}$.

Hydrogen atoms were included in calculated positions, and refined in the riding mode. Weights were optimized in the final cycles. Crystallographic data are given in Table 1.

2.4.2. [Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3${CHBu^{t}Ph})}Cl$_2$] (12a)
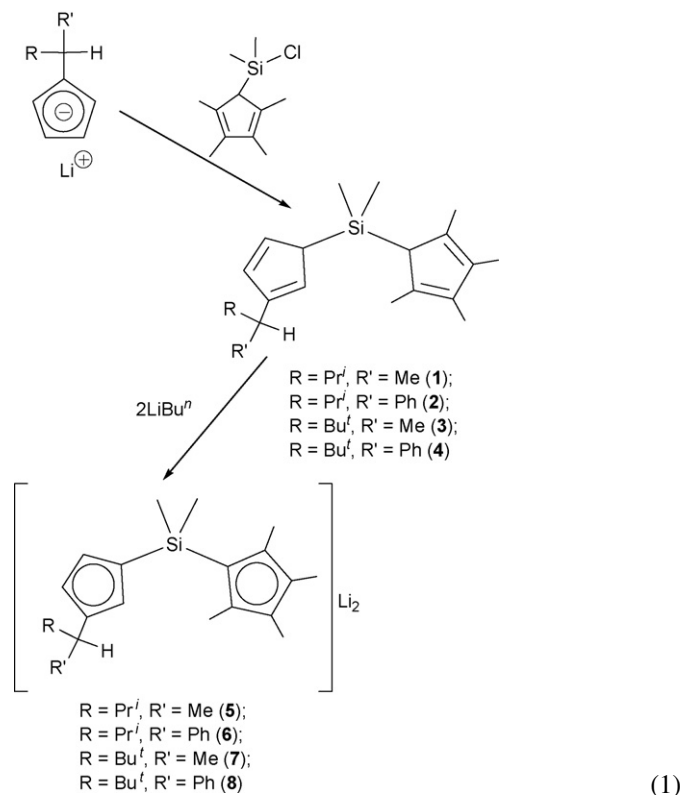
Data were collected on a Bruker SMART CCD-based diffractometer operating at 50 kV and 100 mA, using ω/2θ scan-technique. Absorption corrections were applied using the SAD-ABS program (maximum and minimum transmission coefficients 0.820 and 0.652) [22]. The structure was solved using the SHELXTL Structure Determination Package [23] by direct methods and refined by full-matrix least-squares methods on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions, and refined in the riding mode. Weights were optimized in the final cycles. Crystallographic data are given in Table 1.

3. Results and discussion

3.1. Synthesis and characterization of ansa-precursors

The preparation of the asymmetrically substituted *ansa* ligand precursors, Me$_2$Si(C$_5$Me$_4$H)(C$_5$H$_4${CHRR′}) (R = Pr^i, R′ = Me (**1**); R = Pr^i, R′ = Ph (**2**); R = Bu^t, R′ = Me (**3**); R = Bu^t, R′ = Ph (**4**)), was achieved by the reaction of Li{C$_5$H$_4$(CHRR′)}

with Me$_2$Si(C$_5$Me$_4$H)Cl following previously reported synthetic protocols (Eq. (1)) [10]. **1–4** were isolated as mixtures of the double bond position isomers, with one isomer being predominant as confirmed by ^{1}H NMR spectroscopy. In addition, **1–4** were characterized by electron impact mass spectrometry (see Section 2). The *ansa*-bis(cyclopentadiene) compounds, **1–4**, were lithiated in the traditional manner with *n*-butyllithium to give the dilithium derivatives, Li$_2$\{Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3$\{CHRR′\})\} (R = Pr^i, R′ = Me (**5**); R = Pr^i, R′ = Ph (**6**); R = Bu^t, R′ = Me (**7**); R = Bu^t, R′ = Ph (**8**)) (Eq. (1)):

R = Pr^i, R' = Me (**1**);
R = Pr^i, R' = Ph (**2**);
R = Bu^t, R' = Me (**3**);
R = Bu^t, R' = Ph (**4**)

R = Pr^i, R' = Me (**5**);
R = Pr^i, R' = Ph (**6**);
R = Bu^t, R' = Me (**7**);
R = Bu^t, R' = Ph (**8**)

