Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Organometallic Chemistry 691 (2006) 3089–3097
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Spirane-bridged *ansa* η^5-cyclopentadienyl-η^5-fluorenyl-zirconocene precatalysts

Geir Langli, Christian Rømming, Kjell Undheim *

Department of Chemistry, University of Oslo, Oslo, Norway

Received 4 February 2006; received in revised form 13 March 2006; accepted 13 March 2006
Available online 18 March 2006

Abstract

Synthesis of rigid *ansa*-zirconocene precatalyst systems with a C_2-bridge embedded in a spirane scaffold is described. Fulvenes were key intermediates in regio- and stereoselective preparation of the appropriate spirane ligands. Substitution in the cyclopentadienyl group in the ligand was effected by fulvene methodology. The zirconocenes were active precatalysts for the polymerisation of propene when activated with MAO. The structure of the parent zirconocene dichloride has been verified by X-ray crystal analysis.

Keywords: C_2-spirane-bridged zirconocenes; Spirane scaffold; Rigid *ansa*-zirconocenes; Metallocenes; Stereoselective synthesis

1. Introduction

In a recent report we have described a method for the preparation of a rigid C_2-bridged zirconocene precatalyst system, 2-(η^5-cyclopentadienyl)-1′,2′,3′,4′-tetrahydrospiro[cyclobutane-1,1′-(η^5-fluorenyl)]zirconium dichloride (Fig. 1; **A**), where the C_2-bridge is embedded in a rigid spirane scaffold [1]. A preliminary study of the zirconocene complex as a propene polymerisation precatalyst showed the product to be largely atactic PP resulting from little stereocontrol from the ligand. Inspection of simple models suggested that a regioisomeric fluorenyl zirconocene (Fig 1; **B**) might exert stronger stereocontrol on the course of the polymerisation. When the benzene ring is moved towards the spirobridge, one side of the zirconocene would resemble the isoselective ethylene bridged bisindenyl zirconocene [2]. In this report, we describe a method for the preparation of the zirconocene **B** in Fig. 1, and isopropyl homologues substituted in the cyclopentadienyl moiety of the parent zirconocenes **A** and **B**.

2. Results and discussion

The synthesis of the targeted spirane ligand **6** is outlined in Scheme 1. The substrate was the 4-fluorenone **1** [3], which was to be converted into the spirocyclobutanone **4** via an intermediate cyclopropane **2** and a ring expansion. Lithiated cyclopropyl phenyl sulfide [4], reacted preferentially as a base by extraction of an acidic indene proton. With the less basic reagent derived from the lithiated species and cerium trichloride [5], however, chemoselective addition to the carbonyl carbon was achieved. The ^{1}H NMR spectra of the crude product showed full conversion to the desired product, but part of this material was lost during chromatographic purification probably because of ready elimination of water. Attempts to effect rearrangement of the cyclopropyl phenyl sulfide **2** moiety into a cyclobutanone spirane **4** in the presence of fluoroboric acid according to the methodology reported by Trost et al. [6], failed to provide the cyclobutanone **4**. Instead preferential *endo* elimination of water furnished the dihydrofluorene **3**. Presumably both reaction paths proceed through closely related carbonium ion intermediates after initial hydroxyl elimination. Conditions adapted to Lewis acid catalysis, however, furnished the cyclobutanone **4** in 19% yield using

* Corresponding author.
E-mail address: kjell.undheim@kjemi.uio.no (K. Undheim).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.03.023

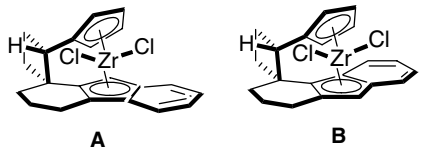


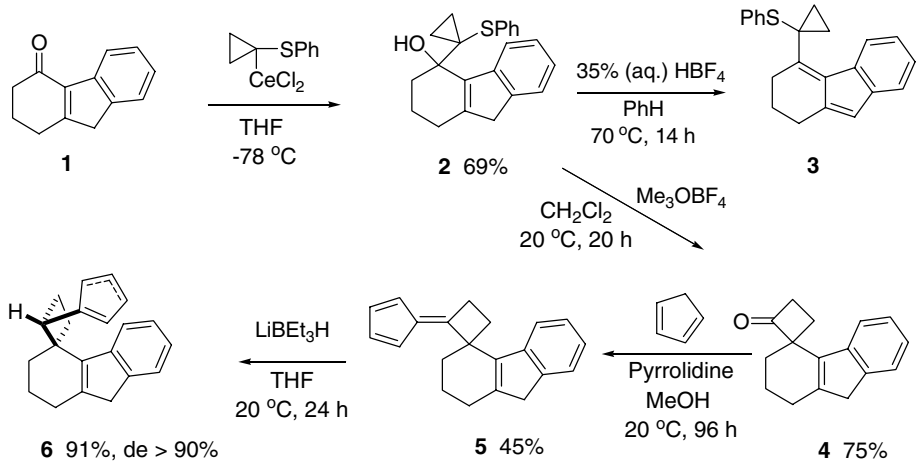
Fig. 1. Rigidly bridged zirconocenes in a spirane scaffold.

$SnCl_4$ whereas the presence of the Meerwein salt Me_3OBF_4 increased the yield to 75%. The ketone **4** was in a subsequent step converted into a fulvene derivative **5** in a modest yield with cyclopentadiene as a reactant in the presence of pyrrolidine as a base.

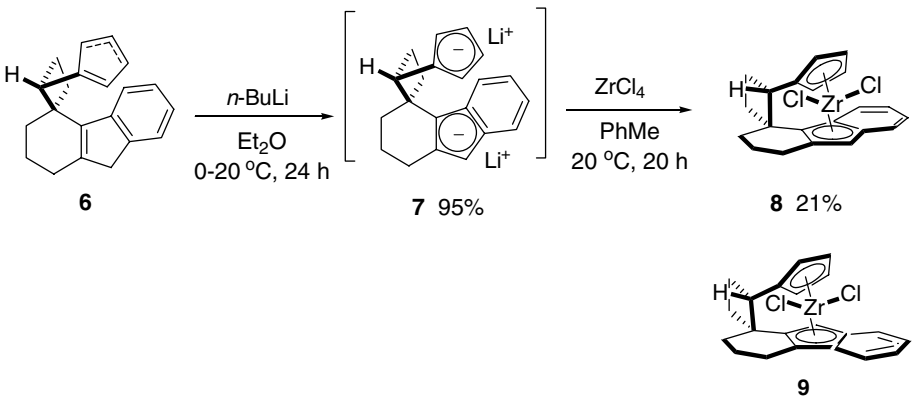
A sandwich zirconocene structure with the zirconium metal coordinated to the fluorenyl and cyclopentadienyl moieties (Fig. 1) requires stereoselective reduction of the exocyclic fulvene double bond. In the structure **5**, the sterical shielding of the two faces of the fulvene moiety differs significantly (Scheme 1). The face pointing away from the major body of fluorene is the less shielded face. Chemoselective and stereoselective *cis*-reduction was achieved by the use of a bulky metal hydride, lithium triethylborohydride. The *cis*-configuration, however, leads to a significant repulsive interaction with the larger part of the fluorene component, and is thermodynamically the less favourable structure of the two geometrical isomers. The cyclobutadienyl substituent is thereby forced into the *cis*-configuration, structure **6**.

