Doubly [SiMe$_2$]-bridged C$_s$- and C$_{2v}$-symmetric zirconocene catalysts for propylene polymerization. Synthesis and polymerization characteristics

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Abstract

The C$_s$- and C$_{2v}$-symmetric doubly dimethylsilylene-bridged zirconocene complexes (Me$_2$Si)$_2$\{η^5-C$_5$H$_2$-4-CHMe$_2$\}\{η^5-C$_5$H-3,5-(SiMe$_3$)$_2$\}ZrCl$_2$, **6a**, and (Me$_2$Si)$_2$\{η^5-C$_5$H-3,5-(CHMe$_2$)$_2$\}$_2$ZrCl$_2$, **6b**, have been synthesized by reaction of corresponding dilithio ligand salts with ZrCl$_4$ in CH$_2$Cl$_2$. When activated with methyl aluminoxane, C$_s$-symmetric zirconocene **6a** catalyzes the polymerization of propylene (liquid propylene, 0°C) to yield a syndiotactic polymer of Mw = 1,000,000 and *rrrr*% = 75.4. By contrast, C$_{2v}$-symmetric zirconocene **6b** displays a low activity and affords an atactic polymer. © 1998 Elsevier Science B.V.

1. Introduction

Stereorigid *ansa*-metallocenes are being actively investigated as stereospecific olefin polymerization catalysts [1–4]. Several types of C$_2$-symmetric *ansa*-metallocenes having a single alkylidene or silylene linker are capable of promoting highly isospecific polymerizations of propylene when combined with methylaluminoxane (MAO) or other types of cocatalyst [1–4]. Moreover, syndiospecific propylene polymerization has been described by Ewen, Jones, Razavi and Ferrara using singly-linked, C$_s$-symmetric metallocenes, e.g., Me$_2$C(η^5-C$_5$H$_4$)($''\eta^3$-$''$C$_{13}$H$_8$)ZrCl$_2$/MAO [5–7]. Although many variations of this ligand combination have been examined, high syndiospecificity is maintained when only relatively minor modifications of cyclopentadienyl and fluorenyl framework are made [8–15].

Doubly-bridged *ansa*-metallocenes, synthesized relatively recently [16–25], may offer new opportunities as olefin polymerization catalysts.

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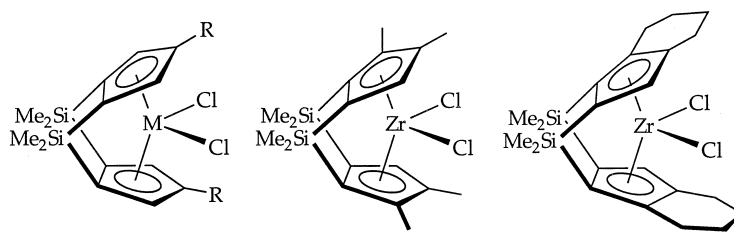
(M = Ti, Zr; R = H, CMe$_3$, SiMe$_3$)

While their potential as Ziegler–Natta catalysts has yet to be fully established, they have been shown to be highly active in ethylene polymerizations, when combined with MAO. Their low activities for propylene polymerizations have been attributed to unfavorable steric interactions between the cyclopentadienyl substituents in the 4-positions of both cyclopentadienyl ligands with the α-olefin substituent. Hence, the ligand substituents for most of those doubly linked metallocenes effectively block coordination of olefins other than ethylene [1–4].

Me$_2$C(η^5-C$_5$H$_4$)($''\eta^3$-$''$C$_{13}$H$_8$)ZrCl$_2$/MAO system, although the activity of a metallocene catalyst, i.e. amount of polymer produced/unit time, varies considerably with temperature, Al/Zr ratio, propylene pressure, as well as with less predictable factors such as the age of methylaluminoxane, so that a direct comparison is often difficult [26].
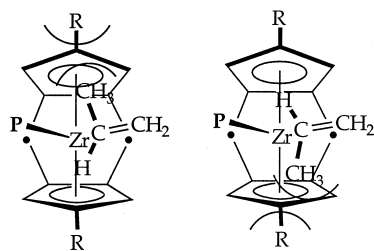
(P = polymer chain; • = -SiMe$_2$-)
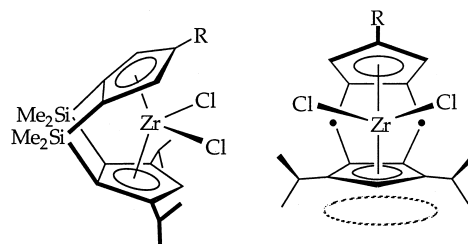
1 (R = CHMe$_2$)

More recently, our group reported that the doubly [SiMe$_2$]-linked, C$_s$-symmetric {Me$_2$Si)$_2$ (η^5-C$_5$H$_2$-4-R}{η^5-C$_5$H-3,5-(CHMe$_2$)$_2$} ZrCl$_2$ (R = CHMe$_2$, 1) and MAO produce highly syndiotactic polypropylene (rrrr% > 98.9) with activities that are comparable to the original

The key design features, in addition to C$_s$ symmetry, are cyclopentadienyls of differing size with the larger cyclopentadienyl having steric bulk flanking the metallocene wedge with an open region in center. Thus, these zirconocenes differ from previous doubly-linked zirconocenes in that they permit alternating enantiospecific approach of α-olefins by accommodating the olefin substituent in the open region between isopropyl groups on the lower cyclopentadienyl ring.

