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# Reduction reactions of the metallocene complex $(\eta^5\text{-}C_5H_4CMe_2C_9H_7)_2ZrCl_2$

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## Abstract

The preparation and characterization of the substituted bis(cyclopentadienyl) zirconium dichloride complexes $(\eta^5\text{-}C_5H_4CMe_2C_9H_7)_2ZrCl_2$ (**1a, b**) is reported. The isomer mixture of **1a, b** was treated with different reducing agents such as sodium and *n*-butyllithium under various reaction conditions. In these reactions CC and CH activation and cleavage reactions were observed. In combination with methylaluminoxane (MAO) **1a, b** and **3** showed low activities as homogeneous ethylene polymerization catalysts and no activities towards propylene. Compounds **2** and **3** were characterized by NMR spectroscopy and X-ray crystallography. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Zirconium; Metallocene complexes; CH activation; CC activation

## 1. Introduction

Recently a large number of metallocene dichloride complexes has been synthesized due to their potential as excellent catalyst precursors for the polymerization of α-olefins [1–7] and their application in syntheses [8–13].

Up to now it was not possible to isolate free zirconocene, although it is described as a highly reactive intermediate [14]. Free zirconocene, '$(C_5H_5)_2Zr$', is unstable, because of its coordinatively and electronically unsaturated nature. On the other side '$(C_5H_5)_2Zr$ in statu nascendi' is able to activate suitable substrates.

However, it is possible to stabilize such metallocenes by substrates like trimethylphosphine [15–17], olefins [17] and *n*-donors [18].

In this paper we describe reduction reactions of the unbridged metallocene complex $(\eta^5\text{-}C_5H_4CMe_2C_9H_7)_2$-$ZrCl_2$ with various substrates.

## 2. Results and discussion

### 2.1. Synthesis of $(\eta^5\text{-}C_5H_4CMe_2C_9H_7)_2ZrCl_2$ (1a, b)

Two equivalents of *n*-butyllithium react with $C_9H_7CMe_2C_5H_5$ to give the corresponding dianion. The reaction of zirconium tetrachloride with the dianion leads to the known ansa metallocene dichloride complex [19].

The reaction of indenyllithium and 6,6-dimethyl fulvene gives the mono anion $[C_9H_7CMe_2C_5H_4]^-$. Two equivalents of this anion can react with one equivalent of $ZrCl_4$ to yield the unbridged metallocene complex **1** that exists as two diastereomers **a** and **b**, due to the endo and exo orientations of the indenyl substituents (Scheme 1).

### 2.2. Reduction of 1a, b with sodium in the presence of trimethylphosphine

The reduction of **1a, b** with sodium sand in tetrahydrofuran leads to the trimethylphosphine olefin com-

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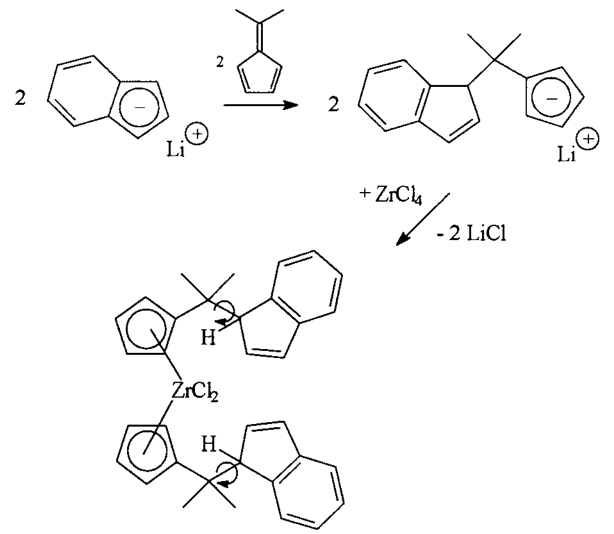


**1a, b**

Scheme 1.

plex **2** (Scheme 2). It is very likely that the first step in this reaction involves the formation of a metallocene as an intermediate. In a second step the metallocene could become stabilized via coordination reactions of the olefin function of one indenyl substituent and one equivalent of trimethylphosphine. The loss of one indenyl substituent could be the consequence of a CC activation reaction induced by sodium [20,21] leading to radicals that can undergo stabilization by intra- or intermolecular hydrogen abstraction [22].