The subsequent conversion of the ligand **6** into the zirconocene **8** is shown in Scheme 2. For the zirconocene formation, the ligand was lithiated. One molar equivalent with *n*-BuLi in diethyl ether produced a clear solution. Addition of a second molar equivalent of *n*-BuLi led to precipitation of a tan powder which was isolated by filtration and washed with pentane. The dilithiated species **7** was added to toluene without any further characterisation and treated with solid $ZrCl_4$, which had been purified by sublimation. The zirconocene **8** was isolated in 21% yield. The product was very sensitive to oxygen and moisture, and the reactions were run in a glove box in preference to the Schlenk equipment.

The performance of the zirconocenes **8** and **9** as precatalysts in the polymerisation of propene was unsatisfactory (vide infra). Attempts were therefore made to modify the properties of the zirconocenes by carbylation in the cyclopentadienyl moiety of the ligands. Initial attempts were



Scheme 1.



Scheme 2.

made to react isopropylcyclopentadiene under conditions for fulvene formation by analogy to the successful reaction **4** → **5** in Scheme 1. The desired fulvene reaction with substituted cyclopentadiene failed. However, when the preformed *cis*-ligands **6** and **12** were subjected to the fulvene methodology with acetone as a reactant and pyrrolidine as base, the isopropylidine products **10** and **13** were obtained in high yields (Scheme 3). The ligand **12** was available from previous work [1]. The exclusive regiochemistry achieved in the substitution reaction is controlled by steric interactions. The fulvene derivative **10** was chemically labile and was used as a crude product in the subsequent reduction. Its isomer **13** was more stable. Exocyclic regiochemical reduction to the isopropyl derivatives **11** and **14** was effected in high yield by lithium triethylborohydride. The NMR spectra of the isopropyl derivatives showed that all the three cyclopentadienyl isomers were present in the products **11** and **14**.

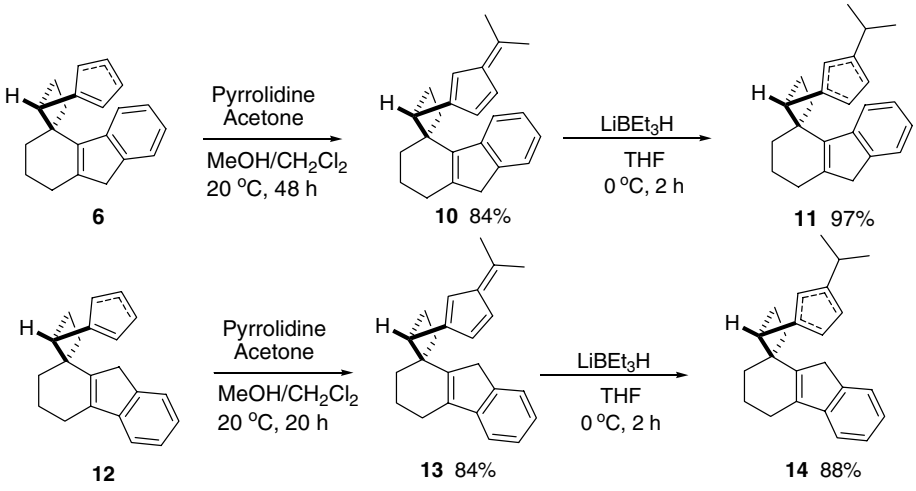
Formation of substituted target zirconocenes is shown in Scheme 4. The isopropyl homologues **11** and **14** were dilithiated by *n*BuLi in diethyl ether in the same manner as the parent compound **6** in Scheme 2. The oily dilithiated products **15** and **17** solidified on trituration with pentane. The lithiated species were further converted by zirconium tetrachloride into the corresponding zirconocenes in 11% and 12% yields, respectively. Isomerism is introduced into the ligands **11** and **14** on metallation because of the unsymmetrical substitution pattern in the cyclopentadienyl moiety, in each case an isomeric pair **16a/16b** (3:5) and **18a/18b** (4:5) was formed depending on which side of the cyclopentadienyl ring was coordinated to the metal. Attempts to increase the selectivity of the reactions by using $Zr(NMe_2)_4$ or $ZrCl_4(THF)_2$ were not successful [7,8]. The solubility of the isopropyl products in toluene, hexane or pentane was significantly higher than for the parent zirconocenes **8** and **9** (Scheme 2). Attempts to separate the individual members in each isomer pair failed. The modest yield in the zirconation may in part be explained by face selectivity. A sandwich complex requires an intramolecular reaction where the zirconium reactant becomes attached to the inner face of the fluorene ring. When the zirconium becomes attached to the other outer face of the ring, intermolecular products are likely to be formed.

The zirconocene structure for the parent molecule **8** has been verified by a single-crystal X-ray analysis. Crystals suitable for X-ray analysis were obtained by slow evaporation of a toluene solution of the zirconocene at room temperature. The ORTEP plots of the crystal structure is shown in Fig. 2.