We have recently begun a systematic study of the effects that differing ligand substitution patterns impose on the activity and stereospecificity of these doubly bridged catalysts. Herein we describe C_s-symmetric **6a**, having two bulky trimethylsilyl substituents at the 3- and 5-positions of the tetra-substituted cyclopentadienyl ring and C_{2v}-symmetric 3,3′,5,5′-tetra-isopropyl-substituted **6b**.

6a   6b
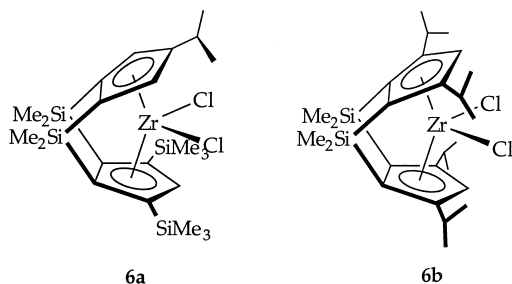
2. Results and discussion

2.1. Synthesis of doubly bridged zirconocene complexes 6a and 6b

Zirconocene dichloride compounds **6a** and **6b** are prepared following synthetic pathways shown in Schemes 1 and 2. Singly-bridged *bis*(cyclopentadiene) derivatives **2a** and **2b** are prepared by the reaction of Me_2SiCl_2 with the corresponding lithium cyclopentadienides in tetrahydrofuran solution. After quenching the reaction mixture with water, **2a** and **2b** are isolated by vacuum distillation as a mixture of double bond isomers in 74 and 77% yield, respectively.

Potassium salt **3a** is obtained as a solid by deprotonation of **2a** with 2 eq of $KN(SiMe_3)_2$ in tetrahydrofuran. The ¹H-NMR spectrum for **3a** shows that it is a mixture of Me_3Si-group positional isomers. The reaction of **3a** with Me_2SiCl_2 in tetrahydrofuran at $-78°C$ yields the doubly-bridged ligands **4a**, which are purified by vacuum distillation at 110–120°C (0.02

Torr) and obtained as mixture of isomers. Interestingly, **4a** can be deprotonated with *n*-BuLi in tetrahydrofuran to yield the C_s-symmetric dianionic ligand **5a** as a petroleum ether insoluble white powder. It appears that the stability of disilacyclohexadiene ring together with cooperative steric interactions between silyl groups cleanly direct the trimethylsilyl substituents to the 3,5 positions, rather than the (undesired) 3,4 positions. For tetrahydrofuran-d_8 solutions of dilithio salt **5a**, two ¹H-NMR singlets at δ 0.11 and δ 0.53 are observed for the two bridging dimethylsilylene groups at $-73°C$ (500 MHz), whereas all four methyl groups appear as a single peak at δ 0.31 at 50°C. We attribute this dynamic NMR behavior to a nonplanar structure **A**, which rapidly interconverts the two types of dimethylsilylene methyl groups via the planar structure **B** (Scheme 3). Indeed, an X-ray structure determination for related $[(SiMe_3)_2(C_5H_3)_2]Li_2(TMEDA)_2$ (TMEDA = tetramethylethylene diammine) reported by Köhler and Hiermeier reveals a planar structure analogous to **B** [27].

3,3′,5,5′ tetra-isopropyl-substituted, doubly-bridged ligand **4b** is prepared by the reaction of lithium salt **3b** with Me_2SiCl_2 in the same manner as for **4a**. Doubly-$[SiMe_2]$-linked **4b** is isolated as crystals in the form of needles from hexane solution. **4b** also can be deprotonated with *n*-BuLi in tetrahydrofuran to yield corresponding dilithio salt **5b** in 85% yield.