(1)

5–8 were characterized by ^{1}H and ^{13}C\{^{1}H\} NMR spectroscopy (see Section 2). In the ^{1}H NMR spectra of **5** and **6**, two doublets and a multiplet were observed for the two diastereotopic methyl groups and proton of the *iso*-propyl fragment, respectively. For **5**, a multiplet at 2.45 ppm and a doublet at 1.09 ppm, were observed, corresponding to the proton and methyl group bonded to the chiral carbon atom of cyclopentadienyl substituent, respectively. For **6**, the proton bonded to the chiral carbon atom gave a doublet signal at 3.31 ppm. Three multiplets (between 6.9 and 7.3 ppm) were recorded for the phenyl moiety. The *tert*-butyl signal in **7** and **8** was observed in the ^{1}H NMR spectra as a singlet at 0.9 ppm. For **7**, a quadruplet, at 2.42 ppm, and a doublet, at 1.15 ppm, were observed corresponding to the proton and methyl group bonded to the chiral carbon atom of cyclopentadienyl substituent, respectively. For **8**, the proton bonded to the chiral carbon atom gave a singlet signal at 3.64 ppm and three multiplets (between 7.0 and 7.5 ppm) were assigned to the phenyl moiety. In addition, the cyclopentadienyl ring protons gave, in the ^{1}H NMR spectra of

5–8, three multiplets between 5.6 and 6.0 ppm. The resolution of the spectra and the small difference in the chemical shift meant the expected four signals for the cyclopentadienyl ring methyl substituents were observed only as two singlets (ca. 1.87 and 2.07 ppm). However, in the ^{13}C\{^{1}H\} NMR spectra of **5–8**, four signals were observed for the methyl carbons (between 10 and 14 ppm). An additional singlet was assigned, in the ^{1}H NMR spectra, to the *ansa* bridge methyl groups (ca. 0.4 ppm). The ^{13}C\{^{1}H\} NMR spectra for **5–8** showed the expected signals (see Section 2).

3.2. Synthesis and characterization of ansa-metallocene complexes

The reaction of **5–8** with either ZrCl$_4$ or HfCl$_4$, yielded the corresponding *ansa*-metallocene(IV) dichloride complexes, [M\{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$\{CHRR′\})\}Cl$_2$] (R = Pr^i, R′ = Me (**9**); R = Pr^i, R′ = Ph (**10**); R = Bu^t, R′ = Me (**11**); R = Bu^t, R′ = Ph (**12**); M = Zr (**a**), Hf (**b**)) (Eq. (2)):

R = Pr^i, R' = Me (**9**);
R = Pr^i, R' = Ph (**10**);
R = Bu^t, R' = Me (**11**);
R = Bu^t, R' = Ph (**12**)

M = Zr (a); Hf (b)

