



ELSEVIER

Journal of Organometallic Chemistry 660 (2002) 161–166

Journal
of Organo
metallic
Chemistry

www.elsevier.com/locate/jorgchem

Synthesis, molecular structure, and polymerization reactivity of ethylenebis(1,3-dimethylcyclopentadienyl)zirconium dichloride

Bun Yeoul Lee^{a,*}, Young Heui Kim^a, Young Chul Won^a, Chang Bo Shim^a, Dong Mok Shin^b, Young Keun Chung^b

^a Department of Molecular Science and Technology, Ajou University, San 5 Wonchondong, Suwon 442-749, Republic of Korea

^b Department of Chemistry and the Center for Molecular Catalysis, College of Natural Sciences, Seoul National University, Seoul 151-742, Republic of Korea

Received 22 April 2002; received in revised form 21 August 2002; accepted 22 August 2002

Abstract

An ethylene-bridged zirconocene complex bearing methyl substituents only on the cyclopentadienyl carbons adjacent to bridge point, ethylenebis(1,3-dimethylcyclopentadienyl)zirconium dichloride (**5**) was synthesized. Crystal structure of **5** was determined. The complex, **5**, when activated with MAO, shows better comonomer incorporation ability than $[\text{Ph}_2\text{C}(\text{Fluo})(\text{Cp})]\text{ZrCl}_2$ in the ethylene–norbornene copolymerization but it is not better than *rac*-Et(Ind)₂ZrCl₂ for the ethylene-1-hexene copolymerization in terms of activity and comonomer incorporation.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Metallocene; Zirconium; Polymerization; Methylaluminoxane

1. Introduction

The metallocene compounds of Group 4 have attracted strong attention from both academic and industrial fields because they can be used as a new generation polyolefin catalyst [1,2]. The ligand structure heavily influences the catalytic activity, comonomer incorporation and distribution, tacticity, and molecular weight [3]. We have shown a novel synthetic route for an *ansa*-zirconocene complex bearing the substituents only on the cyclopentadienyl carbons adjacent to bridge, 2,2'-methylenebis(1,3-dimethylcyclopentadienyl)zirconium dichloride, in which the steric hindrance around reaction site is kept to a minimum. The complex showed excellent activity and comonomer incorporation ability in the ethylene–norbornene copolymerization [4]. In this work, we report synthesis of an ethylene bridged analogue, 2,2'-ethylenbis(1,3-dimethylcyclopentadienyl)zirconium dichloride, and its catalytic reactivity

toward ethylene–norbornene and ethylene-1-hexene copolymerization.

2. Results and discussion

2.1. Synthesis and characterization

The ligand was synthesized by the similar route for 2,2'-methylenebis(1,3-dimethylcyclopentadienyl)zirconium dichloride from 1,5-hexadiyne via the key steps of the Pauson–Khand reaction and the retro-Diels Alder reaction (Scheme 1) [4,5]. The overall yield for the ligand from 1,5-hexadiyne was quite good (38%). The metallation was conducted via trimethyltin-mediated method with rather low yield (31%) [6]. The zirconocene complex was fully characterized by NMR spectroscopy and elemental analysis. ¹H-NMR spectrum of **5** is very simple (6.45 ppm for cyclopentadienyl protons, 3.20 ppm for ethylene bridge protons, and 2.24 ppm for methyl protons). In ¹³C-NMR spectrum, five peaks were observed (129.1, 124.8, and 122.0 ppm for cyclopentadienyl carbons, 26.4 ppm for ethylene bridge carbon, and 14.2 ppm for methyl carbons). The difference

* Corresponding author. Tel.: +82-31-219-1844; fax: +82-31-219-1592

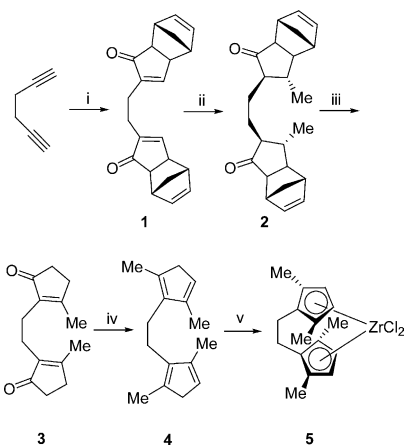
E-mail address: bunyeoul@ajou.ac.kr (B.Y. Lee).

observed in NMR spectra compared with methylene bridged complex is a big downfield shift of the cyclopentadienyl carbon attached to the bridge from 104.1 to 122.0 ppm, which might result from the release of ring strain by the ethylene bridge.