Reaction of the dilithium salts of **5a** and **5b** with $ZrCl_4$ in dichloromethane affords the zirconocene dichloride complexes **6a** and **6b** in approximately 36 and 3% yield, respectively. One possible explanation for the low yield of **6b** is that steric repulsion between methyls of the bridging $[SiMe_2]$ groups with the four neighboring isopropyl substituents favors a more planar structure for dilithio **5b** and thus prevents it from wrapping around the zirconium center as required for its coordination. **6a** and **6b** are soluble in aromatic hydrocarbons, dichloromethane and tetrahydrofuran and insoluble in alkanes (hexane, petroleum ether).
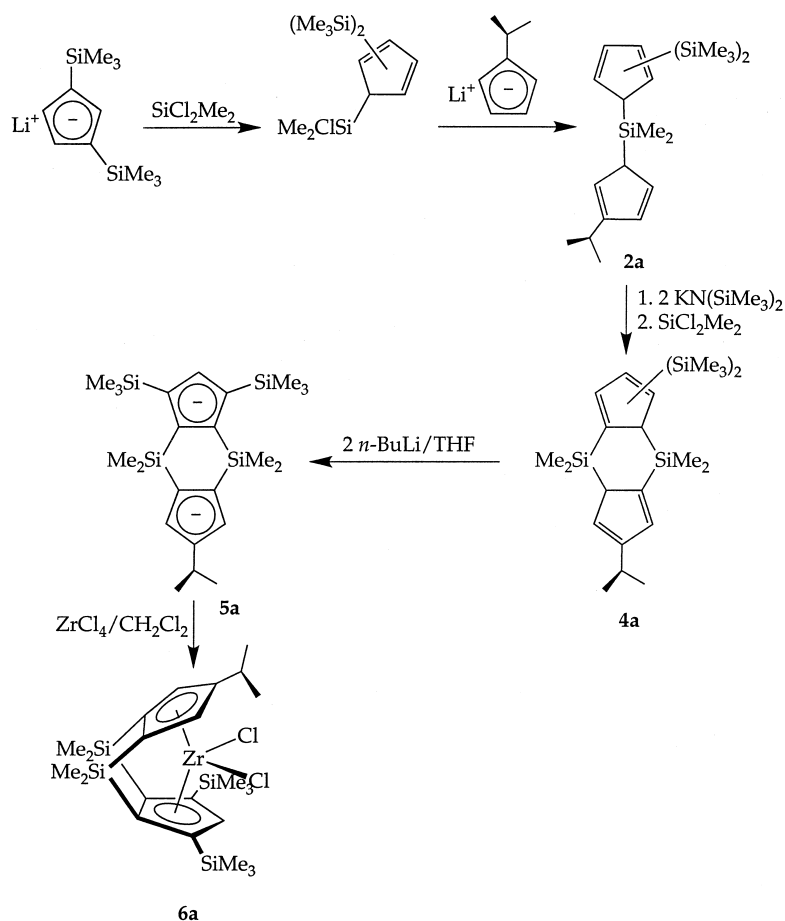
2.2. Propylene polymerization catalysis

The properties of complexes **6a** and **6b** as catalysts for the polymerization of propylene have been studied in liquid propylene at 0°C using with methyl aluminoxane (MAO, Al/Zr = 1200) as co-catalyst. The productivities of these catalysts and properties of the polymers that they produce are listed in Table 1. Corresponding data for $(Me_2Si)_2(\eta^5-C_5H_2-4-CHMe_2)\{\eta^5-C_5H-3,5-(CHMe_2)_2\}ZrCl_2$ (**1**) are included for comparison.

C_s-symmetric **6a** yields relatively highly syndiotactic polymer with an [$rrrr$] value of 75.4%. Although its stereospecificity is less than that for **1**, the productivity of **6a** is higher than that for **1** and the molecular weight of polymer

obtained with **6a** is comparable. On the other hand, C_{2v}-symmetric **6b** affords nearly atactic polypropylene with relatively low productivity and relatively low molecular weight. As we and others have anticipated, C_s symmetry is important for syndiospecific polymerization. Furthermore, 3,5-substitution of *both* cyclopentadienyl rings is expected to inevitably block the motion of the polymer chain segment out of the zirconcene wedge, as is required in the transition state for chain propagation. Indeed, in consideration of these features it is somewhat surprising that **6b** is as active as it is.

The pentad distributions of the polypropylenes prepared with **6a** and **1** are summarized in Table 2. In both spectra, *rmrr* and *rmmr* signals are observed, while *mrmr* is not. This

Scheme 1.
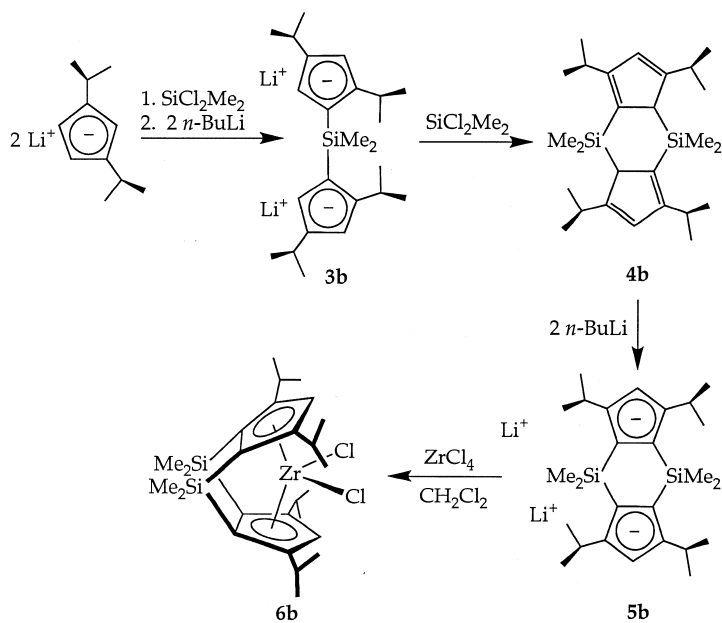
Scheme 2.