(2)
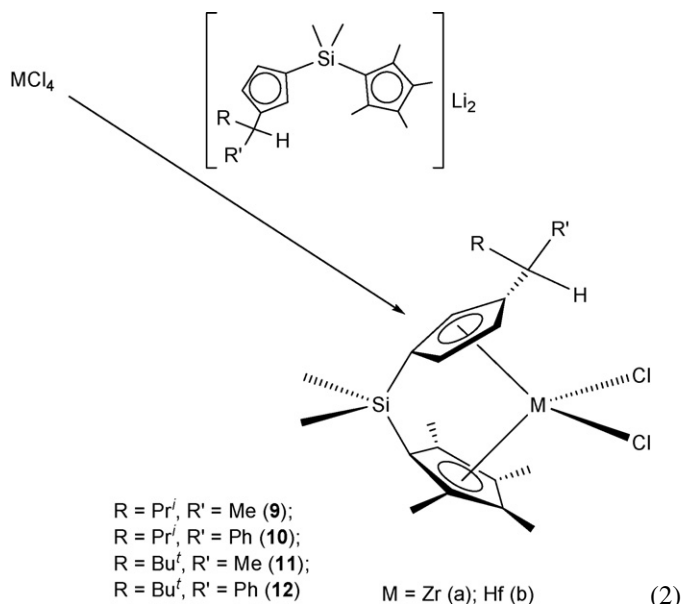
9–12 were isolated as crystalline solids and characterized spectroscopically. There exists planar chirality about the monosubstituted cyclopentadienyl ring in **9–12** and this combined with the presence of a chiral centre in the bulky substituent gives rise to the possibility of the formation of two diastereoisomers (Fig. 1). NMR spectroscopy confirmed the presence of the two diastereoisomers in the isolated products. The separation of one of the isomers from the mixture was achieved by fractional recrystallization. The ^{1}H NMR spectra for the diastereoisomers of **9–12** gave three multiplets for the protons of the monosubstituted C$_5$ ring (between 4.9 and 7.1 ppm), four singlets for the methyl groups of the tetramethyl-substituted C$_5$ ring (between 1.8 and 2.2 ppm), and two singlets corresponding to the methyl groups of the SiMe$_2$ bridging unit (between 0.6 and 0.9 ppm). Additional signals were observed for the chiral alkyl substituent with similar chemical shifts and identical spectral patterns to those observed in the lithium precursors **5–8**. The ^{13}C\{^{1}H\}
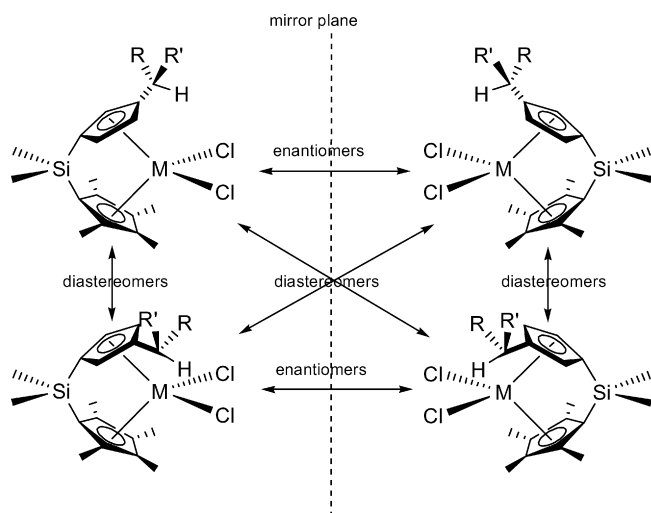
Fig. 1. Stereoisomers for **9**–**12**.

NMR spectra of **9**–**12** showed the expected signals (see Section 2).

The molecular structures, of one of the diastereomers, of **11a** and **12a** were established by single-crystal X-ray diffraction studies. The two enantiomers, related by symmetry, were located in the asymmetric unit. The molecular structures and atomic numbering schemes of one of the enantiomers are shown in Figs. 2 and 3. The absolute configuration due to the planar chirality of the C_5 ring is defined by the substituent arrangement
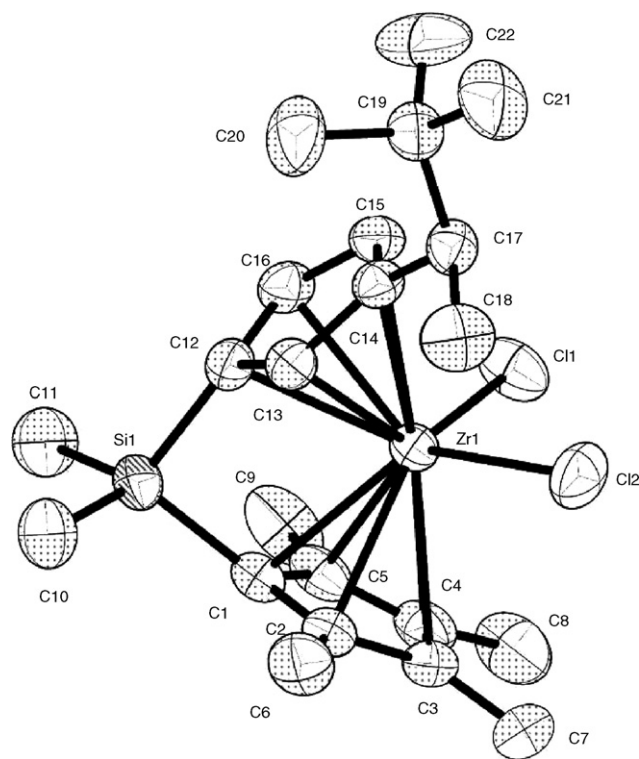

Fig. 3. Molecular structure and atom-labeling scheme for $R,R'_{(cp)}$-$[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CHBu^tPh\})\}Cl_2]$ (**12a**), with thermal ellipsoids at 50% probability.

about the C^3 carbon of the cyclopentadienyl moiety. In the case of **12a**, a toluene molecule was also located in the asymmetric unit. Selected bond lengths and angles for **11a** and **12a** are given in Table 2.