This reaction depends very much on the solvent: in toluene no reaction could be observed; obviously because intermediates cannot be stabilized. A similar behaviour is known from the reduction reactions of ($\eta^5$-$C_5H_5$)$_2$ZrCl$_2$ [23] and ($\eta^5$-$C_5H_5$)($\eta^5$-$C_5H_4CMe_2$-$C_9H_7$)ZrCl$_2$ [24] with sodium in the presence of trimethylphosphine.

### *2.3. Reduction of **1a, b** with two equivalents of n-butyllithium*

Metallocene dichloride complexes like ($\eta^5$-$C_5H_5$)$_2$-ZrCl$_2$ react with 2 equiv. of *n*-butyllithium to give di(butyl) complexes. These complexes are not stable and undergo $\beta$-H elimination to give butane, butene and zirconocene [24–27].

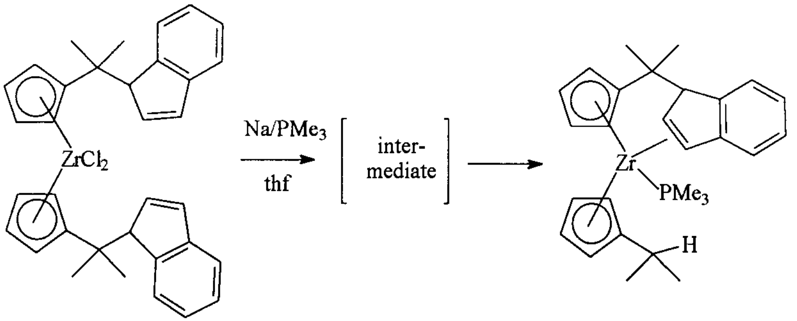
In a similar manner **1a, b** were reacted with two equivalents of *n*-butyllithium in toluene to give a mixture of products from which metallacycle **3** could be isolated and characterized by an X-ray structure analysis. Scheme 3 suggests a reaction pathway that could explain the formation of **3**. The di(butyl) intermediate could eliminate butane and butene to form an intermediate stabilized by either one or two olefin functions of the two indenyl groups. Analogous results are known from similar reactions [26]. A subsequent CH activation at the five membered ring of one indenyl moiety could be responsible for the formation of the Zr-$\sigma$-bond. Simultaneously the hydrido ligand at the metal could be transferred to the other indenyl moiety to give the $\eta^1$-indanyl ligand. Such a hydrogen shift reaction can also be explained as a retro-$\beta$-H elimination step and is known from similar cases [28].

### *2.4. Crystal structure of ($\eta^5$-$C_5H_4CMe_2H$) ($\eta^5$:$\eta^2$-$C_5H_4CMe_2C_9H_7$)Zr($PMe_3$) (2)*

The molecular structure of **2** is shown in Fig. 1. Selected bond lengths and internal bond angles are given in Tables 1 and 2.

The structure of **2** can be compared with a similar compound [24]. The additional isopropyl group at one cyclopentadienyl ligand causes only little differences in the structural parameters.

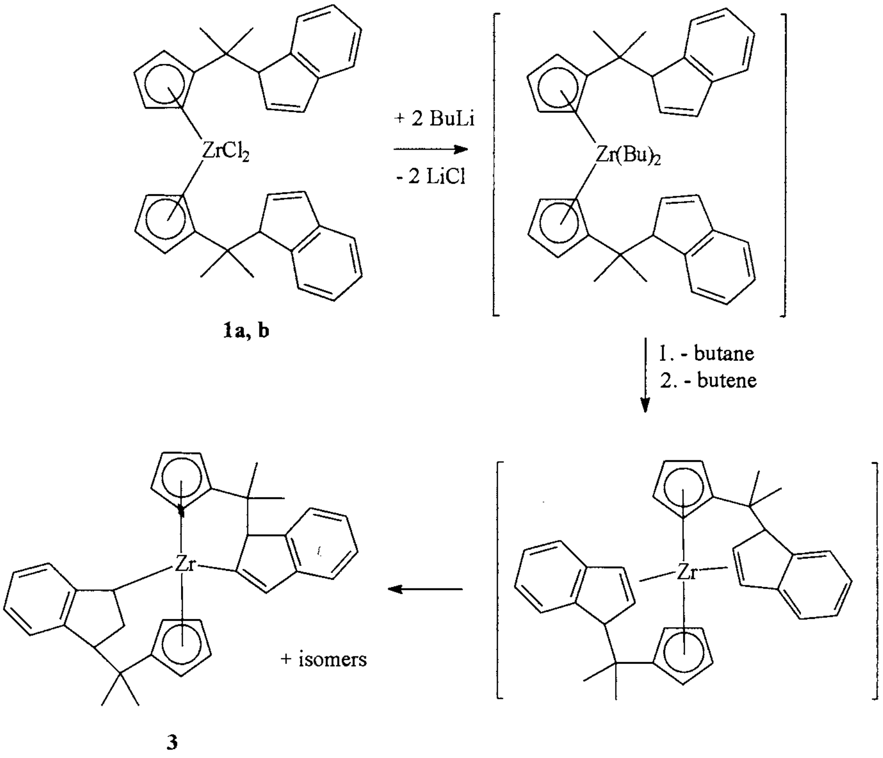
The orientation of the olefinic bond (C17–C18) is remarkable, because it lies in the plane that bisects the $Cp_2Zr$ fragment. Analogous orientations of olefin ligands are observed in other zirconocene olefin complexes [23,29–33] like ($\eta^5$-$C_5H_5$)$_2$Zr($C_2H_4$)($PMe_3$)