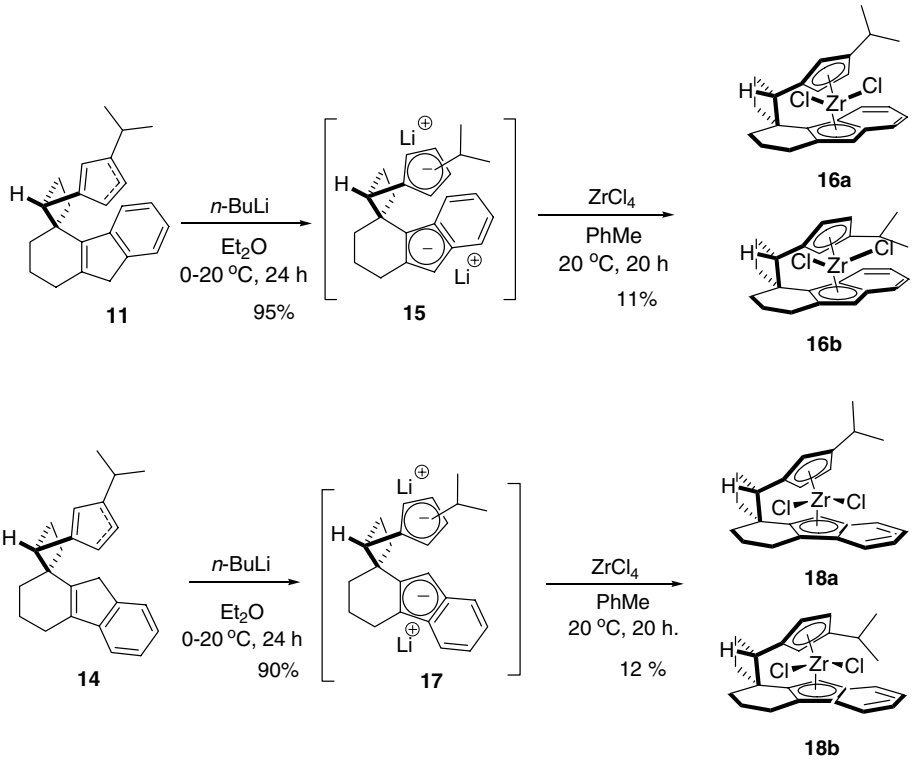
The bite angle between the two Cp-moieties is 126.6°. For comparison, this value is very close to the bite angle 125.8° of the regioisomeric zirconocene **9** [1] (Scheme 2), and the bite angle 125.3° in the ethylene bridged bisindenyl zirconocene [2]. The bite angle between the cyclopentadienyl units in the two η^5-coordinated aromatic ligands in *ansa*-zirconocene dichloride complexes have a profound influence on the catalytic properties of such complexes [9–11].

2.1. Propene polymerisation

The parent zirconocenes **8** and **9** (Scheme 2) as well as their isopropyl isomers **16** and **18** (Scheme 4) were all active precatalysts for the polymerisation of propene when the catalyst system was activated with a large excess of MAO (1:1000). The polymerisation reactions were performed in toluene at 30 °C with propene, pressure 1.1 bar. The parent precatalyst **9** (Scheme 2) yielded essentially an atactic oligomer with an average of 15 monomer units. The other parent precatalyst **8** (Scheme 2) yielded a viscous oily PP which was slightly isotactic ([mmmm] = 17.6%) with an average of 100 units [1]. The zirconocene **8** showed a twofold increase in activity over the regioisomeric system **9**. The isomeric pairs **16a/16b** and **18a/18b** were used as such. The results were much better than for the unsubstituted zirconocenes, but uncertainties are



Scheme 3.



Scheme 4.

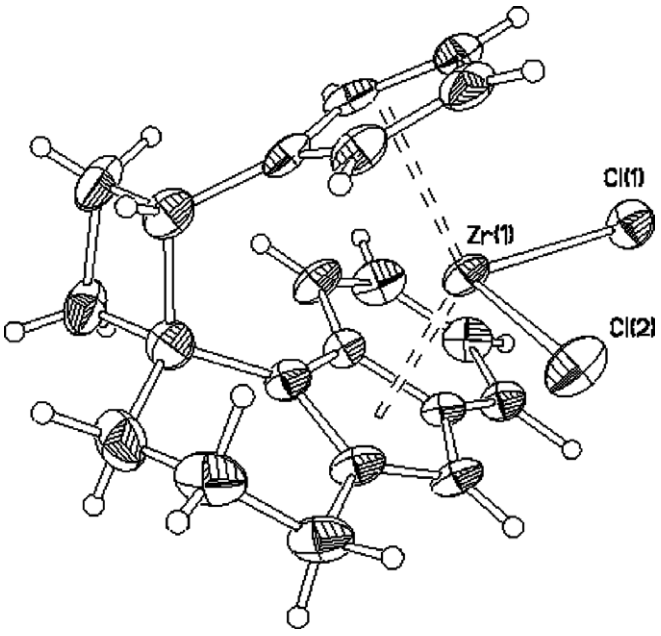


Fig. 2. The ORTEP plot of compound **8**. Ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°) in the molecules: Zr(1)–Cl(1) = 2.431, Zr(1)–Cl(2) = 2.443, Zr(1)–X(1A) = 2.201, Zr(1)–X(1B) = 2.224; X(1A)–Zr(1)–X(1B) = 126.6, Cl(1)–Zr(1)–Cl(2) = 97.8. Estimated standard deviations are 0.001 Å in bond lengths and 0.1° in angles.

associated with which regioisomer in each pair is the more active, and which isomer is the more stereoselective. Both catalyst systems produced complex polypropylene products which were extracted with diethyl ether to remove atactic PP (40–60%). The ether extractions will increase the apparent isotacticity values due to the removal of the atactic PP. The zirconocene pair **16** yielded a crystalline powder with a relatively high isotacticity ([mmmm] = 81.6%), while the zirconocene pair **18** yielded a waxy PP with intermediate isotacticity. The molecular weights for both polymers were low.

3. Conclusion

In conclusion, a method for the preparation of C_2-rigidified *ansa*-zirconocene precatalysts is described. The C_2-bridge is part of a spirane system which is substituted by a cyclopentadienyl and a fluorenyl moiety. *cis*-Spirane ligands appropriate for conversion into metallocenes were prepared by stereochemically controlled reactions. The precatalyst zirconocenes together with a large excess of MAO constitute a moderately active catalyst system for PP formation.

4. Experimental

The ^{1}H NMR spectra were recorded at 500 MHz with a Bruker DPX 500, at 300 MHz with a Bruker DPX 300 instrument. The ^{13}C NMR spectra were recorded at 125 or 75 MHz using the above instruments. ^{1}H and ^{13}C spectra were referenced to residual protons in the solvent. Mass spectra were recorded at 70 eV ionising voltage and are presented as *m*/*z* (% rel. int.).