Table 1
Propylene polymerization with catalysts derived from **6a** and **6b**

Catayst precursor	**6a**	**6b**	**1**
Productivity[a]	18 000	2070	10 200
[rrrr][b]	75.4	12.9	98.9
[r][c]	93.7	61.6	99.6
Mw[d]	1 000 000	430 000	1 100 000
Mw/Mn	3.03	2.11	3.14

[a] Liquid propylene at 0°C, polymer isolated (g)/Zr (g)/h.
[b] Percentage of [rrrr] pentad by ^{13}C NMR analysis.
[c] [r = [rr] + 0.5[mr].
[d] By GPC, calibrated with standard polystyrene.

Table 2
Pentad distribution of polypropylenes prepared with **6a** and **1**

Catalyst	mmmm	mmmr	rmmr	mmrr	rmrr	mrmr	rrrr	mrrr	mrrm
6a	0.0	0.4	1.8	3.8	4.1	0.2	75.4	14.2	0.1
1	0.0	0.0	0.1	0.3	0.5	0.0	98.9	0.3	0.0

distribution is indicative of at least two kinds of stereochemical defects corresponding to . . . *rrrrrmrrrr* . . . (single *m* defects) and . . . *rrrrrm*
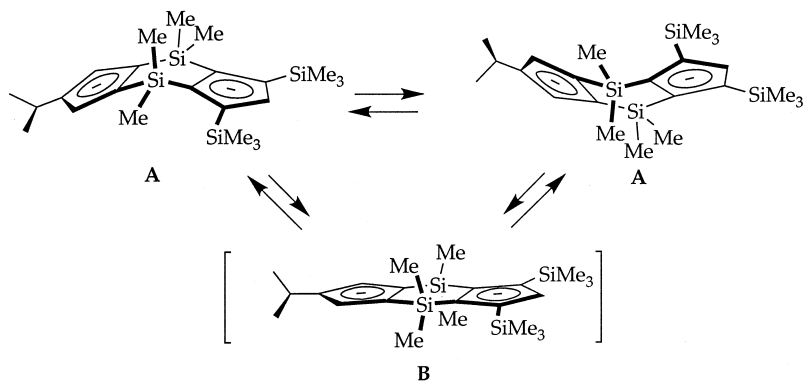
Scheme 3.

mrrrrrr... (double *m* defects) for these syndio-tactic polymers, likely produced by two types of mechanisms: site epimerization (Scheme 4) and enantiofacial mis-insertion (Scheme 5), respectively [1]. The percentages of stereochemical defects can be estimated from only two pentads since $mm = rmmr$ and $m = 1/2 [rmrr]$ [2]. Thus, the polymer produced by **6a** has eight times as many single *m* defects and eighteen times as many *mm* defects as the polymer made by **1**. Interestingly, site epimerization and enantiofacial mis-insertion occur with roughly equal frequency for both catalysts **6a** (2.1 versus 1.8%) and **1** (0.3 versus 0.1%) [3]. The introduction of bulky trimethylsilyl groups at the 3- and 5-positions for **6a** (vis-a-vis the smaller isopropyl substituents for **1**) likely encourages the polymer chain to move more to the center of the zirconcene wedge after each insertion of propylene. As a consequence, site epimerization by chain swinging is expected to occur more frequently for **6a**, leading to a reduction in the alternating monomer enantiofacial discrimination and lower syndiospecificity (Scheme 4).

3. Experimental

3.1. General considerations

All operations were performed under argon using Schlenck techniques. Tetrahydrofuran, toluene, petroleum ether, used in organometallic reactions were all dried over sodium benzophenone ketyl. Dichloromethane was dried over calcium hydride. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM500 (500.13 MHz) spectrometer.

Isopropylcyclopentadiene, 1,3-diisopropylcyclopentadiene and *bis*(trimethylsilyl)cyclopentadiene were prepared by literature methods [29–31].

3.2. Synthesis

3.2.1. [(Me₂Si)(C₅H₃-3-CHMe₂)(C₅H₂(SiMe₃)₂)]H₂, 2a

3.2.1.   [(Me₂Si)(C₅H₃-3-CHMe₂)(C₅H₂(SiMe₃)₂)]H₂, 2a

A 200 ml round bottom flask, charged with $C_5H_4(SiMe_3)_2$ (10.0 g, 47.5 mmol) and tetrahydrofuran (50 ml), was equipped with a reflux condenser and a 180° needle valve and cooled to 0°C with an ice bath. *n*-BuLi (1.6 M hexane solution, 32 ml, 51 mmol) was added via a syringe pump at a rate 1.5 ml/min to the cold solution and the solution was allowed to warm to 25°C with stirring as the ice melted overnight. 12 h after *n*-BuLi addition, the solution was heated and allowed to reflux for 3 h. The tetrahydrofuran solution of $Li^+[C_5H_3(SiMe_3)_2]^-$ was then cooled to 25°C and used as a solution.

A stirring bar, 400 ml of petroleum ether and $C_5H_5(CHMe_2)$ (8 g, 73.3 mmol) were added to a 1 l flask equipped with a glass filter. *n*-BuLi (1.6 *M* hexane solution, 45.8 ml, 73.3 mmol) was added to this solution at 0°C. A white precipitate was observed immediately. After stirring for 1 h at 0°C, stirring was continued for 3 h at 25°C. The precipitate was filtered off and dried under vacuum overnight.