**1a, b**

**2**

Scheme 2.



Scheme 3.

[23,33]. The symmetry of the hybrid orbitals of zirconium determines the steric orientation of the olefin. This orientation is important for the stereoselective propylene polymerization with metallocene catalysts [34]. The bond lengths Zr–C(18) (231.7(2) pm) and Zr–C(17) (239.5(2) pm) are comparable with the corresponding Zr–C distances in ($\eta^5$-$C_5H_5$)$_2$Zr($C_2H_4$)($PMe_3$) (233.4 and 237.7 pm). The large bond distance C(17)–C(18) (146.1(3) pm) indicates a metallacyclopropane structure rather than an olefin complex.

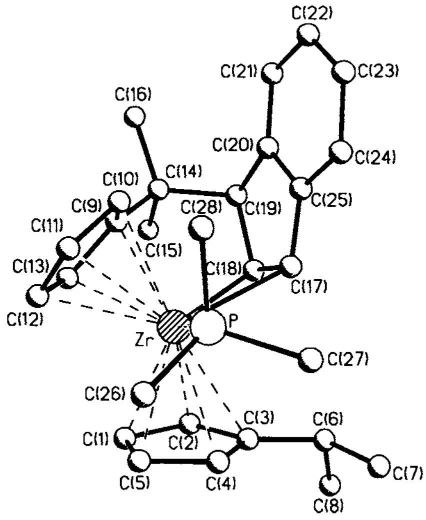


Fig. 1. X-ray structure of **2**

## 2.5. *Crystal structure of* ***3***

The molecular structure of **3** is shown in Fig. 2. Selected bond lengths and internal bond angles are given in Tables 3 and 4.

Table 1
Atom distances of **2**

| Atoms | Distance (pm) | Atoms | Distance (pm) |
|---|---|---|---|
| Zr–P | 271.8(1) | Zr–C(1) | 248.8(2) |
| Zr–C(2) | 252.5(2) | Zr–C(3) | 262.1(2) |
| Zr–C(4) | 257.4(2) | Zr–C(5) | 248.6(2) |
| Zr–C(11) | 253.2(2) | Zr–C(12) | 252.7(2) |
| Zr–C(13) | 249.7(2) | Zr–C(17) | 239.5(2) |
| Zr–C(18) | 231.7(2) | P–C(26) | 183.0(3) |
| P–C(27) | 182.2(3) | P–C(28) | 182.7(2) |
| C(1)–C(2) | 141.3(4) | C(1)–C(5) | 139.2(4) |
| C(2)–C(3) | 141.7(4) | C(3)–C(4) | 141.1(3) |
| C(3)–C(6) | 151.1(3) | C(4)–C(5) | 142.0(4) |
| C(6)–C(7) | 151.1(4) | C(6)–C(8) | 151.9(3) |
| C(9)–C(10) | 142.3(3) | C(9)–C(13) | 141.7(3) |
| C(9)–C(14) | 151.8(3) | C(10)–C(11) | 141.5(3) |
| C(11)–C(12) | 139.4(3) | C(12)–C(13) | 140.7(4) |
| C(14)–C(15) | 152.7(4) | C(14)–C(16) | 153.7(4) |
| C(14)–C(19) | 155.3(4) | C(17)–C(18) | 146.1(3) |
| C(17)–C(25) | 146.5(2) | C(18)–C(19) | 155.1(3) |
| C(19)–C(20) | 151.4(3) | C(20)–C(21) | 138.2(3) |
| C(20)–C(25) | 141.0(3) | C(21)–C(22) | 138.0(4) |
| C(22)–C(23) | 138.2(5) | C(23)–C(24) | 139.1(3) |
| C(24)–C(25) | 138.7(3) | | |