Table 2
Selected bond lengths (Å) and angles (°) for **11a** and **12a**

	11a	**12a**
Zr–Cent(1)	2.220	2.215
Zr–Cent(2)	2.227	2.232
av Zr–C[C(1)–C(5)][a]	2.528	2.522
av Zr–C[C(12)–C(16)][a]	2.532	2.540
Zr–Cl(1)	2.4424(5)	2.4420(7)
Zr–Cl(2)	2.4177(6)	2.4222(8)
Cent(1)–Zr–Cent(2)	126.8	127.60
Si(1)–C(1)–Cent(1)	163.0	163.39
Si(1)–C(12)–Cent(2)	162.7	162.72
C(1)–Si(1)–C(12)	94.25(8)	94.11(13)
Cl(1)–Zr–Cent(1)	106.3	106.9
Cl(1)–Zr–Cent(2)	106.5	106.35
Cl(2)–Zr–Cent(1)	107.5	105.34
Cl(2)–Zr–Cent(2)	109.2	106.48
Cl(1)–Zr–Cl(2)	96.03(2)	102.37(3)
C(17)–C(14)–Cent(2)	174.9	170.26
C(17)–C(18)–Cent(3)		176.92

Cent(1) and Cent(2) are the centroids of C(1)–C(5) and C(12)–C(16), respectively. For **12a** Cent(3) is the centroid of C(18)–C(23).

[a] Average bond distance between Zr(1) and the carbon atoms of the C_5 ring of the corresponding cyclopentadienyl moiety.

Fig. 2. Molecular structure and atom-labeling scheme for $R,S'_{(cp)}$-$[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\{CHBu^tMe\})\}Cl_2]$ (**11a**), with thermal ellipsoids at 50% probability.

Table 3
Selected structural data of some *ansa*-zirconocene complexes

Complex	Zr–Cp (Å)[a]	Zr–Cl (Å)	Cp–Zr–Cp (°)	Cl–Zr–Cl (°)	$C_{(cp)}$–Si–$C_{(cp)}$ (°)	Reference
$[Zr\{Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)\}Cl_2]$	2.202 Cp, 2.198 Cp*	2.451(1)	128.10	104.60(7)	95.2(2)	[10]
$[Zr\{Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3Me)\}Cl_2]$	2.194 Cp^R, 2.184 Cp*	2.414(4)	126.25	101.1(2)	92.4(8)	[10]
$[Zr\{Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3Et)\}Cl_2]$	2.214 Cp^R, 2.207 Cp*	2.429(4)	126.5	100.4(2)	93.3(7)	[11]
$[Zr\{Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3Pr^i)\}Cl_2]$	2.223 Cp^R, 2.230 Cp*	2.429	126.9	98.2(1)	94.2(2)	[11]
R-$[Zr\{Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3\{menthyl\})\}Cl_2]$		2.419	126.6	98.6(2)	93.6(4)	[8,9]
R,S'-$[Zr\{Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3\{CHBu^tMe\})\}Cl_2]$ (**11a**)	2.227 Cp^R, 2.220 Cp*	2.4301	126.8	96.03(2)	94.25(8)	This work
R,R'-$[Zr\{Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3\{CHBu^tPh\})\}Cl_2]$ (**12a**)	2.232 Cp^R, 2.215 Cp*	2.4321	127.60	102.37(3)	94.11(13)	This work
$[Zr\{Me_2Si(\eta^5-C_5Me_4)_2\}Cl_2]$	2.329	2.4334(7)	128.6	99.28(3)	95.7(1)	[24,25]

[a] Cp* refers to the C_5Me_4 moiety; Cp^R refers to the C_5H_3R moiety.