Me_2SiCl_2 (6.3 g, 49 mmol) was dissolved to 300 ml of tetrahydrofuran. Solutions of $Li^+[C_5H_3(SiMe_3)_2]^-$ and $Li^+[C_5H_4(CHMe_2)]^-$ were added in this order dropwise to the Me_2SiCl_2 solution at −78°C by cannula. After additions were completed, stirring was continued for 2 h at room temperature. Water and hexane were added to the reaction mixture. The organic phase was separated, dried and the por-

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[1] Similar analyses of the origins of single *m* and double *m* defects for the $Me_2C(\eta^5\text{-}C_5H_4)(''\eta^3\text{-}''C_{13}H_8)ZrCl_2$ /MAO catalyst system have been previously described by Ewen and co-workers (see Ref. [4]).

[2] A more complete statistical analysis according to the model described by Farina leads to similar conclusions (see Ref. [28]).

[3] These conclusions are based on the assumption that defects arise only by the mechanisms shown in Schemes 4 and 5. Alternative mechanisms for stereoerror production clearly are also possible; for example, site epimerization could be much faster following an enantiofacial mis-insertion (also leading to a single *m* defect). Chain epimerization by β-H elimination/olefin rotation/re-insertion sequences could give rise to either a double *m* or a single *m* defect.

tion that distilled at 115–125°C and 0.1 mm Hg was collected. Yield: 13.4 g (74%).

3.2.2. $[[(Me_2Si)_2(C_5H_2\text{-}4\text{-}CHMe_2)(C_5H(SiMe_3)_2)]H_2$, 4a

$[(Me_2Si)(C_5H_3\text{-}3\text{-}CHMe_2)(C_5H_2(SiMe_3)_2)]H_2$, 2a (5 g, 13.3 mmol) and $K[N(SiMe_3)_2]$ (5.33 g, 26.6 mmol) were solved in tetrahydrofuran (200 ml) and the reaction mixture was heated at reflux for 2 days. The solvent was removed under high vacuum

for 12 h at 60°C. The resultant solid, $[Me_2Si(C_5H_2\text{-}4\text{-}CHMe_2)(C_5H_2(SiMe_3)_2)]K_2$, 3a, was used in this form. Me_2SiCl_2 (1.72 g) was vacuum transferred at −78°C onto a tetrahydrofuran solution (100 ml) of $[Me_2Si(C_5H_2\text{-}4\text{-}CHMe_2)(C_5H_2(SiMe_3)_2)]K_2$, 3a (13.3 mmol). The reaction mixture was stirred, the temperature was allowed to warm to 25°C and the mixture was stirred overnight. After water and hexane were added, the hexane phase was separated and dried over $MgSO_4$. $MgSO_4$ was
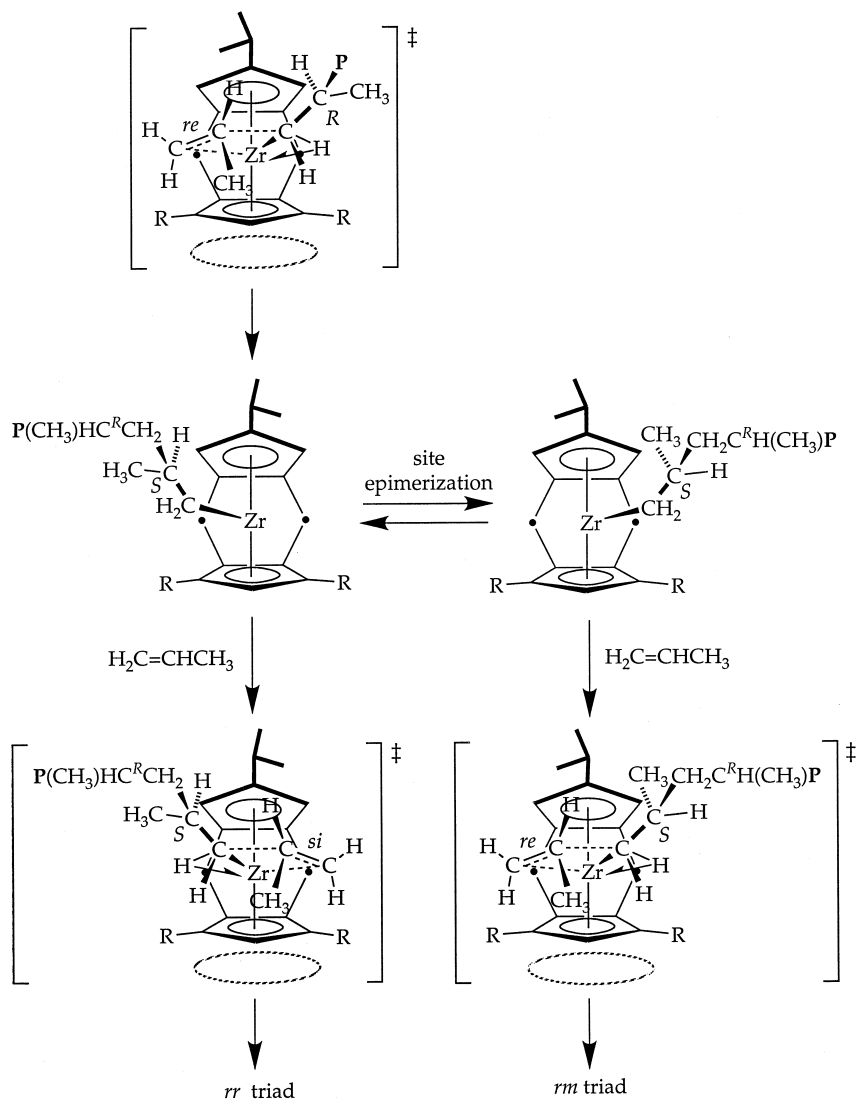
Scheme 4.