Table 2
Selected angles of **2**

| Atoms | Angles (°) | Atoms | Angles (°) |
|---|---|---|---|
| P–Zr–C(1) | 118.2(l) | C(14)–C(l9)–C(20) | 118.2(2) |
| P–Zr–C(4) | 76.2(1) | C(21)–C(20)–C(25) | 119.9(2) |
| C(1)–Zr–C(10) | 132.0(1) | P–Zr–C(17) | 80.6(1) |
| C(3)–Zr–C(17) | 84.0(1) | C(3)–Zr–C(18) | 81.2(l) |
| P–Zr–C(18) | 116.5(1) | C(10)–Zr–C(18) | 85.6(l) |
| Zr–P–C(26) | 116.0(1) | Zr–P–C(27) | 118.1(1) |
| C(26)–P–C(27) | 100.8(1) | Zr–P–C(28) | 117.3(l) |
| C(2)–C(1)–C(5) | 108.2(2) | Zr–C(3)–C(6) | 127.1(1) |
| C(2)–C(3)–C(4) | 106.6(2) | C(3)–C(6)–C(8) | 109.9(2) |
| C(2)–C(3)–C(6) | 125.7(2) | C(10)–C(9)–C(14) | 126.3(2) |
| C(3)–C(4)–C(5) | 108.7(2) | C(9)–C(10)–C(R) | 108.7(2) |
| C(3)–C(6)–C(7) | 113.0(2) | C(9)–C(14)–C(15) | 110.6(2) |
| C(7)–C(6)–C(8) | 110.2(2) | C(15)–C(14)–C(16) | 108.6(2) |
| C(13)–C(9)–C(14) | 127.5(2) | C(15)–C(14)–C(19) | 107.2(2) |
| C(10)–C(11) C(12) | 107.9(2) | Zr–C(17)–C(18) | 69.0(1) |
| C(9)–C(13)–C(12) | 109.0(2) | C(18)–C(17)–C(25) | 108.1(2) |
| C(9)–C(14)–C(16) | 109.9(2) | Zr–C(18)–C(19) | 117.7(l) |
| C(9)–C(14)–C(19) | 107.0(2) | C(14)–C(19)–C(18) | 109.9(2) |
| C(16)–C(14)–C(19) | 113.6(2) | C(18)–C(19)–C(20) | 103.3(2) |
| Zr–C(17)–C(25) | 122.0(1) | C(19)–C(20)–C(25) | 110.4(2) |
| Zr–C(18)–C(17) | 74.9(l) | C(17)–C(25)–C(20) | 110.0(2) |
| C(17)–C(18)–C(19) | 108.1(2) | | |

Complex **3** consists of two metallacyclic systems. As a consequence both cyclopentadienyl ligands are tilted and the distances of their carbon atoms to the metal vary in a wider range (248.7(3)–257.8(3) pm and 248.0(3)–254.8(3) pm) than in **2** (248.8(2)–252.7(2) pm). In a similar way the bond angles at the isopropylidene bridges of **3** differ considerably (105.1°(3) and 112.1°(2)). The metal carbon σ-bonds Zr–C(11) and Zr–C(27) are in an expected range (230.0(3) and 229.4(3) pm).

### 2.6. *Olefin polymerisation*

Complexes **1a, b** and **3** have been activated with MAO and tested for the polymerization of ethylene and propylene. The activities of both catalysts are low towards ethylene; propylene could not be polymerized. In the ethylene polymerization a slurry of **1a, b** or **3** and MAO in pentane solution had an activity of only 1.8 or 1.9 kg PE mmol $h^{-1}$ (10 bar ethylene, 60°C). The produced polyethylene had a molecular weight, $M_\eta$, of 590 and 280 kg $mol^{-1}$, respectively.