All organometallic reactions were run under an argon atmosphere using Schlenk or glovebox techniques. THF, Et_2O and toluene were distilled from sodium/benzophenone, and CH_2Cl_2 from CaH_2. $CeCl_3$ was bought as the heptahydrate and dried according to the literature [12].

4.1. X-ray crystallographic analysis for zirconocene **8**

X-ray data were collected on a Siemens SMART CCD diffractometer [13] using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection method: ω-scan, range 0.6°, crystal to detector distance 5 cm. Data reduction and cell determination were carried out with the SAINT and XPREP programs [13]. Absorption corrections were applied by the use of the SADABS program [14]. The structures were determined and refined using the SHELXTL program package [15]. The non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were located from difference Fourier maps and refined with isotropic thermal parameters.

The structure was found to contain one disordered molecule of toluene per unit cell. Structural data have been deposited at the Cambridge Crystallographic Data Centre with Deposition No. CCDC 269765.

4.2. Crystal data for $C_{21}H_{20}Cl_2Zr$ (**8**) + $C_{3.5}$

$M = 476.52$, triclinic, $P\bar{1}$, $a = 8.227(2)$ Å, $b = 10.746(3)$ Å, $c = 12.956(3)$ Å, $\alpha = 114.30(1)°$, $\beta = 97.05(1)°$, $\gamma = 96.63(1)°$, $V = 1018.5(5)$ Å^3, $Z = 2$, $D_x = 1.554$ Mg m^{-3}, $\mu = 0.809$ mm^{-1}, $T = 103(2)$ K, measured 11,096 reflections in 2θ range 4.2–52.8°, $R_{int} = 0.129$. 325 Parameters refined against $4166F^2$, $R = 0.046$ for $I_0 > 2\sigma(I_0)$ and 0.079 for all data.

4.3. 2,3,4,9-Tetrahydro-4-[1-(phenylthio)cyclopropyl]-1H-fluoren-4-ol (**2**)

1.6 M *n*-BuLi in hexane (113 mL, 180 mmol) was added to a solution of cyclopropyl phenyl sulfide (26.8 g, 180 mmol) in THF (250 mL) at 0 °C, and the mixture stirred at this temperature for 90 min. The temperature was lowered to −78 °C, and the solution cannulated into a solution of anhydrous $CeCl_3$(51.8 g, 210 mmol) in THF (500 mL) at −78 °C. The $CeCl_3$/THF mixture had been vigorously stirred overnight. The mixture was stirred at −78 °C for 3 h before a solution of 3,4-dihydro-2*H*-fluoren-1(9*H*)-one (**1**) (24.9 g, 135 mmol) in THF (80 mL) was added dropwise, and the reaction mixture allowed to reach room temperature overnight. Water (50 mL) was added, the organic phase collected, evaporated to dryness and the residual material triturated with dichloromethane (1.0 L). The organic solution was washed with water (3×100 mL), dried ($MgSO_4$), the solution evaporated and the residual material subjected to flash chromatography on silica gel using EtOAc:hexane 1:10; yield 29.3 g (65%) of a light yellow oil. HRMS(EI): M 334.1385. Calc. for $C_{22}H_{22}OS$: 334.1391. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.92–0.97 (m, 1H), 1.26–1.41 (m, 3H), 1.73–1.86 (m, 2H), 1.95–2.13 (m, 1H), 2.45–2.50 (m, 3H), 2.60–2.68 (m, 1H), 3.25 (dd, $J = 22.5$, 22.5 Hz, 2H), 7.13–7.39 (m, 6H), 7.55–7.59 (m, 2H), 7.84 (d, $J = 7.6$ Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.9, 17.0, 19.7, 25.7, 34.2, 37.7, 40.8, 75.1, 121.8, 123.1, 123.5, 125.8, 126.2, 128.2, 130.4, 136.1, 137.3, 142.0, 143.8, 146.5. MS(EI): 334 (M^+, 18%), 316 (59), 207 (77), 185 (100), 165 (37), 150 (57), 129 (19).

4.4. 2,3-Dihydro-4-[1-(phenylthio)cyclopropyl]-1H-fluorene (**3**)

The product (**3**) (yield 78%) was a viscous dark yellow oil. HRMS(EI): M 316.1284. Calc. for $C_{22}H_{20}S$: 316.1286. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.06–1.24 (m, 1H), 1.41–1.55 (m, 2H), 1.61–1.76 (m, 1H), 1.80–1.98 (m, 2H), 6.46 (s, 1H), 6.98–7.03 (m, 1H), 7.19–7.22 (m, 2H), 7.25–7.34 (m, 3H), 7.46 (dd, 1H, $J = 0.47$, 7.6 Hz), 7.60–7.63 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.6, 25.2, 31.2, 31.6, 65.7, 119.3, 122.9, 123.3, 124.5, 126.6, 128.57, 128.63, 132.5, 133.6, 135.2, 137.4, 140.0, 143.4, 146.5. MS(EI): 316 (M^+, 62%), 283 (5), 239 (6), 207 (100), 191 (27), 178 (23), 165 (33), 152 (9).

4.5. 1′,2′,3′,4′-Tetrahydro-9′H-spiro[cyclobutane-1,4′-fluoren]-2-one (**4**)

Triethyloxonium tetrafluoroborate (99 mg, 0.52 mmol) was added to a solution of 2,3,4,9-tetrahydro-4-[1-(phenylthio)cyclopropyl]-1*H*-fluoren-4-ol (**2**) (167 mg, 0.5 mmol) in anhydrous dichloromethane (15 mL) under argon at room temperature. The mixture was stirred at room temperature for 20 h before water (20 mL) and diethyl ether (100 mL) were added. The organic layer was collected, washed with saturated $NaHCO_3$ (20 mL), dried ($MgSO_4$), the solution evaporated and the residual material subjected to flash chromatography on silica gel using EtOAc:hexane 1:10; yield 84 mg (75%) of a light yellow solid. HRMS(EI): M 224.1209. Calc. for $C_{16}H_{16}O$: 224.1201. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.69–1.82 (m, 1.5H), 1.89–2.05 (m, 3.5H), 2.41–2.45 (m, 2H), 2.51–2.61 (m, 1H), 3.16–3.39 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.0, 23.5, 25.9, 33.0, 40.7, 43.1, 64.9, 118.6, 123.8, 124.0, 126.0, 134.1, 142.7, 143.2, 144.6, 213.9. MS(EI): 224 (M^+, 10%), 196 (8), 182 (100), 167 (29), 152 (14), 128 (10), 115 (7).