removed by filtration. After concentration of the mixture, the resultant oil was distilled under high vacuum. Yield: 4.2 g (73%).
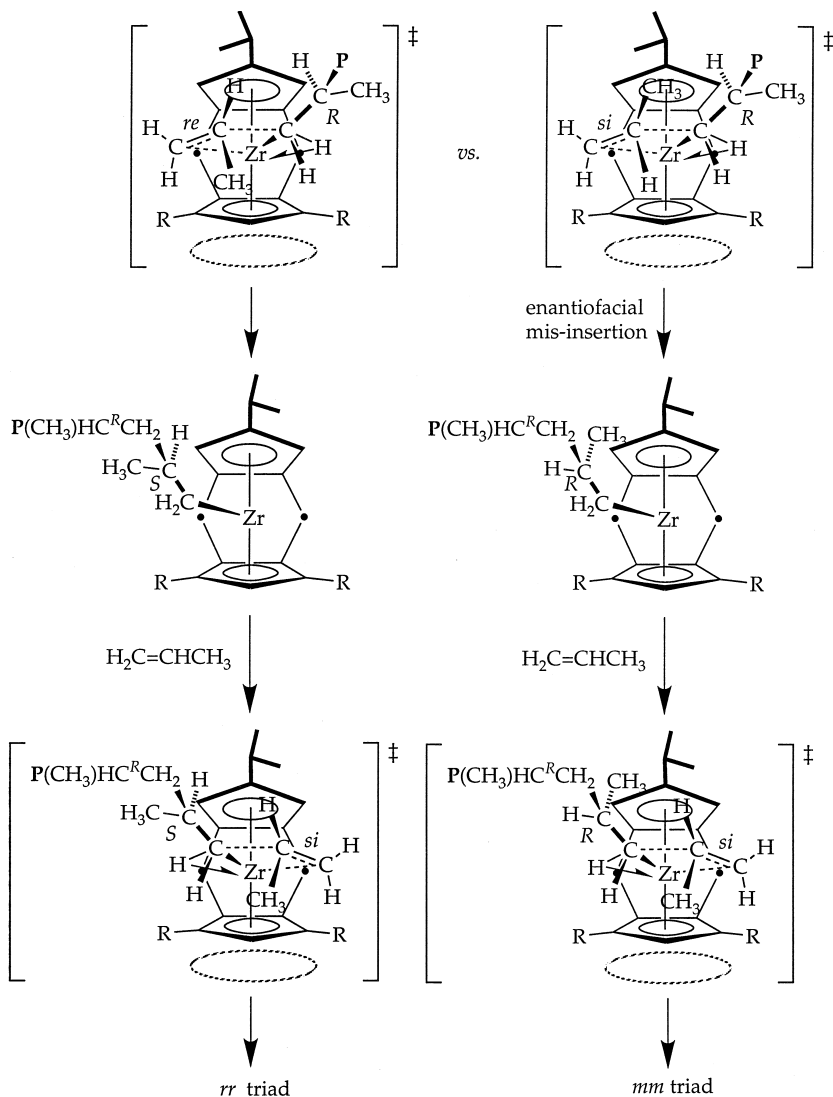
3.2.3. [(Me₂Si)₂(C₅H₂-4-CHMe₂)(C₅H-3, 5-(SiMe₃)₂)]Li₂, 5a

n-BuLi (1.6 *M* hexane solution, 9.4 ml, 15 mmol) was added to a tetrahydrofuran solution of [(Me₂Si)₂(C₅H₂-4-CHMe₂)(C₅H(SiMe₃)₂)]H₂, **4a** (3.25 g, 7.54 mmol) at 0°C. After 1 h the reaction temperature was allowed to warm to 25°C. The solvent was

removed in vacuo and the oily residue was washed with petroleum ether and filtered to yield a white solid of **5a** (1.2 g).

^{1}H-NMR (tetrahydrofuran-d_8 at −73°C): δ 6.58 (s, 1H, C₅**H**); 6.04 (s, 2H, C₅**H**₂), 3.61(THF), 2.88 (h, 1H, -C**H**(CH₃)₂); 1.79(THF); 1.27 (d, 6H, -CH(C**H**₃)₂); 0.52 (s, 6H, Si(C**H**₃)₂); 0.20 (s, 18H, Si(C**H**₃)₃); 0.15 (s, 6H, Si(C**H**₃)₂).

^{1}H-NMR (tetrahydrofuran-d_8 at 50°C): δ 6.74 (s, 1H, C₅**H**); 6.10 (s, 2H, C₅**H**₂), 3.61(THF), 2.92 (h, 1H, -C**H**(CH₃)₂); 1.78(THF); 1.21 (d,

Scheme 5.