Single crystals of **5** for X-ray crystallography were grown by vapor phase diffusion of pentane to a toluene solution. Fig. 1 shows the structure of **5** with selected bond lengths and angles. The angle of two centroids of cyclopentadienyl and zirconium atom, the value of which usually indicates how far the zirconium atom displaces from the cyclopentadienyl ligand, is 124.29° . The value is much bigger compared with those observed for 2,2'-methylenebis(1,3-dimethylcyclopentadienyl)zirconium dichloride **6** (117.15°) [4] and $[\text{Ph}_2\text{C}(\text{Fluo})(\text{Cp})]\text{ZrCl}_2$ (117.6°) [7] but it is comparable to that of *rac*-Et(Ind) $_2\text{ZrCl}_2$ (125.3°) [8]. The Cl–Zr–Cl angle is $98.29(10)^\circ$, which is also close to that of *rac*-Et(Ind) $_2\text{ZrCl}_2$ ($99.09(3)^\circ$). The ten Zr–C(Cp) distances are almost the same (average, $2.518(9)$ Å). This feature contrasts with the methylene bridged complex **6**, in which the Zr–C(Cp) distance increases progressively from bridge head carbon (average, $2.450(4)$ Å), to α -carbon (average, $2.496(4)$ Å) and β -carbon (average, $2.544(6)$ Å). The Zr–Cl distance ($2.447(3)$ and $2.451(2)$ Å) is longer than that of *rac*-Et(Ind) $_2\text{ZrCl}_2$ ($2.3884(5)$ Å).

2.2. Copolymerization studies

The catalyst was tested for ethylene–norbornene copolymerization [9] under identical conditions previously carried out in our laboratory to compare the reactivity with methylene bridged complex **6** and $[\text{Ph}_2\text{C}(\text{Fluo})(\text{Cp})]\text{ZrCl}_2$, which has been proved to be one of the best for the copolymerization in terms of activity and comonomer incorporation [10,11]. The polymerization results are summarized in Table 1 and



Scheme 1. (i) (Indenyl)Co(COD) (1 mol%), CO (15 bar); (ii) Me_2CuLi ; (iii) 420°C (4.5 min); (iv) MeLi, then aq. HCl; (v) (a) *n*-BuLi (2.0 equivalents), then Me_3SnCl , (b) ZrCl_4 .

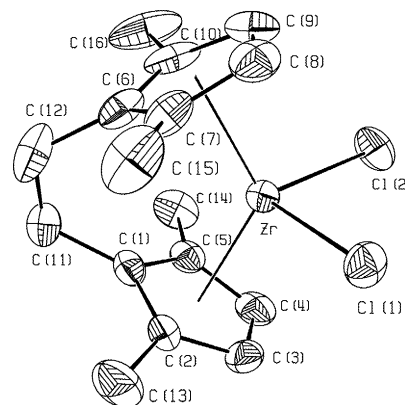


Fig. 1. ORTEP view of **5**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): Zr–Cl(1), $2.447(3)$; Zr–Cl(2), $2.451(2)$; Zr(1)–C(1), $2.503(9)$; Zr(1)–C(2), $2.521(10)$; Zr(1)–C(3), $2.519(11)$; Zr(1)–C(4), $2.517(10)$; Zr(1)–C(5), $2.508(9)$; Cl(1)–Zr–Cl(2), $98.29(10)$; C(1)–C(11)–C(12), $115.2(9)$; C(6)–C(12)–C(11), $114.7(9)$; Cp(centroid)–Zr–Cp(centroid), 124.29 .