4.6. 2-(Cyclopenta-2,4-dienylidene)-1′,2′,3′,4′-tetrahydro-9′H-spiro[cyclobutane-1,4′-fluorene] (**5**)

Pyrrolidine (6.4 mL, 74 mmol) was added dropwise to a solution of 1′,2′,3′,4′-tetrahydro-9′*H*-spiro[cyclobutane-1,4′-fluoren]-2-one (**4**) (2.05 g, 9.2 mmol) and cyclopentadiene (6.1 mL, 74 mmol) in a 1:5 mixture of dichloromethane and methanol (50 mL) at 0 °C. The mixture was stirred at room temperature for 96 h and was subsequently poured

into 0.5 M HCl (100 mL) at 0 °C. The mixture was extracted with hexane (3 × 150 mL), the extracts dried ($MgSO_4$), evaporated and the residual material subjected to flash chromatography on silica gel with EtOAc:hexane 1:100; yield 1.12 g (45%) of a dark yellow oil. HRMS(EI): M 272.1558. Calc. for $C_{21}H_{20}$: 272.1565. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.70–1.84 (m, 1H), 1.91–2.00 (m, 1H), 2.00–2.13 (m, 2H), 2.23–2.31 (m, 1H), 2.50–2.56 (m, 2H), 2.6–2.72 (m, 1H), 3.23–3.45 (m, 4H), 5.98 (dt, $J = 1.7$, 5.2 Hz, 1H), 6.19–6.21 (m, 1H), 6.37 (dt, $J = 1.7$, 5.1 Hz, 1H), 6.41–6.44 (m, 1H), 7.07–7.19 (m, 3H), 7.40 (d, $J = 6.6$ Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.1, 26.3, 27.0, 29.1, 38.3, 40.7, 49.6, 119.7, 119.88, 119.92, 123.3, 123.4, 125.8, 130.1, 130.3, 138.8, 139.6, 142.3, 142.7, 143.9, 164.0. MS(EI): 272 (M^+, 100), 257 (17), 243 (70), 229 (28), 215 (65), 202 (23), 182 (15), 165 (29), 115 (18), 49 (5).

4.7. *cis*-2-(Cyclopentadienyl)-1′,2′,3′,4′-tetrahydro-9′*H*-spiro[cyclobutane-1,4′-fluorene] (**6**)

1.0 M $LiBEt_3H$ in THF (0.4 mL) was added dropwise to a solution of 2-(cyclopenta-2,4-dienylidene)-1′,2′,3′,4′-tetrahydro-9′*H*-spiro[cyclobutane-1,4′-fluorene] (**5**) (71 mg, 0.26 mmol) in THF (5 mL) at 0 °C. The mixture was stirred at room temperature for 22 h, poured into a mixture of water/ice (50 mL) and dichloromethane (50 mL). The layers were separated, the water phase extracted with dichloromethane (2 × 30 mL), the combined organic solutions washed with water (3 × 10 mL), dried ($MgSO_4$), and the solution evaporated to furnish the crude title compound which was used as such in the subsequent reaction; yield 65 mg (91%) of a light yellow oil as a 1:1 mixture of two double bond isomers in the cyclopentane ring. HRMS(EI): M 274.1710. Calc. for $C_{21}H_{22}$: 274.1721. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.70–3.30 (m, 1.5H), 6.03–6.14 (m, 1.5H), 6.25–6.29 (m, 1H), 6.49–6.55 (m, 0.5H), 7.00–7.66 (m, 4H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 19.3, 19.4, 20.6, 21.5, 26.5, 26.6, 28.3, 28.5, 40.4, 40.6, 40.7, 41.1, 41.6, 42.9, 44.6, 45.4, 46.6, 48.3, 120.0, 121.2, 122.6, 122.8, 123.0, 123.1, 125.1, 125.5, 125.9, 126.6, 131.2, 131.6, 132.3, 134.4, 139.3, 139.4, 139.7, 142.6, 142.7, 142.9, 145.2, 145.6, 148.3, 150.9. MS(EI): 274 (M^+, 8%), 195 (12), 182 (100), 167 (17), 153 (7), 141 (7), 91 (7).

4.8. 2-(η^5-Cyclopenta-2,4-dienyl)-1′,2′,3′,4′-tetrahydrospiro[cyclobutane-1,4′-(η^5-fluorenyl)]zirconium dichloride (**8**)

1.6 M *n*-BuLi in hexane (4.6 mL, 7.4 mmol) was added to solution of *cis*-2-(cyclopenta-dienyl)-1′,2′,3′,4′-tetrahydro-9′*H*-spiro[cyclobutane-1,4′-fluorene] (**6**) (842 mg, 3.1 mmol) in diethyl ether (20 mL) under argon at 0 °C. The reaction mixture was allowed to reach room temperature overnight. A dilithium salt was precipitated as a tan yellow solid which was filtered off, washed with pentane (5 mL), dried in vacuo and stored in a glovebox; yield: 860 mg (98%). Solid, sublimated zirconium tetrachloride (233 mg, 1.0 mmol) was added to a suspension of the dilithiated product (286 mg, 1.0 mmol) in toluene (20 mL) at −20 °C. The mixture was stirred at room temperature overnight, filtered through a glass sinter and the clear dark yellow filtrate concentrated to 1 mL before addition of pentane (20 mL). A light yellow solid precipitate was formed. The solid was filtered off, washed with a small amount of pentane and dried in vacuo; yield: 90 mg (21%), of a light yellow solid. The product was crystallised for X-ray analysis by slow evaporation of a solution in toluene. HRMS(EI): M 431.9978. Calc. for $C_{21}H_{20}Cl_2Zr$: 431.9989. ^{1}H NMR (CD_2Cl_2, 300 MHz): $\delta = 1.65$ (dt, $J = 3.0$, 13.6, 1H), 1.94–2.25 (m, 4H), 2.50–2.68 (m, 2H), 2.95–3.09 (m, 2H), 3.19 (dd, $J = 5.1$, 17.0 Hz, 1H), 4.04 (t, $J = 8.7$ Hz, 1H), 6.20 (q, $J = 2.4$, 3.1 Hz, Cp, 1H), 6.29 (s, fluorene, 1H), 6.30–6.37 (m, Cp, 2H), 6.43 (q, $J = 2.5$, 2.8 Hz, Cp, 1H), 7.16–7.31 (m, Ar, 2H), 7.58 (dd, $J = 1.2$, 8.3 Hz, Ar, 1H), 8.26 (dd, $J = 0.6$, 8.5 Hz, Ar, 1H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 19.3, 20.3, 27.0, 27.8, 41.0, 50.5, 52.1, 107.1, 107.5, 114.4, 119.2, 120.1, 123.9, 124.3, 124.8, 125.2, 125.8, 126.4, 133.2, 135.7, 139.6. MS(EI): 432 (M^+, 68%), 341 (54), 303 (10), 251 (100), 215 (18), 181 (32), 165 (56), 152 (21).