6H, -CH(C**H**$_3$)$_2$); 0.34 (s, 12H, Si(C**H**$_3$)$_2$); 0.26 (s, 18H, Si(C**H**$_3$)$_3$).

3.2.4. $(Me_2Si)_2(\eta^5$-C_5H_2-4-$CHMe_2)(\eta^5$-C_5H-3,5-$(SiMe_3)_2)ZrCl_2$, **6a**

(Me$_2$Si)$_2$(C$_5$H$_2$-4-CHMe$_2$)(C$_5$H-3, 5-(SiMe$_3$)$_2$)]Li$_2$(THF)$_2$ (0.5 g, 1 mmol) and ZrCl$_4$ (0.23 g, 1 mmol) were placed in a 50 ml flask equipped with a glass filter. Dichloromethane (20 ml) was vacuum transferred to the flask at −78°C and the temperature was allowed to increase to 25°C. After dichloromethane was removed in vacuo, toluene (50 ml) was vacuum transferred onto the residue. The resultant yellow–brown suspension was filtered and a clear toluene filtrate was obtained. This solution was concentrated and white microcrystals were obtained. The product was filtered off, washed with cold toluene and dried. The crude product was recrystallized from toluene. Yield: 250 mg.

^{1}H-NMR (benzene-d_6): δ 6.96 (s, 1H, C$_5$**H**); 6.72 (s, 2H, C$_5$**H**$_2$), 3.22 (h, 1H, -C**H**(CH$_3$)$_2$); 1.33 (d, 6H, -CH(C**H**$_3$)$_2$); 0.72 (s, 6H, Si(CH$_3$)$_2$); 0.48 (s, 6H, Si(C**H**$_3$)$_2$); 0.30 (s, 18H, Si(C**H**$_3$)$_3$). ^{13}C-NMR (benzene-d_6): δ 156.9, 137.3, 136.6, 129.7, 117.4, 106.8 (Cp C's); 28.4 (-**C**H(CH$_3$)$_2$); 23.7 (-CH(**C**H$_3$)$_2$); 3.6 (Si-**C**H$_3$); 2.4 (Si-**C**H$_3$); 0.1 (Si-**C**H$_3$). Elemental anal. found: C, 45.96; H, 6.63. Calculated for C$_{23}$H$_{40}$Cl$_2$Si$_4$Zr: C, 46.74; H, 6.82.

3.2.5. $[(Me_2Si)(C_5H_2$-2,4-$(CHMe_2)_2)_2]H_2$, **2b**

n-BuLi (1.6 M hexane solution, 93.8 ml, 151 mmol) was added to a tetrahydrofuran solution (250 ml) of C$_5$H$_4$(CHMe$_2$)$_2$ (22.5 g, 150 mmol) at 0°C. The reaction temperature was allowed to rise to 25°C and the mixture was stirred for an additional 2 h. Me$_2$SiCl$_2$ (9.7 g, 75 mmol) was dissolved to 250 ml of tetrahydrofuran and the solution of Li$^+$[C$_5$H$_3$(CHMe$_2$)$_2$]$^-$ was added dropwise at −78°C by cannula. After addition, stirring was continued for 2 h at room temperature. Water and hexane were added to the reaction mixture and the organic phase was separated and dried over MgSO$_4$. MgSO$_4$ was removed by filtration. After concentration of the

mixture, the resulting oil was distilled under vacuum. Yield: 20.6 g (77%).

3.2.6. $(Me_2Si)(C_5H_2$-2,4-$(CHMe_2)_2)_2]Li_2$ (THF), **3b**

n-BuLi (1.6 M hexane solution, 52 ml, 83.2 mmol) was added to a petroleum ether solution (200 ml) of [(Me$_2$Si)(C$_5$H$_2$-2,4-(CHMe$_2$)$_2$)$_2$]H$_2$, **3a** (14.2 g, 40 mmol) at 0°C. The reaction temperature was allowed to warm to 25°C and the mixture was stirred for 3 h. After concentration of the reaction mixture to 100 ml, tetrahydrofuran (6 ml) was added to the clear solution with stirring. The precipitated white powder was filtered off and dried. Yield: 16.1 g (91.3%).

^{1}H-NMR (tetrahydrofuran-d_8): δ 5.65 (s, 2H, C$_5$**H**$_2$); 5.60 (s, 2H, C$_5$**H**$_2$), 3.56 (m, 4H, THF); 3.07 (br, 2H, -C**H**(CH$_3$)$_2$); 2.74 (h, 2H, -C**H**(CH$_3$)$_2$); 1.75 (m, 4H, THF); 1.12 (d, 24H, -CH(C**H**$_3$)$_2$); 0.32 (s, 6H, Si(C**H**$_3$)$_3$).