comparative reactivity is summarized in Fig. 2. The activity is the least among the three catalysts under the same condition but the norbornene incorporation ability is better than that of $[\text{Ph}_2\text{C}(\text{Fluo})(\text{Cp})]\text{ZrCl}_2$ although it is less than that of **6**. However, both activity and comonomer incorporation are much better when compared with the ethylene-bridged complex, *rac*-Et(Ind) $_2\text{ZrCl}_2$. *rac*-Et(Ind) $_2\text{ZrCl}_2$ gave 4.5×10^6 g $\text{mol}^{-1} \text{h}^{-1}$ activity and 47% norbornene content (T_g , 146°C) while complex **5** gave 6.6×10^6 g $\text{mol}^{-1} \text{h}^{-1}$ activity and 57% norbornene content (T_g , 190°C) under the same conditions at 50 psig. ^{13}C -NMR spectra of the copolymers were recorded (Fig. 3). The spectra are too complicated to be analyzed unambiguously even though extensive study of the assignment of the ^{13}C -NMR spectra of the copolymers has been recently carried out [12]. However, the main pattern of the spectrum (51 mol% norbornene, A in Fig. 3) is similar to that observed for the polymer (50.8 mol% norbornene) prepared with *rac*-Et(Ind) $_2\text{ZrCl}_2$ [12]. More severe splitting is observed in the C2/C3 signal region (47–50 ppm), which might be attributed to the atactic placement of the norbornene unit. With the C_2 symmetric catalyst, *rac*-Et(Ind) $_2\text{ZrCl}_2$, isotactic placement is predominant and hence the signals are relatively simple. Mole fraction of norbornene in the copolymers and mole fraction of norbornene in the feeding monomers are well fitted to Fineman–Ross plot ($R = 0.997$). The reactivity ratios, r_N and r_E are determined to be 0.040 and 1.5, respectively. Narrow molecular weight distribution (1.9–2.4) were observed and the molecular weights are comparable to those obtained with methylene bridged complex **6**. Usually, the molecular weight increases by the increase of the norbornene content because, after

Table 1
Ethylene–norbornene polymerization results ^a

Pressure (psig)	[E] ^b (mol l ⁻¹)	Yield (g)	A ^c	T _g (°C)	N incorp (mol%) ^d	M _w	M _w /M _n
100	0.13	2.6	16	158	51	177 000	2.0
75	0.27	1.6	9.6	170	54	161 000	2.1
50 ^e	0.41	1.1	6.6	190	57	118 000	1.9
25	0.55	0.60	3.6	209	65	70 000	2.4

^a Polymerization condition: 30 ml norbornene solution in toluene (3.54 M), 0.5 μmol catalyst, Al/Zr = 4000, 60 °C, 20 min.

^b Ethylene concentration measured with thermal mass flowmeter.

^c Activity in unit of 10⁶ g mol⁻¹ h⁻¹.

^d Norbornene incorporated in the copolymer by ¹³C-NMR.

^e *rac*-Et(Ind)₂ZrCl₂ gave 4.5 × 10⁶ g mol⁻¹ h⁻¹ activity and 47% norbornene content (T_g, 146 °C) under the same condition.

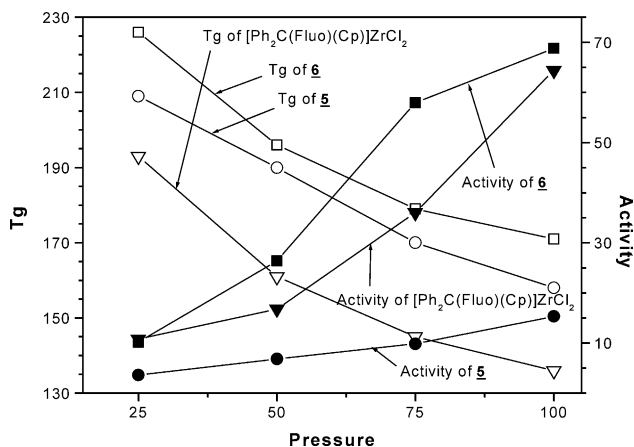


Fig. 2. Comparative reactivity for norbornene–ethylene copolymerization of **5**, **6** (2,2'-methylenebis(1,3-dimethylcyclopentadienyl)zirconium dichloride), and [Ph₂C(Fluo)(Cp)]ZrCl₂.

norbornene insertion, the chain transfer via β-elimination is impossible [11]. However, the molecular weight decreases in this case by the increase of norbornene content, which cannot be explained clearly in this stage.