4.9. *cis*-2-(3-Isopropylidenecyclopenta-2,4-dienyl)-1′,2′,3′,4′-tetrahydro-9′*H*-spiro[cyclobutane-1,4′-fluorene] (**10**)

Acetone (1.5 mL, 17.7 mmol) and pyrrolidine (1.8 mL, 20.7 mmol) were added to a solution of *cis*-2-(cyclopenta-dienyl)-1′,2′,3′,4′-tetrahydro-9′*H*-spiro[cyclobutane-1,4′-fluorene] (**6**) (1.62 g, 5.9 mmol) in methanol (40 mL) and dichloromethane (10 mL) under argon at 0 °C. The mixture was allowed to reach room temperature and stirred for 48 h before the mixture was poured into ice/water (100 mL). The resultant mixture was extracted with hexane (3 × 50 mL), the organic phase collected and washed with water (3 × 10 mL). The dried ($MgSO_4$) solution was evaporated to leave a dark yellow oil which was used in the subsequent reaction without further purification; yield 1.57 g (84%). HRMS(EI): M 314.2025. Calc. for $C_{24}H_{26}$: 314.2034. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 1.75–1.96 (m, 5H), 2.02 (s, CH_3, 3H), 2.05 (s, CH_3, 3H), 2.15–2.25 (m, 2H), 2.43–2.63 (m, 4H), 2.87–3.00 (m, 1H), 3.16 (d, $J = 3.0$ Hz, 1H), 6.05–6.08 (m, Cp, 1H), 6.14–6.18 (m, Cp, 2H), 7.03 (dt, $J = 1.0$, 7.4 Hz, Ar, 1H), 7.15 (dt, $J = 1.3$, 7.6 Hz, Ar, 1H), 7.31 (dd, $J = 0.5$, 7.3 Hz, Ar, 1H), 7.66 (d, $J = 7.7$ Hz, Ar, 1H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 19.9, 21.8, 22.7 (double, CH_3), 27.0, 29.0, 41.0, 42.2, 45.7, 48.0, 115.9, 120.6, 121.5, 123.2, 123.4, 125.8, 132.7, 139.9, 142.3, 143.4, 143.5, 146.1, 146.2, 148.5. MS(EI): 314 (M^+, 20%), 272 (12), 182 (100), 167 (27), 154 (11), 141 (16), 132 (46), 115 (12), 91 (10).

4.10. cis-2-(3-Isopropylcyclopentadienyl)-1′,2′,3′,4′-tetrahydro-9′H-spiro[cyclobutane-1,4′-fluorene] (11)

A 1.0 M solution of $LiBEt_3H$ in THF (6.3 mL, 6.3 mmol) was added to a solution of *cis*-2-(3-isopropylidenecyclopentadienyl)-1′,2′,3′,4′-tetrahydro-9′*H*-spiro[cyclobutane-1,4′-fluorene] (**10**) (1.31 g, 4.2 mmol) in THF (40 mL) under argon at 0 °C. The mixture was stirred at 0 °C for 2 h and poured into ice/water (100 mL) and dichloromethane (50 mL). The organic phase was separated, the water phase extracted with dichloromethane (2 × 50 mL) and the combined organic solutions washed with water (3 × 20 mL). The dried ($MgSO_4$) solution was evaporated to leave a light yellow oil which was used in the subsequent reaction without any further purification; yield 1.28 g (97%). HRMS(EI): M 316.2192. Calc. for $C_{24}H_{28}$: 316.2191. MS(EI): 316 (M^+, 15%), 273 (6), 182 (100), 167 (25), 141 (10), 134 (48), 119 (22), 91 (6).

4.11. cis-2-(3-Isopropylidenecyclopenta-2,4-dienyl)-1′,2′,3′,4′-tetrahydro-9′H-spiro[cyclobutane-1,1′-fluorene] (13)

Acetone (0.44 mL, 5.9 mmol) and pyrrolidine (0.6 mL, 7.2 mmol) were added to a solution of *cis*-2-(cyclopentadienyl)-1′,2′,3′,4′-tetrahydro-9′*H*-spiro[cyclobutane-1,1′-fluorene] (**12**) [1] (1.0 g, 3.6 mmol) in methanol (20 mL) and dichloromethane (5 mL) under argon at 0 °C. The mixture was allowed to reach room temperature overnight and poured into ice/water (50 mL). The mixture was extracted with hexane (3 × 20 mL), the hexane solution washed with water (2 × 10 mL), dried ($MgSO_4$) and evaporated to leave a dark yellow oil which was used in the subsequent reaction without further purification; yield 954 mg (84%). HRMS (EI): M 314.2026. Calc. for $C_{24}H_{26}$: 314.2034. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 1.77–2.01 (m, 5H), 2.09 (s, CH_3, 3H), 2.14 (s, CH_3, 3H), 2.29–2.64 (m, 6H), 3.29–3.44 (m, 2H), 6.14 (dd, $J = 1.4$, 5.3 Hz, 1H), 6.24 (dd, $J = 2.0$, 3.9 Hz, 1H), 6.34 (dd, $J = 2.2$, 5.2 Hz, 1H), 7.07 (dt, $J = 2.0$, 7.1 Hz, 1H), 7.17–7.22 (m, 2H), 7.30 (d, $J = 7.4$ Hz, 1 H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 20.4, 21.5, 22.9, 23.0 (2 shifts), 32.3, 38.8, 40.0, 46.6, 47.9, 115.2, 118.1, 121.6, 123.5, 124.0, 126.2, 132.1, 136.9, 142.3, 143.7, 146.5 (2 shifts), 147.1, 148.6. MS (EI): *m*/*z* (%) 314 (M^+, 21), 195 (7), 182 (100), 167 (34), 153 (11), 141 (14), 132 (21), 117 (8), 91 (5).