## 3. Experimental

All operations were performed routinely under an argon atmosphere with freshly distilled anhydrous solvents. The NMR spectra were recorded with a Bruker ARX 250 instrument.

### 3.1. *Preparation of* **1a, b**

A 2.25 ml volume (20.0 mmol) of indene was dissolved in 200 ml of tetrahydrofuran and treated with 12.5 ml (20.0 mmol) *n*-butyllithium (1.6 M in hexane) at −78°C. The mixture was allowed to warm up to r.t. and stirred for additional 4 h and then cooled to −78°C. Then 2.41 ml (20.0 mmol) of 6,6-dimethylfulvene were added and the solution was stirred for another 1 h. At −78°C 2.33 g (10.0 mmol) $ZrCl_4$ were added and the slurry was stirred for additional 8 h. Subsequently, the solvent was reduced to 50 ml and the remaining suspension was filtered over sodium sulfate. The filtrate was washed with pentane and the remaining residue was extracted with $CH_2Cl_2$. After evaporation of the solvent, 4.5 g of **1a, b** remained as pale microcrystalline powder. Yield: 9.07 g (75%).

$^1$H-NMR ($CDCl_3$): δ 7.09 (m, 16 H), 6.56 (m, 16 H), 6.09 (m, 24 H), 6.06 (m, 8 H), 5.86 (m, 4 H), 5.77 (m, 4 H), 5.63 (m, 4 H), 5.55 (m, 4 H), 3.24 (m, 8 H), 1.59 (s, 12 H), 1.57 (s, 12 H), 1,40 (s, 12 H), 137 (s, 12 H) ppm $^{13}$C-NMR ($CDCl_3$): δ 145.3, 144,3, 141.2, 136.7, 132.3, 126.7, 124.6, 124.3, 120.9, 118.4, 118.3, 117.5, 117.4, 113.2, 112.3, 110.4, 109.4, 63.9, 39.4, 27.2, 26.8, 23.5, 23.0 ppm; MS, *m*/*e* 605 ($M^+$).

### 3.2. *Preparation of* **2**

A 1.52 g mass (2.52 mmol) of **1a, b** were dissolved in 100 ml tetrahydrofuran and cooled to −78°C. Then 0.46 g (20.0 mmol) sodium and 0.96 ml (12.55 mmol) $PMe_3$ were added and the slurry was warmed up to r.t. within 2 h and stirred for additional 30 h (colour change from colourless to black). The solvent was evaporated and the residue washed with pentane and then extracted with toluene. The orange extract was filtered over sodium sulfate and crystallized at −78°C. yield 0.31 g (25%).

$^1$H-NMR ($C_6D_6$): δ 7.16 (m, 2 H), 6.92 (m, 2 H), 5.46 (m, 1 H), 5.39 (m, 1 H), 5.26 (m, 1 H), 4.93 (m, 2 H), 4.81 (m, 1 H), 4.52 (m, 1 H), 4.36 (d, 3J(1H,1H) 8.2 Hz, 1 H), 3.69 (m, 1 H), 2.86 (dt, $^3J(^1H,^1H)$ 8.2 and 1.8 Hz, 1 H), 2.20 (q, $^3J(^1H,^1H)$ 6.8 Hz, 1 H), 2.07 (dd, $^3J(^1H,^1H)$ 8.2 and 5.8 Hz, 1 H), 1.78 (s, 3 H), 1.44 (s, 3 H), 1.12 (d, $^3J(^1H,^1H)$ 6.8 Hz, 3 H), 1.03 (d, $^3J(^1H,^1H)$ 6.8 Hz, 3 H), 0.85 (d, $^3J(^1H,^1H)$ 15.5 Hz, 9 H) ppm; $^{13}$C-NMR ($C_6D_6$): δ 161.5, 145.9, 143.1, 126.8, 125.6, 119.8, 119.1, 103.1, 102.8, 102.4, 100.0, 98.2, 98.1, 97.3, 97.2, 96.9, 96.0, 74.1, 54.1, 54.0, 53.9, 43.5, 31.3, 28.7, 27.4, 24.3, 23.7, 17.1, 16.9 ppm; $^{31}$P-NMR ($C_6D_6$): δ 2.3 ppm.