The catalyst was tested for the copolymerization of ethylene and 1-hexene. The polymerization results are summarized in Table 2. *rac*-Et(Ind)₂ZrCl₂ was used for comparison. Both complexes follow the general trend of the copolymerization reactivity: activity increase by addition of comonomer; molecular weight decrease by the increase of comonomer content; narrow molecular weight distribution [13]. The activity is not as good as that of *rac*-Et(Ind)₂ZrCl₂ under the same conditions. Comonomer content in the copolymer, which can be estimated by T_m value, is less than that obtained by *rac*-Et(Ind)₂ZrCl₂. Copolymers obtained at 0.25 M 1-hexene concentration were analyzed by ¹³C-NMR study [14]. Analysis of the spectrum gave a value of 4.4 mol% hexene content for the copolymer obtained by complex **5** (T_m, 108.1 °C) while 6.0 mol% hexene content was obtained by *rac*-Et(Ind)₂ZrCl₂ (T_m, 102.0 °C). Slightly higher molecular weight polymer is obtained with *rac*-Et(Ind)₂ZrCl₂.

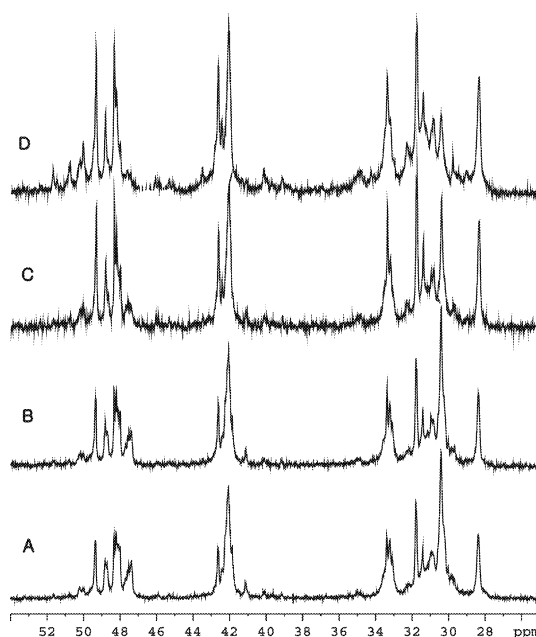


Fig. 3. ¹³C-NMR spectra of norbornene–ethylene copolymers prepared with **5**, with norbornene mol percent: 51% (A); 54% (B); 57% (C); 65% (D).

3. Experimental

3.1. General considerations

All manipulations were performed under an inert atmosphere (dinitrogen or Ar) using a standard Schlenk technique or a VAC glove box. Pentane, toluene, and Et₂O were distilled from benzophenone ketyl. Anhydrous grade toluene was purchased from Aldrich for polymerization and purified by distillation over Na/K alloys. Methylaluminoxane (MAO) was purchased as a solution in toluene from Akzo (6.4 w% of Al, MMAO type 4). Ethylene with a high purity grade 99.9% was purchased from Conley Gas (99.9%) and purified by passing through columns of activated molecular sieves and copper. NMR spectra were obtained on a Bruker

Table 2
Ethylene-1-hexene copolymerization results ^a

[1-Hex] (mol l ⁻¹)	Catalyst	Yield (g)	Activity (10 ⁶ g mol ⁻¹ h ⁻¹)	<i>M_w</i>	<i>M_w/M_n</i>	<i>T_m</i> (°C)
0	5	1.7	14	244 000	1.67	
0.060	5	3.6	29	127 000	1.74	123.9
0.13	5	3.7	30	105 000	1.80	116.1
0.25	5	3.7	30	110 000	1.67	108.1 ^c
0.50	5	4.9	39	74 000	1.73	91.9
0	(EBI)ZrCl ₂ ^b	3.1	25	383 000	1.74	
0.060	(EBI)ZrCl ₂	5.9	47	148 000	1.84	116.4
0.13	(EBI)ZrCl ₂	4.8	38	119 000	1.76	108.9
0.25	(EBI)ZrCl ₂	4.9	39	132 000	1.74	102.0 ^d
0.50	(EBI)ZrCl ₂	7.3	58	89 000	1.75	n.d.