4.12. cis-2-(3-Isopropylcyclopentadienyl)-1′,2′,3′,4′-tetrahydro-9′H-spiro[cyclobutane-1,1′-fluorene] (14)

A 1.0 M solution of $LiBEt_3H$ in THF (4.5 mL, 4.5 mmol) was added to a solution of *cis*-2-(3-isopropylidenecyclopenta-2,4-dienyl)-1′,2′,3′,4′-tetrahydro-9′*H*-spiro [cyclobutane-1,1′-fluorene] (**13**) (900 mg, 2.7 mmol) in THF (40 mL) under argon at 0 °C. The stirring was continued at this temperature for 1.5 h and the mixture poured into ice/water (100 mL) and dichloromethane (50 mL). The organic phase was separated, the water phase extracted with dichloromethane (2 × 50 mL) and the combined organic solutions washed with water (3 × 20 mL). The dried ($MgSO_4$) solution was evaporated to leave a light yellow oil which was used in the subsequent reaction without any further purification; yield 753 mg (88%). HRMS (EI): M 316.2199. Calc. for $C_{24}H_{28}$: 316.2191. MS (EI): *m*/*z* (%) 316 (M^+, 9), 182 (100), 167 (14), 154 (6), 141 (7), 119 (9).

4.13. 2-(η^5-3-Isopropylcyclopenta-2,4-dienyl)-1′,2′,3′,4′-tetrahydrospiro[cyclobutane-1,4′-(η^5-fluorenyl)]zirconium dichloride (16)

1.6 M *n*-BuLi in hexane (5.6 mL, 8.9 mmol) was added to *cis*-2-(3-isopropylcyclopenta-2,4-dienyl)-1′,2′,3′,4′-tetrahydro-9′*H*-spiro[cyclobutane-1,4′-fluorene] (**11**) (1.28 g, 3.9 mmol) in diethyl ether (40 mL) under argon at 0 °C. The reaction mixture was allowed to reach room temperature overnight. The solvent was decanted from the precipitated red syrup. The sirup was triturated with pentane (15 mL). The dilithiated light yellow solid was isolated by filtration, and dried in vacuo; yield 1.30 g (98%). Freshly sublimed solid zirconium tetrachloride (466 mg, 2.0 mmol) was added to a suspension of the dilithiated product (632 mg, 1.9 mmol) in toluene (40 mL) at −20 °C. The mixture was stirred at room temperature overnight, filtered through a glass sinter, and the filtrate evaporated. The residual material was extracted with pentane (3 × 15 mL), the pentane solution concentrated to ca. 3 mL and cooled to −20 °C. A light yellow solid was precipitated, filtered off and dried in vacuo; yield 100 mg (11%). The product was a 3:5 mixture of the two isomeric products **16a** and **16b**. HRMS(EI): M 474.0464. Calc. for $C_{24}H_{26}Cl_2Zr$: 474.0459. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 0.84 (d, $J = 6.8$ Hz, CH_3, major), 0.97 (d, $J = 6.9$ Hz, CH_3, major), 1.08 (d, $J = 6.8$ Hz, CH_3, minor), 1.12 (d, $J = 6.9$ Hz, CH_3, minor), 1.2–4.0 (series of m, 19.2 H), 5.92 (t, $J = 2.7$ Hz, Cp, major, 1H), 6.02–6.06 (m, Cp double intensity of minor, 1.2H), 6.23–6.25 (m, Cp and fluorene major, 2H), 6.27 (t, $J = 2.9$ Hz, major, 1H), 6.30 (s, fluorene minor, 0.6H), 6.41 (t, $J = 3.0$ Hz, Cp minor, 0.6H), 7.16–7.27 (m, Ar, 3.2H), 7.56–7.62 (m, Ar, 1.6H), 8.26 (d, $J = 8.6$ Hz, Ar major, 1H), 8.31 (d, $J = 8.6$ Hz, Ar minor, 0.6H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 18.9, 19.1, 20.2, 20.5, 22.6 (2 shifts), 23.5, 23.8, 24.3, 25.3, 28.7, 29.2, 29.9, 30.6, 37.3, 38.4, 48.9, 49.3, 51.1, 51.4, 95.1, 95.5, 107.4, 107.7, 113.1 (2 shifts), 116.5, 118.9, 119.4, 119.6, 123.4, 125.0 (2 shifts), 125.6, 126.0, 126.2, 126.3, 126.6, 128.6, 129.4, 132.2, 132.6, 137.2, 138.2, 140.9, 141.8, 141.9, 144.6. MS(EI): 474 (M^+, 43%), 341 (11), 293 (100), 255 (13), 181 (16), 165 (23), 91 (6).

4.14. 2-(η^5-3-Isopropylcyclopenta-2,4-dienyl)-1′,2′,3′,4′-tetrahydro-spiro[cyclobutane-1,1′-(η^5-fluorenyl)]zirconium dichloride (**18**)