The structural determinations of **11a** and **12a** reveal, in the absence of any symmetry planes or axes, the C_1 symmetric nature of the *ansa*-metallocene complexes. In both structures the usual bent metallocene conformation was observed with the geometry around the metal atom being pseudo-tetrahedral as defined by the two chlorine atoms and the two cyclopentadienyl moieties. The *ansa* ligand chelates the zirconium atom and both C_5 rings are bound to the metal in an η^5 mode. The centroids of the C_5 rings form an angle with the zirconium atom of 126.8° **11a** and 127.60° **12a**, which are typical values for dichloride group four *ansa*-metallocene complexes. The chiral carbon atom (C17) of the alkyl substituent is located, 5.1° for **11a**, and 9.74° for **12a**, out of the plane defined by the cyclopentadienyl unit. The bulky chiral substituent is situated more or less above one of the chlorine atoms (dihedral angle θ Cl(2)–Zr···C(14)–C(17) 2.9(2)° for **11a** and −17.2(2)° for **12a**) and should therefore be influential in controlling the coordination mode of the olefin monomer at this site during polymerization. Selected structural data of **11a** and

12a can be compared with similar *ansa*-zirconocene complexes using Table 3.

3.3. Polymerization of ethylene

The polymerization of ethylene using the isolated diastereomer of the zirconium derivatives as catalyst with a MAO cocatalyst–metal catalyst ratio of 1000:1 has been carried out. The polymerization experiments were conducted at 20 °C and at olefin pressure of 2 bar during 15 min. Polymerization was also carried out with the reference compound $[Zr(\eta^5-C_5H_5)_2Cl_2]$ under the same experimental conditions. The catalytic activities and polymer molecular weight and distribution values are given in Table 4. The hafnium derivatives **9b**–**12b** were also tested but gave very low catalytic activities.

The catalytic activities for the *ansa*-zirconocene complexes, **9a**–**12a**, are all slightly lower than the reference compound $[Zr(\eta^5-C_5H_5)_2Cl_2]$ except for **11a** which exhibited an activity

Table 4
Ethylene polymerization results for **9a**–**12a** and $[Zr(\eta^5-C_5H_5)_2Cl_2]$[a,b]

Catalyst	Activity[b]	M_w (g mol^{-1})	M_w/M_n
$[Zr(\eta^5-C_5H_5)_2Cl_2]$	1730	275050	3.0
$[Zr\{Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3\{CHPr^iMe\})\}Cl_2]$ (**9a**)	1367	150490	2.7
$[Zr\{Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3\{CHPr^iPh\})\}Cl_2]$ (**10a**)	1500	158970	3.0
$[Zr\{Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3\{CHBu^tMe\})\}Cl_2]$ (**11a**)	4720	153240	2.9
$[Zr\{Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3\{CHBu^tPh\})\}Cl_2]$ (**12a**)	1233	162610	3.2

[a] At 20 °C, 2 bar monomer pressure, 200 mL toluene, [Al] = 3×10^{-2} mol L^{-1}, [Zr] = 3×10^{-5} mol L^{-1}, t_{Pol} = 15 min.
[b] In kg Pol (mol Zr h)$^{-1}$.

Table 5
Propylene polymerization results for **9a**–**12a** and $[Zr(\eta^5-C_5H_5)_2Cl_2]$[a,b]

Catalyst	Activity[b]	M_w (g mol^{-1})	M_w/M_n	[mmmm] (%)
$[Zr(\eta^5-C_5H_5)_2Cl_2]$	565	204800	3.2	3.5
$[Zr\{Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3\{CHPr^iMe\})\}Cl_2]$ (**9a**)	550	218320	3.8	60.5
$[Zr\{Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3\{CHPr^iPh\})\}Cl_2]$ (**10a**)	557	221610	3.6	56.1
$[Zr\{Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3\{CHBu^tMe\})\}Cl_2]$ (**11a**)	613	198570	3.3	65.0
$[Zr\{Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3\{CHBu^tPh\})\}Cl_2]$ (**12a**)	350	203320	3.2	54.9

[a] At 20 °C, 2.5 bar monomer pressure, 200 mL toluene, [Al] = 6×10^{-2} mol L^{-1}, [Zr] = 3×10^{-5} mol L^{-1}, t_{Pol} = 30 min.
[b] In kg Pol (mol Zr h)$^{-1}$.