^a Polymerization condition: Al/Zr = 4200, 0.5 μmol catalyst, 250 ml hexane, 15 min, 80 °C, 30 psig.

^b *rac*-Et(Ind)₂ZrCl₂.

^c 4.4 mol% of [C6] was calculated by the analysis of ¹³C-NMR spectrum.

^d 6.0 mol% [C6].

ARX-300. IR spectra were recorded on a BIO-RAD FTA-60A instrument. Elemental analyses were carried out on a Perkin–Elmer 2400 CHN microanalyzer. Gel permeation chromatograms (GPC) were obtained at 140 °C in trichlorobenzene using Waters Model 150-C + GPC and the data were analyzed using a polystyrene analyzing curve. Differential scanning calorimetry (DSC) was performed on a Thermal Analysis 3100. Ethylene–norbornene copolymerizations were conducted by the same method and conditions previously reported [4]. The ¹³C-NMR spectra of norbornene copolymers were recorded according to the literature method at 100 °C on a Bruker DRX 600 spectrometer operating at 150 MHz in 5 mm tubes and the norbornene content in the copolymers were calculated according to the formula established in the literature [11]. Ethylene concentrations were measured by thermal mass flowmeter. The reactivity ratios, *r_N* and *r_E* were calculated by the Fineman–Ross method [15].

3.2. 4,4'-Ethylenebis(3-oxotricyclo[5.2.1.0^{2,6}]deca-4,8-diene) (1)

Compound **1** was synthesized according to the literature method and conditions [16]. The compound was purified by dissolving in hot hexane and EtOAc (v/v, 3:1), filtering it over short silica gel pad and then recrystallization in a freezer (ca. -30 °C) for 1 day. Solids were deposited, collected by removing the solvent, and dried in a vacuum. Yield was 79%. White solid. M.p. 108–112 °C. Anal. Calc. for C₂₂H₂₂O₂: C, 82.99; H, 6.96. Found: C, 83.03; H, 7.08%. ¹H-NMR (CDCl₃): 7.14 (d, *J* = 2 Hz, 1H, C(O)C=C-*H*), 6.23 (dd, *J* = 5.6, 3.0 Hz, 1H, vinyl-*H*), 6.15 (dd, *J* = 5.6, 3.0 Hz, 1H, vinyl-*H*), 2.86 (s, 1H), 2.66 (s, 1H), 2.60 (s, 1H), 2.35 (s, 2H, bridge-CH₂CH₂), 2.25 (d, *J* = 5 Hz, 1H), 1.32 (d, *J* = 9.3 Hz, 1H), 1.12 (d, *J* = 9.3 Hz, 1H). ¹³CMR (CDCl₃): δ 209.6 (carbonyl), 159.2, 49.5, 138.3, 137.0,

52.5, 47.7, 43.6, 42.9, 41.1 (bridge-CH₂CH₂), 22.9. IR (KBr pellet): 1705, 1622 cm⁻¹.

3.3. 2,2'-Ethylenebis(3-methyl-2-cyclopenten-1-one) (3)

To a Schlenk flask containing a slurry of CuI (8.61 g, 45.2 mmol) in Et₂O (150 ml) was added MeLi (60 ml, 1.5 M in Et₂O solution, 90 mmol) at -20 °C. The solution was stirred at -20 °C for 30 min and cooled to -78 °C. A solid **1** (6.00 g, 18.8 mmol) was added to the solution in one portion. The resulting solution was allowed to warm to room temperature (r.t.). After the solution was stirred at r.t. for 5 h, it was poured to the chilled water (100 ml). The mixture was filtered over celite and the ethereal solution was separated. The aq. soln was extracted with Et₂O (50 ml). The ethereal solutions were combined, dried over anhydrous MgSO₄, and evaporated to give white solid, which was used for further reaction without further purification. The solid was placed in a quartz tube which was connected via a flexible tube to a Schlenk flask. After the system was purged with nitrogen, the quartz tube was placed in a furnace whose temperature had been set at 420 °C and the Schlenk flask was immersed in liquid nitrogen bath. After 4.5 min, the quartz tube was removed from the furnace and was cooled to r.t. Purification of a crude product was carried out by column chromatography on a silica gel eluting with hexane and EtOAc (v/v, 1:1). Overall yield from **1** was 81% (3.33 g). White solid. M.p. 108–109 °C. Anal. Calc. for C₁₄H₁₈O₂: C, 77.03; H, 8.31. Found: C, 77.26; H, 8.48%. ¹H-NMR (CDCl₃): δ 2.43–2.32 (m, 2H), 2.33–2.28 (m, 2H), 2.29 (s, 2H, bridge-CH₂CH₂), 2.97 (s, 3H, CH₃). ¹³C-NMR (CDCl₃): δ 209.4 (carbonyl), 171.0, 139.6, 34.2, 31.5, 21.5 (bridge-CH₂CH₂), 17.2 (CH₃). IR (KBr pellet): 1691, 1640 cm⁻¹.