1.6 M *n*-BuLi in hexane (3.0 mL, 4.8 mmol) was added to a solution of *cis*-2-(3-isopropylcyclopentadienyl)-1′,2′,3′,4′-tetrahydro-9′*H*-spiro[cyclobutane-1,1′-fluorene] (**14**) (695 mg, 2.2 mmol) in diethyl ether (20 mL) under argon at 0 °C. The reaction mixture was allowed to reach room temperature overnight. A red syrup-like precipitate was formed. The solvent was decanted off, the residue triturated with hexane (10 mL), and a light yellow solid was formed. The solid was filtered off and dried in vacuo; yield 686 mg (95%). Freshly sublimed zirconium tetrachloride (466 mg, 2.0 mmol) was added to a suspension of the dilithiated ligand (656 mg, 2.0 mmol) in toluene (40 mL) under argon at room temperature. The mixture was stirred at room temperature overnight, filtered through a glass sinter and the solution evaporated. The residual material was extracted with pentane (3 × 15 mL), the pentane extracts concentrated to ca. 3 mL and cooled to −20 °C. A light yellow solid was precipitated and was filtered off and dried in vacuo; yield 114 mg (12%) of a 4:5 mixture of two isomeric products **18a** and **18b**. HRMS (EI): M 474.0479. Calc. for $C_{24}H_{26}Cl_2Zr$: 474.0459. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 1.06 (d, $J = 6.8$ Hz, CH_3, minor), 1.07 (d, $J = 6.9$ Hz, CH_3, major), 1.11 (d, $J = 7.0$ Hz, CH_3, minor), 1.15 (d, $J = 6.9$ Hz, CH_3, major), 1.20–2.50 (m, 11.2H), 2.64–2.83 (m, 3.6H), 2.95–3.09 (m, 1.8H), 3.19–3.32 (m, 1.8H), 3.73–3.79 (m, 1.8H), 5.81 (t, $J = 2.6$ Hz, Cp–H, minor, 0.8H), 6.05–6.09 (m, Cp–H, double intensity of major, 2H), 6.42 (t, $J = 2.8$ Hz, Cp–H, minor, 0.8H), 6.54 (t, $J = 2.6$ Hz, Cp–H, major, 1H), 6.81 (t, $J = 3.0$ Hz, Cp–H, minor, 0.8H), 6.86 (s, fluorene-H, major, 1H), 6.98 (s, fluorene-H, minor, 0.8H), 7.14–7.30 (m, Ar–H, 3.6H), 7.42–7.61 (m, Ar–H, 3.6H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 19.5, 19.6, 20.3, 20.6, 22.5, 22.7, 23.6, 23.9, 24.2, 25.5, 28.9, 29.2, 30.4, 30.6, 38.3, 38.6, 49.3, 49.5, 50.6, 50.7, 95.2, 95.4, 107.6, 107.8, 113.0, 113.2, 117.0, 119.2, 119.4, 119.8, 123.5, 124.9, 125.1, 125.6, 126.0, 126.2, 126.3, 126.6, 128.6, 129.4, 132.2, 132.6, 137.2, 138.2, 140.9, 141.7, 142.0, 145.7. MS (EI): *m*/*z* (%) 474 (M^+, 64), 312 (35), 293 (66), 269 (23), 239 (28), 182 (76), 178 (95), 165 (100), 91 (33).

4.15. Polymerisation reactions

The polymerisation experiments in toluene were carried out in a 500 mL glass reactor equipped with a magnetic stirrer, thermocouple and a monomer inlet tube. The reactor was evacuated, filled with propene, and charged with 200 mL of dry toluene. The precatalysts (approximately 0.02 mmol) were incubated with MAO (20 mmol) in toluene (13 mL) for 5 min before the polymerisation was started by injection of the active catalyst into the reactor. The temperature was kept at 30 °C and the propene pressure at 1.1 bar during the reaction. A solution of 1% HCl in MeOH (200 mL) was added after 1 h to quench the reaction. The polymers from the parent zirconocenes **8** and **9** (Scheme 2) were separated from methanol by decantation, washed with methanol and dried at 60 °C in a rotary evaporator overnight. The polymers from the isopropyl substituted isomers **16** and **18** were collected by filtration, washed with methanol, dried and extracted with Et_2O (50 mL) to remove atactic PP.

4.16. Polymer analysis

The properties of the zirconocene complexes as a propene polymerisation precatalyst were briefly studied with MAO in toluene under a propene pressure of 1.1 bar at 30 °C. Molecular weights and molecular weight distributions were determined by gel-permeation chromatography (GPC, Waters 150CVplus, 140 °C in 1,2,4-trichlorobenzene) for the polymers from the isopropyl substituted isomers **16** and **18**. The molecular weights for polymers from **8** and **9** (Scheme 1) were calculated by ^{1}H NMR end-group analysis [16]. ^{1}H NMR spectra were recorded at 300 MHz on a Bruker DPX 300 instrument ($C_2D_2Cl_4$, 363 K and 256 scans). ^{13}C NMR spectra were recorded at 75 MHz on the same instrument ($C_2D_2Cl_4$, 363 K, 3000 scans and a delay time of 12 s) and analysed by known methods [17].

References

[1] G. Langli, C. Rømming, K. Undheim, J. Organomet. Chem. 691 (2006) 356–360.
[2] F. Piemontesi, I. Camurati, L. Resconi, D. Balboni, A. Sironi, M. Moret, R. Zeigler, N. Piccolrovazzi, Organometallics 14 (1995) 1256–1266.
[3] D. Binder, C.R. Noe, Monatsh. Chem. 107 (1976) 1145–1151.
[4] K. Tanaka, H. Uneme, S. Matsui, A. Kaji, Bull. Chem. Soc. Jpn. 55 (1982) 2965–2972.
[5] T. Imamato, Pure Appl. Chem. 62 (1990) 747–752.
[6] (a) B.M. Trost, Acc. Chem. Res. 7 (1974) 85–92;
(b) B.M. Trost, D.E. Keeley, H.C. Arndt, M.J. Bogdanowicz, J. Am. Chem. Soc. 99 (1977) 3088–4000.
[7] J.N. Christopher, R.F. Jordan, J.L. Petersen, V.G. Young, Organometallics 16 (1997) 3044–3050.
[8] I.M. Lee, W.J. Gauthier, J.M. Ball, B. Iyengar, S. Collins, Organometallics 11 (1992) 2115–2122.
[9] L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, Chem. Rev. 100 (2000) 1253–1345.
[10] H.G. Alt, Chem. Rev. 100 (2000) 1205–1221.
[11] P. Schertl, H.G. Alt, J. Organomet. Chem. (1997) 545–546, 553–557.
[12] N. Takeda, T. Imamoto, Org. Synth. 76 (1999) 228–238.
[13] SMART and SAINT, Area-Detector Control and Integration Software Version 5.054, Bruker Analytical X-ray Instruments Inc., Madison, WI, USA, 1998.
[14] G.M. Sheldrick, SADABS Version 2.01. Program for Empirical Correction of Area Detector Data, University of Göttingen, Germany, 2000.
[15] G.M. Sheldrick, SHELXTL, Structure Determination Programs Version 5.10, Bruker Analytical X-ray Instruments Inc., Madison, WI, USA, 1997.

[16] (a) J.A. Ewen, J. Am. Chem. Soc. 106 (1984) 6355–6364;
(b) G. Moscardi, L. Resconi, Organometallics 20 (2001) 1918–1931;
(c) C.J. Schaverien, R. Ernst, P. Schut, T. Dall'Occo, Organometallics 20 (2001) 3436–3452.

[17] (a) J. Inoue, Y. Itabashi, R. Chujo, Y. Doi, Polymer 25 (1984) 1640–1644;
(b) G. Erker, R. Nolte, R. Aul, S. Wilker, C. Krüger, R. Noe, J. Am. Chem. Soc. 113 (1991) 7594–7602.