### 3.3. *Preparation of* **3**

A 0.83 g mass (1.37 mmol) of **1a, b** were dissolved in 40 ml toluene. After the addition of 1.72 ml (2.76

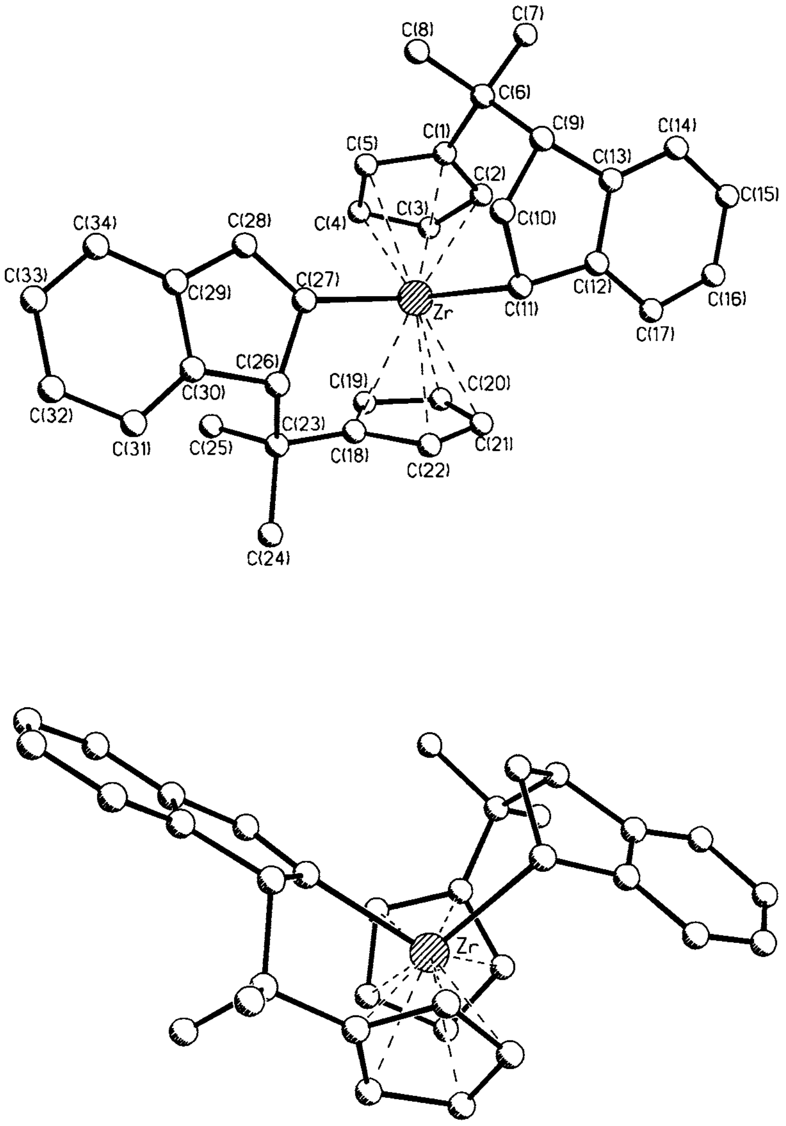


Fig. 2. X-ray structure of **3** (two different views)

mmol) *n*-butyllithium (1.6 M in hexane) the solution was stirred for 7 h at r.t. (the yellow solution turned orange immediately). The reduction of the volume of the solution to 10 ml gave an orange microcrystalline powder (Section 2.2); complex **3** was recrystallized at − 20°C. Yield: 0.23 g (31%).

$^1$H-NMR ($C_6D_6$): $\delta$ 6.74 (m, 1 H), 6.41 (m, 1 H), 6.07 (m, 1 H), 5.58 (m, 1 H), 5.17 (m, 1 H), 4.82 (m, 2 H), 4.31 (m, 1 H), 1.71 (s, 3 H), 1.41 (s, 3 H), 1.38 (s, 3 H), 0.55 (s, 3 H) ppm (because of isomerisation reactions not all signals could be assigned).

### 3.4. X-ray analysis of the crystal structures of 2 and 3

A Siemens P4 diffractometer (Mo–K$_\alpha$-Strahlung; $\lambda = 0.71073$ Å) with a graphite monochromator was used for the measurement of the reflection intensities. The structure solution was done with Siemens SHELXTL PLUS (VMS).