3.4. 2,2'-Ethylenebis(1,3-dimethyl-1,3-cyclopentadiene) (4)

To a Schlenk flask containing **3** (1.32 g, 6.05 mmol) in 50 ml of Et₂O was added MeLi (12 ml, 1.5 M in Et₂O, 18 mmol) at –78 °C. The solution was allowed to warm to r.t. After the solution was stirred for 20 h, 10 ml of water was added carefully. Volatiles were removed by rotary evaporator and EtOAc (60 ml) was added to the residue. The mixture was poured into a separatory funnel. The aq. layer was removed and aq. 2 N HCl solution (60 ml) was added. The separatory funnel was vigorously shaken for 2 min. The aq. layer was removed and the organic layer was washed with aq. concd NaHCO₃ (30 ml). The organic layer was collected and dried over anhyd MgSO₄. After removal of the solvent by rotary evaporator, the residue was purified by column chromatography on silica gel eluting with hexane and benzene (v/v, 10:1). Yield: 0.767 g (59%). ¹H-NMR (CDCl₃): δ 5.80 (d, *J* = 1 Hz, 1H, vinyl-*H*), 2.73–2.71 (m, 2H, CH₂), 2.31 (s, 2H, bridge-CH₂CH₂), 1.93 (s, 3H, CH₃), 1.85 (s, 3H, CH₃). ¹³C-NMR (CDCl₃): δ 143.8, 139.9, 137.7, 123.5, 43.8, 25.6 (bridge-CH₂CH₂), 14.1 (CH₃), 13.5 (CH₃).

3.5. 2,2'-Ethylenebis(1,3-dimethylcyclopentadienyl)zirconium dichloride (5)

To a Schlenk flask containing **4** (0.728 g, 3.40 mmol) in 20 ml Et₂O was added *n*-BuLi (2.7 ml, 2.5 M in hexane, 6.8 mmol) at –78 °C. The solution was allowed to warm to r.t. After the solution was stirred for 20 h, chlorotrimethyltin (1.49 g, 7.48 mmol) in 10 ml Et₂O was added at –40 °C. After stirring at r.t. for 2 h, all volatiles were removed under reduced pressure. The residue was dissolved in anhydrous hexane (60 ml) and filtered. Removal of hexane gave a white crystalline solid. To a flask containing the solid was added 30 ml toluene and the flask was placed in a –30 °C bath. A slurry of ZrCl₄ (0.781 g, 3.35 mmol) in toluene (20 ml) was added via cannula. The mixture was allowed to warm to r.t. and stirred for 20 h. After the solution was stirred in addition for 3 h at 80 °C; all volatiles were removed under vacuum at that temperature. The complex was extracted with hot hexane (150 ml). White solid was deposited by cooling the solution to –30 °C (0.401 g, 31%). Single crystals for X-ray crystallography were obtained by slow diffusion of pentane vapor to a toluene solution. White crystals. M.p. > 200 °C (dec.). Anal. Calc. for C₁₆H₂₀Cl₂Zr: C, 51.31; H, 5.38. Found: C, 51.54; H, 5.04%. ¹H-NMR (CDCl₃): δ 6.45 (s, 2H, Cp-*H*), 3.20 (s, 2H, bridge-CH₂CH₂), 2.24 (s, 6H, CH₃). ¹³C-NMR (75 MHz, CDCl₃): δ 129.1, 124.8, 122.0, 26.4 (bridge-CH₂CH₂), 14.2 (CH₃).