Table 6
Pentad distribution, calculated from $^{13}C\{^1H\}$ NMR spectroscopy, for polypropylenes synthesized from **9a** to **12a**

Catalyst	[mmmm] (%)	[mmmr] (%)	[rmmr] (%)	[mmrr] (%)	[mmrm] + [rmrr] (%)	[mrmr] (%)	[rrrr] (%)	[mrrr] (%)	[mrrm] (%)
[Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$\{CHPr^{i}Me\})}Cl$_2$] (**9a**)	60.5	11.8	2.4	7.8	5.2	3.2	2.2	2.8	4.1
[Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$\{CHPr^{i}Ph\})}Cl$_2$] (**10a**)	56.1	12.3	2.9	8.8	7.2	3.5	2.0	2.9	4.3
[Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$\{CHBu^{t}Me\})}Cl$_2$] (**11a**)	65.0	12.5	1.9	8.0	4.5	1.4	1.6	1.1	4.0
[Zr{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$\{CHBu^{t}Ph\})}Cl$_2$] (**12a**)	54.9	12.9	3.8	9.1	6.5	3.9	2.4	2.1	4.4

nearly three times greater than the reference compound. The polymer molecular weights are of the order of 150,000.

3.4. Polymerization of propylene

The polymerization of propylene using the isolated diastereomer of the zirconium derivatives with a MAO cocatalyst–metal catalyst ratio of 2000:1 has been carried out. The polymerization experiments were conducted at 20 °C and at olefin pressure of 2.5 bar during 30 min. Polymerization was also carried out with the reference compound [Zr(η^5-C$_5$H$_5$)$_2$Cl$_2$] under the same experimental conditions. The catalytic activities, polymer molecular weight and distribution values and tacticity are given in Table 5. Pentad distribution percentages are given in Table 6. The hafnium derivatives **9b–12b** were also tested but gave very low catalytic activities.

The catalytic activities for the *ansa*-zirconocene complexes, **9a–12a**, are all of the same order to that recorded for the reference compound [Zr(η^5-C$_5$H$_5$)$_2$Cl$_2$] except **12a** whose activity is somewhat lower. The polymer molecular weights are of the order of 200,000.

The isotacticity of the polymers was measured by the pentad method using $^{13}C\{^1H\}$ NMR spectroscopy. The [mmmm] pentad for the *ansa*-metallocene catalysts, **9a–12a**, were of the order of 60% and are comparable (if not somewhat lower) than those reported previously for similar C_1 symmetric complexes [8,9,11].
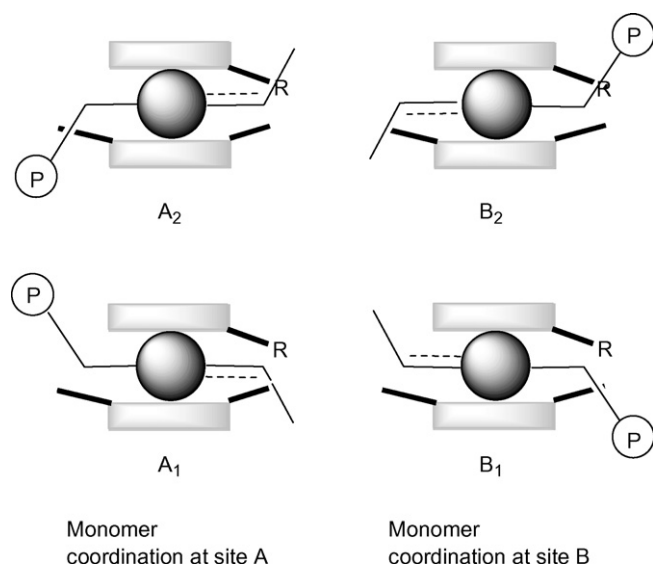