$C_{28}H_{37}PZr$ (**2**), orange prism of dimensions 0.50 × 0.22 × 0.20 mm; monoclinic; space group, $P2_1/n$; $a = 10.662(2)$ Å, $b = 11.428(2)$ Å, $c = 20.498(2)$ Å; $\beta = 102.19(2)°$; $V = 2441.2(7)$ Å$^3$; $Z = 4$; $D_{calc} = 1.349$ Mg m$^{-3}$; $F(000) = 1040$; measured reflexions; 5716; independent and observed reflections ($F > 0.0\sigma(F)$) 4212 with $R_{int} = 1.15\%$; number of refined parameters 272; $R = 3.59\%$ and $wR = 2.13\%$; all non hydrogen atoms anisotropic; maximum residual electron density, 0.36 e Å$^{-3}$; minimum residual electron density, − 0.25 e Å$^{-3}$.

$C_{34}H_{34}Zr \cdot 0.6C_6D_6$ (**3**), orange plate of dimensions 0.45 × 0.35 × 0.08 mm; triclinic; space group, $P\bar{1}$; $a = 9.465(2)$ Å, $b = 12.312(2)$ Å, $c = 13.088(2)$ Å; $\alpha = 104.05(2)°$, $\beta = 102.19(2)°$; $\gamma = 96.78(2)°$; $V = 1416.0(4)$ Å$^3$; $Z = 2$; $D_{calc} = 1.252$ Mg m$^{-3}$; $F(000) = 556$; measured reflexions; 7579; independent and observed reflections ($F > 0.0\sigma(F)$) 6418 with $R_{int} = 5.45\%$; number of

Table 3
Atom distances of **3**

| Atoms | Distance (pm) | Atoms | Distance (pm) |
|---|---|---|---|
| Zr–C(1) | 257.8(3) | Zr–C(2) | 254.2(3) |
| Zr–C(3) | 250.7(3) | Zr–C(4) | 248.7(3) |
| Zr–C(5) | 253.1(2) | Zr–C(ll) | 230.0(3) |
| Zr–C(18) | 252.5(3) | Zr–C(19) | 248.0(3) |
| Zr–C(20) | 249.7(4) | Zr–C(21) | 253.7(3) |
| Zr–C(22) | 254.8(3) | Zr–C(27) | 229.4(3) |
| C(l)–C(2) | 142.6(4) | C(l)–C(5) | 142.2(5) |
| C(l)–C(6) | 152.1(4) | C(2)–C(3) | 139.1(5) |
| C(3)–(4) | 140.9(6) | C(4)–C(5) | 141.6(5) |
| C(6)–C(7) | 153.3(5) | C(6)–C(8) | 154.6(5) |
| C(6)–C(9) | 155.2(3) | C(9)–C(10) | 152.9(4) |
| C(9)–C(13) | 152.5(4) | C(l0)–C(ll) | 155.4(4) |
| C(1l)–C(12) | 147.4(5) | C(12)–C(13) | 141.0(4) |
| C(12)–C(17) | 140.1(4) | C(13)–C(14) | 136.7(5) |
| C(14)–C(15) | 139.8(5) | C(15)–C(16) | 138.5(5) |
| C(16)–C(17) | 137.0(6) | C(18)–C(19) | 140.2(4) |
| C(18–C(22) | 142.0(4) | C(18)–C(23) | 152.2(5) |
| C(19)–C(20) | 141.5(6) | C(20)–C(21) | 136.5(5) |
| C(2l)–C(22) | 142.1(6) | C(23)–C(24) | 153.9(4) |
| C(23)–C(25) | 151.9(4) | C(23)–C(26) | 157.4(4) |
| C(26)–C(27) | 152.2(4) | C(26)–C(30) | 152.2(5) |
| C(27)–C(28) | 136.1(4) | C(28)–C(29) | 143.8(5) |
| C(29)–C(30) | 140.3(4) | C(29)–C(34) | 140.6(5) |
| C(30)–C(31) | 136.8(5) | C(31)–C(32) | 138.9(6) |
| C(32)–C(33) | 137.9(5) | C(33)–C(34) | 136.3(6) |

refined parameters 329; $R = 5.27\%$ and $wR = 3.72\%$; all non hydrogen atoms, anisotropic; semiempirical absorption correction; max./min. transmission factor, (0.4414/0.5349), maximum residual electron density, 1.03 e Å$^{-3}$; minimum residual electron density, $-0.59$ e Å$^{-3}$.