3.6. Ethylene-1-hexene copolymerization

To a dried 500 ml glass reactor was added a solution of 1-hexene in hexane (250 ml). The nitrogen atmosphere was replaced by ethylene by purging with ethylene gas. The reactor was immersed in an oil bath (80 °C) for 15 min. The activated catalyst, which had been prepared by mixing MAO (1.0 ml, 2.1 mmol Al, 6.4 w% Al in toluene) with zirconocene complex (0.5 μmol) in 10 ml of toluene for 15 min at r.t., was added via syringe. Ethylene was fed immediately under the pressure of 30 psig. After stirring for 15 min under that pressure, the reaction was quenched by releasing the ethylene pressure and addition of 5 ml of MeOH. White solid was obtained by filtration and dried under vacuum. *T_m* values were determined with DSC on a second heating at a heating rate of 10 °C min^{–1}.

3.7. Crystallographic studies

Crystals coated with grease (Apiezon N) were mounted inside a thin glass tube with epoxy glue and placed on an Enraf–Nonius CCD single crystal X-ray diffractometer using graphite-monochromated Mo–K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97) [17] and refined against all *F*² data (SHELXS-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as idealized contributions.

3.7.1. Crystal data for **1**

C₁₆H₂₀Cl₂Zr, *M* = 377.44, white crystals, crystal size 0.3 × 0.3 × 0.2 mm, orthorhombic, space group *P*212121, temperature 293(2) K, *a* = 8.5291(3), *b* = 13.2531(5), *c* = 14.2340(6) Å, *V* = 1608.97(11) Å³, *Z* = 4, *D*_{calc} = 1.546 Mg m^{–3}, *F*(000) = 760, 3581 reflections collected in *h*(–11/11), *k*(–17/17), *l*(–18/18), measured in the range 2.10 < θ < 27.45°, *R*_{int} = 0.0000, 177 parameters, 0 restraints, *R*₁ = 0.0590, ω*R*₂ = 0.1289 (for reflections with *I* > 2σ(*I*)), *R*₁ = 0.1118, ω*R*₂ = 0.1792, goodness-of-fit = 1.021, largest difference peak and hole: 1.007/–1.628 e Å^{–3}.

4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 184277 for compound **5**. 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 www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

This work was supported by grant No. (R05-2002-000-00155-0) from the Basic Research Program of the Korea Science and Engineering Foundation.