3.2.7. $[(Me_2Si)_2(C_5H_2$-2,4-$(CHMe_2)_2)_2]H_2$, **4b**

[(Me$_2$Si)(C$_5$H$_2$-2,4-(CHMe$_2$)$_2$)Li$_2$(THF), **3b** (16 g 36.3 mmol) was placed in a flask and tetrahydrofuran (120 ml) was vacuum transferred onto the solid. Me$_2$SiCl$_2$ (5.3 ml, 43.4 mmol) was also vacuum transferred to the reaction flask at −78°C. The reaction mixture was allowed to warm to room temperature and stirred for 3 h (white precipitate was observed). Water and hexane, and the hexane phase were separated and dried over MgSO$_4$. MgSO$_4$ was removed by filtration. The organic phase was concentrated and white needle-shaped crystals were obtained from this hexane solution. Yield: 4.6 g (31%).

^{1}H-NMR (CDCl$_3$): δ 6.35 (s, 2H, C$_5$**H**$_2$); 1.76 (m, 2H, C$_5$**H**$_2$), 3.10 (h, 2H, -C**H**(CH$_3$)$_2$); 2.68 (h, 2H, -C**H**(CH$_3$)$_2$); 1.1–1.3 (m, 24H, -CH(C**H**$_3$)$_2$); 0.59 (s, 6H, Si(C**H**$_3$)$_2$); 0.59 (s, 6H, Si(C**H**$_3$)$_2$).

3.2.8. $[(Me_2Si)_2(C_5H_2$-2,4-$(CHMe_2)_2)_2]Li_2$, **5b**

n-BuLi (1.6 M hexane solution, 8.5 ml, 13.6 mmol) was added to a tetrahydrofuran solution

of $[(Me_2Si)_2(C_5H_2\text{-}2,4\text{-}(CHMe_2)_2)_2]H_2$, **4b** (2.8 g, 6.8 mmol) at 0°C and the reaction mixture was stirred for 1 h. The reaction temperature was allowed to warm to 25°C. The white suspension was stirred for 2 h and the solid was filtered off, washed with petroleum ether and dried. Yield: 3.3 g (85%).

^{1}H-NMR (tetrahydrofuran-d_8): δ 6.02 (s, 2H, C$_5$**H**), 3.61(THF), 3.14 (h, 4H, -C**H**(CH$_3$)$_2$); 1.78(THF); 1.20 (d, 24H, -CH(C**H**$_3$)$_2$); 0.33 (s, 12H, Si(C**H**$_3$)$_2$).

3.2.9. $[(Me_2Si)_2(\eta^5\text{-}C_5H(CHMe_2)_2)_2]ZrCl_2$, 6b

$[(Me_2Si)_2(C_5H(CHMe_2)_2)_2]Li_2(THF)_2$ (3.24 g, 5.7 mmol) and ZrCl$_4$ (1.3 g, 5.6 mmol) were placed in a 50 ml flask equipped with a glass filter. Dichloromethane (50 ml) was vacuum transferred into the flask at -78°C and the temperature was allowed to warm to 25°C while the reaction mixture was stirred. After dichloromethane was removed in vacuo, toluene (50 ml) was vacuum transferred onto the residue. The resultant yellow–brown suspension was filtered and the clear toluene filtrate was obtained. The solution was concentrated to 2 ml and a small amount of petroleum ether was vacuum transferred onto the solution. White microcrystals were obtained. Yield: 80 mg.

^{1}H-NMR (benzene-d_6): δ 6.60 (s, 2H, C$_5$**H**); 2.97 (h, 4H, -C**H**(CH$_3$)$_2$); 1.42 (d, 12H, -CH(C**H**$_3$)$_2$); 1.02 (d, 12H, -CH(C**H**$_3$)$_2$); 0.66 (s, 6H, Si(C**H**$_3$)$_2$); 0.62 (s, 6H, Si(C**H**$_3$)$_2$); ppm. ^{13}C-NMR (benzene-d_6): δ 162.8, 114.1, 109.7 (Cp C's); 29.8, 29.0 (-CH(C**H**$_3$)$_2$); 21.1 (-**CH** (CH$_3$)$_2$); 6.2 (Si-**CH**$_3$); 1.3 (Si-**CH**$_3$). Elemental anal. found: C, 54.93; H, 7.44. Calculated for C$_{26}$H$_{42}$Cl$_2$Si$_2$Zr: C, 54.51; H, 7.39.

3.3. Polymerization and polymer analysis

Polymerizations were carried out in a 100 ml high pressure glass reactor equipped with a pressure gauge, a safety release-valve, an injection port and a magnetic stirrer. A typical polymerization process follows: MAO (Arbemarle, 500 mg) was placed in the reactor in a nitrogen-filled dry box. A propylene line was connected to the reactor and liquid propylene was condensed on the MAO at 0°C, 120 psi. After the propylene inlet valve was closed, a 2 ml toluene solution of the metallocene (7 μmol/1 ml) was injected into the vigorously stirred MAO/propylene suspension at 0°C. The polymerization was quenched with methanol, followed by drying in vacuo.

The molecular weight of the polymers were determined by gel permeation chromatography on a Waters 150C instrument (Shodex-AT80M/S; eluent 1,2,4-trichlorobenzene at 135°C). ^{13}C-NMR measurements for the polypropylene samples were performed on a Bruker AM500 (500.13MHz) spectrometer at 100°C (solvent: 1,2,4-trichlorobenzene/benzene-d_6; volume ratio, 3/1).

Acknowledgements

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