Fig. 4. Diastereomeric intermediates in the polymerization of propylene.
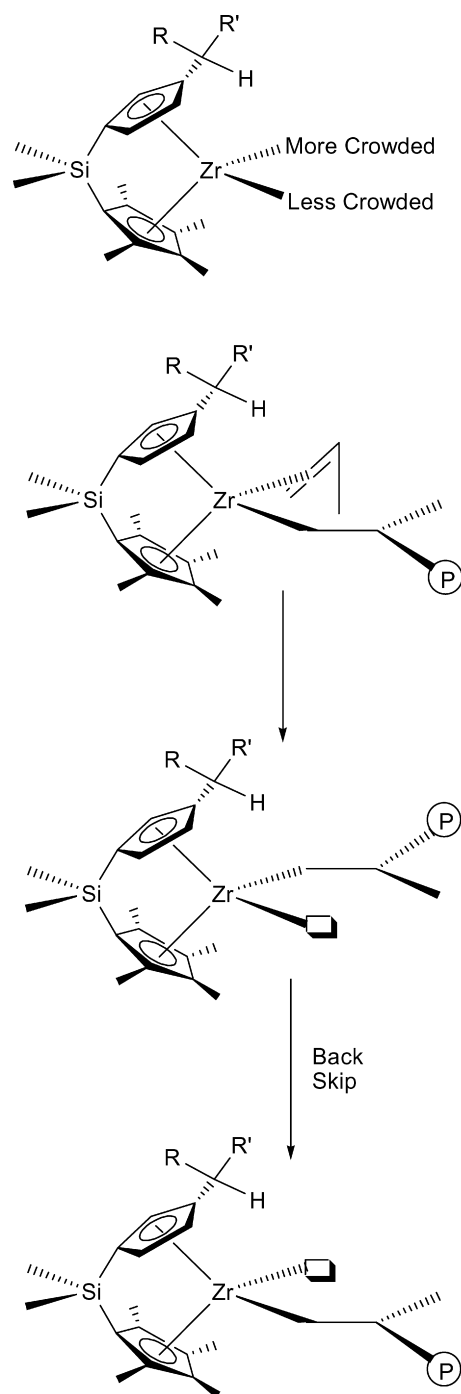

Fig. 5. Polymer chain back-skip mechanism in the *ansa*-zirconocene complexes **9a–12a**.

A Cossee–Arlman site control mechanism can be used to explain the stereoselectivity of the C_1 catalysts, **9a–12a**. During the polymerization of propylene, four possible diastereomeric intermediates (two at each binding site) are possible. The two binding sites A and B can be considered as isoselective with the growing polymer chain being preferentially located in the less sterically hindered positions, intermediates A1 and B1 (see Fig. 4). Thus, and in a similar way to that predicted and observed for C_2 *ansa*-metallocene catalysts [26], isotactic polypropylene should be produced.

A back-skip mechanism may alternatively be applied to explain the stereoselectivity of **9a–12a** in the polymerization of propylene. Morokuma proposed that the presence of a bulky alkyl cyclopentadienyl β-substituent prohibits the growing polymer chain to be situated in the more crowded position [27]. In the absence of monomer molecule, as probably occurs at the end of each insertion step, the steric pressure imposed by the ligand may force the growing chain to skip back to the less crowded position. Insertion, therefore, occurs with the same relative disposition of the monomer and the growing polymer chain and thus leads to isotactic polypropylene (see Fig. 5). Several examples of the back-skip mechanism in the polymerization of propylene have been reported [9,11,28–30].

The pentad distribution percentages for **9a–12a** are in agreement with enantiamorphic site control in the stereoselective polymerization. Isolated stereoerrors in site control polymerization should produce [rr] triads and give relative triad distributions of [mr] ≈ 2[rr]; and relative pentad distributions of [mmmr] ≈ [mmrr] ≈ 2[mrrm] [31].

4. Conclusions

We have prepared new group 4 *ansa*-metallocene complexes containing bulky chiral substituents. The zirconium derivatives have proved to be active as catalysts in the polymerization of ethylene and propylene. The stereoselective polymerization of propylene with the *ansa*-metallocene catalysts gave polymers with moderate isotacticity. The rational design of the catalyst should open up the possibility of modulating the properties of polypropylene.

5. Supplementary material

Crystallographic data for the structural analysis of **11a** and **12a** have been deposited with the Cambridge Crystallographic Data Centre, CCDC-611901 & 611902. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

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