Table 4
Selected bond angles of **3**

| Atoms | Angle (°) | Atoms | Angle (°) |
|---|---|---|---|
| C(1)–Zr–C(11) | 79.8(1) | C(l)–Zr–C(21) | 81.8(1) |
| C(4)–Zr–C(27) | 93.8(l) | C(l)–Zr–C(22) | 161.7(l) |
| C(1l)–Zr–C(27) | 102.8(l) | C(5)–Zr–C(27) | 81.3(l) |
| C(2)–C(l)–C(5) | 105.8(3) | C(18)–Zr–C(27) | 69.4(l) |
| C(2)–C(l)–C(6) | 127.1(3) | Zr–C(l)–C(6) | 125.8(l) |
| C(l)–C(2)–C(3) | 109.0(3) | C(2)–C(3)–C(4) | 109.0(3) |
| C(l)–C(6)–C(7) | 108.9(2) | C(l)–C(6)–C(8) | 110.2(3) |
| C(7)–C(6)–C(8) | 107.6(2) | C(l)–C(6)–C(9) | 112.1(2) |
| C(7)–C(6)–C(9) | 110.1(3) | C(8)–C(6)–C(9) | 107.9(2) |
| C(6)–C(9)–C(I0) | 113.3(3) | C(6)–C(9)–C(13) | 115.0(2) |
| C(10)–C(9)–C(13) | 102.3(2) | C(9)–C(l0)–C(ll) | 104.8(2) |
| Zr–C(11)–C(10) | 107.1(2) | Zr–C(11)–C(12) | 117.6(2) |
| C(10)–C(1l)–C(12) | 102.2(2) | C(11)–C(12)–C(13) | 111.5(2) |
| C(9)–C(13)–C(12) | 108.8(3) | C(19)–C(18)–C(22) | 107.3(3) |
| Zr–C(18)–C(23) | 116.9(2) | C(19)–C(18)–C(23) | 128.2(3) |
| C(22)–C(18)–C(23) | 124.4(2) | C(20)–C(2l)–C(22) | 108.1(4) |
| C(18)–C(22)–C(21) | 107.6(3) | C(18)–C(23)–C(24) | 109.6(2) |
| C(18)–C(23)–C(25) | 110.9(2) | C(24)–C(23)–C(25) | 109.9(3) |
| C(18)–C(23)–C(26) | 105.1(3) | C(24)–C(23)–C(26) | 110.6(2) |
| C(25)–C(23)–C(26) | 110.7(2) | C(23)–C(26)–C(27) | 109.8(2) |
| C(23)–C(26)–C(30) | 116.0(3) | C(27)–C(26)–C(30) | 104.9(2) |
| Zr–C(27)–C(26) | 117.1(2) | Zr–C(27)–C(28) | 135.8(2) |
| C(26)–C(27)–C(28) | 106.9(3) | C(27)–C(28)–C(29) | 112.2(2) |
| C(2)–Zr–C(11) | 85.0(1) | C(26)–C(30)–C(29) | 106.8(3) |

Complete lists of crystal structure data, bond length and angles, and thermal parameters are available on request from the Cambridge Crystallographic Data Centre on quoting the names of the authors journal citation and the reference number CCDC-101022.

### *3.5. Polymerization reactions*

#### *3.5.1. Activation of the catalyst precursor*

A 5 mg mass of the metallocene were dissolved in 5 ml MAO solution (Witco, 30 mass% MAO in toluene, Mw = 1100) and 45 ml toluene were added. A change of colour gave indication for the activation reaction.

#### *3.5.2. Polymerization conditions*

For all polymerization reactions a 1 l Büchi steel autoclave was used. Ethylene was polymerized in pentane solution at 60°C with an ethylene pressure of 10 bar. Liquid propylene was applied for polymerization without any solvent at 60°C.

#### *3.5.3. Polymer characterization by viscosimetry*

The molecular weight of the polymers was determinated by an Ubbelohde viscosimeter in *cis*/*trans* decahydronaphtalene at 135 ($\pm$0.1)°C. The samples were dried in vacuo before the measurement and diluted in *cis*/*trans* decahydronaphtalene for 3–4 h at 140–150 °C. The determination of $M_\eta$ was accomplished with a calibration curve ($c = 0.1$ g dl$^{-1}$).

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