References

- [1] Review: (a) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1143; (b) G. Fink, R. Mülhaupt, H.H. Brintzinger (Eds.), *Ziegler Catalysts*, Springer-Verlag, Berlin, 1995; (c) A. Togni, R.L. Halterman (Eds.), *Metallocenes*, Wiley-VCH, New York, 1998; (d) M. Bochmann, *J. Chem. Soc. Dalton Trans.* 3 (1996) 255; (e) W. Kaminsky, *Macromol. Chem. Phys.* 197 (1996) 3907.
- [2] Recent progress: (a) B.Y. Lee, G.C. Bazan, *J. Organomet. Chem.* 642 (2002) 275; (b) N.E. Grimmer, N.J. Coville, C.B. de Koning, *J. Organomet. Chem.* 642 (2002) 195; (c) H. Schumann, D.F. Karasiak, S.H. Mühle, W. Kaminsky, U. Weingarten, *J. Organomet. Chem.* 636 (2001) 31; (d) E.J. Thomas, M.D. Rausch, J.C.W. Chien, *J. Organomet. Chem.* 631 (2001) 29; (e) T. Dreier, R. Fröhlich, G. Erker, *J. Organomet. Chem.* 621 (2001) 197; (f) H.G. Alt, A. Reb, W. Milius, A. Weis, *J. Organomet. Chem.* 628 (2001) 169; (g) A. Razavi, U. Thewalt, *J. Organomet. Chem.* 621 (2001) 267; (h) H.G. Alt, A. Reb, K. Kundu, *J. Organomet. Chem.* 628 (2001) 211; (i) P. Jutzi, C. Müller, B. Neumann, H.-G. Stammer, *J. Organomet. Chem.* 625 (2001) 180; (j) R.L. Haltermann, D.R. Fahey, V.P. Marin, D.W. Dockter, M.A. Khan, *J. Organomet. Chem.* 625 (2001) 154.
- [3] Review: (a) H. Alt, A. Köppl, *Chem. Rev.* 100 (2000) 1205; (b) L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, *Chem. Rev.* 100 (2000) 1253; (c) G.W. Coates, *Chem. Rev.* 100 (2000) 1223.
- [4] B.Y. Lee, Y.H. Kim, Y.C. Won, J.W. Han, I.S. Lee, W.H. Suh, Y.K. Chung, K.H. Song, *Organometallics* 21 (2002) 1500.
- [5] (a) B.Y. Lee, J.W. Han, H. Seo, I.S. Lee, Y.K. Chung, *J. Organomet. Chem.* 627 (2001) 233; (b) B.Y. Lee, J.W. Han, Y.K. Chung, S.W. Lee, *J. Organomet. Chem.* 587 (1999) 181; (c) B.Y. Lee, H. Moon, Y.K. Chung, N. Jeong, *J. Am. Chem. Soc.* 116 (1994) 2163; (d) B.Y. Lee, H. Moon, Y.K. Chung, N. Jeong, G.B. Carpenter, *Organometallics* 12 (1993) 3879.
- [6] (a) I.E. Nifant'ev, P.V. Ivchenko, *Organometallics* 16 (1997) 713; (b) A.Y. Agarkov, V.V. Izmer, A.N. Riabov, L.G. Kuz'mina, J.A.K. Howard, I.P. Beletskaya, A.Z. Voskoboinikov, *J. Organomet. Chem.* 619 (2001) 280.
- [7] A. Razavi, J.L. Atwood, *J. Organomet. Chem.* 459 (1993) 117.
- [8] F. Piemontesi, I. Camurati, L. Resconi, D. Balboni, A. Sironi, M. Moret, R. Zeigler, N. Piccolrovazzi, *Organometallics* 14 (1995) 1256.
- [9] (a) C. Janiak, P.G. Lassahn, *Macromol. Rapid. Commun.* 22 (2001) 479; (b) H. Lasarov, T.T. Pakkanen, *Macromol. Rapid. Commun.* 22 (2001) 434; (c) A.L. McKnight, R.M. Waymouth, *Macromolecules* 32 (1999) 2816.
- [10] (a) W. Kaminsky, A. Noll, *Polym. Bull.* 31 (1993) 175; (b) W. Kaminsky, A. Bark, M. Arndt, *Makromol. Chem. Makromol. Symp.* 47 (1991) 83.
- [11] (a) D. Ruchatz, G. Fink, *Macromolecules* 31 (1998) 4669; (b) D. Ruchatz, G. Fink, *Macromolecules* 31 (1998) 4681; (c) D. Ruchatz, G. Fink, *Macromolecules* 31 (1998) 4674; (d) D. Ruchatz, G. Fink, *Macromolecules* 31 (1998) 4684.
- [12] I. Tritto, C. Marestin, L. Boggioni, L. Zetta, A. Provasoli, D.R. Ferro, *Macromolecules* 33 (2000) 8931.
- [13] (a) S.E. Reybuck, A. Meyer, R.M. Waymouth, *Macromolecules* 35 (2002) 637; (b) P. Lehmus, E. Kokko, O. Härkki, R. Leino, H.J.G. Luttikhedde, J.H. Näsman, J.V. Seppälä, *Macromolecules* 32 (1999) 3547; (c) R. Quijada, J. Dupont, M.S.L. Miranda, R.B. Scipioni, G.B. Galland, *Macromol. Chem. Phys.* 196 (1995) 3991.
- [14] (a) E. Hsieh, J.C. Randall, *Macromolecules* 15 (1982) 1402; (b) J.C. Randall, *Macromol. Chem. Phys.* C29 (1989) 201.
- [15] P. Altamura, A. Grassi, *Macromolecules* 34 (2001) 9197.
- [16] B.Y. Lee, Y.K. Chung, N. Jeong, Y. Lee, S.H. Hwang, *J. Am. Chem. Soc.* 116 (1994) 8793.
- [17] G.M. Sheldrick, *SHELXL-97*, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.