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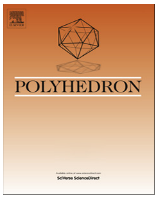

Zirconium complexes with pendant aryloxy groups attached to the metallocene moiety by ethyl or hexyl spacers

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ABSTRACT

Four zirconium complexes with pendant aryloxy groups attached to the metallocene moiety by ethyl or hexyl spacers have been synthesized and characterized by spectroscopic methods and HR-MS or elemental analysis. The solid state structure of bis[{6-(2,6-dimethylphenoxy)hexyl}cyclopentadienyl]zirconium dichloride was determined by single crystal X-ray diffraction. The prepared complexes were tested as catalyst precursors in the polymerization of ethylene upon activation with MAO. The results showed a marked effect of the spacer length on the catalytic activity, while only a minor effect of the substitution on the aryl group, which affected its steric properties.

1. Introduction

Since catalysts for ethylene and propylene polymerization were pioneered by Ziegler and Natta in the 1950s [1,2], complexes of group IV elements with ligands such as mono-cyclopentadienyl (Cp), bis-Cp, and *ansa*-type bridged Cp have been tested to catalyze olefin polymerization [3–6]. The development of new metallocene compounds with ether functionalized side chain attached to Cp ring is also attractive as such catalysts could avoid the infringement of existing patents. The side chains may also act as coordinating groups during catalysis [7–10]. Side chains have been imputed to stabilize unstable active species, prolonging their lifetimes, and to alter the electronic and steric environments around the metal centers [7–10]. Ether linkage could also be used for anchorage to silica supports to make heterogeneous catalysts [11].

There are few reported metallocene compounds with ether functionalized side chains. Examples include $(ROCH_2CH_2Cp)_2MCl_2$ (M = Ti and Zr; R = Me [12,13], R = isobornyl, menthyl, and fenchyl [13]), $[CH_3CH_2CH_2OCH_2CH_2O(CH_2)_nCp]_2ZrCl_2$ ($n = 2, 4, 6, 8$) [14], $(MeO\text{-}4\text{-}PhCH_2Cp)_2TiCl_2$ [15], $(MeOCH_2CH_2CH_2Cp)_2MCl_2$ (M = Ti and Zr) [16], $(R\text{-}MeO(CH_2)_nCHMeCp)_2MCl_2$ ($n = 0, 1$; M = Ti and Zr) [17], $(2\text{-}MeOPhCR_2Cp)_2TiCl_2$ ($R_2 = Me_2$, MeEt, and Et_2) [18], $(2\text{-}THF\text{-}CH_2Cp)_2ZrCl_2$ [19], $(R_3SiOCp)_2TiCl_2$ ($R_3 = Me_2Bu^t$, Et_3, and $i\text{-}Pr_3$) [20], and $(4\text{-}C_5H_{11}\text{-}4\text{-}C_6H_{10}PhOCH_2CH_2CH_2CH_2CH_2CH_2Cp)_2TiCl_2$ [21]. Most reports of metallocene with pendant ether functionalized Cp ligands have focused on compounds containing one or two methylene spacers between the Cp and ether groups [12–19]; much less attention has been directed towards longer methylene spacers and/or aryloxy group attached to Cp ring [21,22]. Only two examples of titanocene [21] or zirconocene [22] complexes with hexyl spacers between the Cp ring and aryloxy groups have been reported in the literature. However, in the case of zirconocene complexes, their exact synthetic routes and spectroscopic data were not provided in the patent literature [22].

This work reports the development of zirconocene complexes with Cp ring and aryloxy group linked by ethyl or hexyl spacers such as (2-phenoxyethyl)cyclopentadienyl, {2-(2,6-dimethylphenoxy)ethyl}cyclopentadienyl, (6-phenoxyhexyl)cyclopentadienyl, and [6-(2,6-dimethylphenoxy)hexyl]cyclopentadienyl ligands. Novel zirconocene chloride complexes containing these functionalized Cp rings were synthesized here and their catalysis of the polymerization of ethylene was investigated. In addition, the solid state structure of zirconium complex with [6-(2,6-dimethylphenoxy)hexyl]cyclopentadienyl ligand was confirmed by single crystal X-ray diffraction.

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2. Experimental

2.1. General procedure

All manipulations were carried out under a dinitrogen atmosphere using standard Schlenk and glove box techniques. [23]. All other chemicals were from Aldrich and were used as supplied unless otherwise indicated. MAO was from Albemarle (Albemarle PMAO 10% solution, 1.5 M concentration). $Zr(NMeEt)_4$ was from DNF Co., Ltd., in Korea. All solvents such as toluene, diethyl ether, and *n*-hexane were dried by distillation from sodium diphenylketyl under dinitrogen and were stored over 3 Å activated molecular sieves [24]. $CDCl_3$ was dried over 4 Å activated molecular sieves and used after vacuum transfer to a Schlenk tube equipped with a J. Young valve [24].

2.2. Measurements

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at ambient temperature on AVANCE III-400 or Bruker DPX-300 NMR spectrometer using standard parameters. All chemical shifts are reported in δ units with reference to the residual peaks of $CDCl_3$ for proton (7.24 ppm) and carbon (77.0 ppm) chemical shifts. HRMS was performed by maXis 4G (Hybrid LC/Q-TOF system). Elemental analyses were performed using an EA 1110-FISONS analyzer (CE Instruments). The polymers' thermal properties were investigated by Thermal Analyst Q200 differential scanning calorimetry (DSC) under dinitrogen at a heating rate of 10 °C/min. The results of the second scan were recorded to eliminate differences from the sample history. The polymers' molecular weights and molecular weight distributions were determined at 140 °C in 1,2,4-trichlorobenzene by PL 220 + 220R GPC (Polymer Laboratories) calibrated with standard polystyrenes.

2.3. Synthesis

Compounds $C_6H_5OCH_2CH_2Cp$ (**1L4**) [25], $Me_2C_6H_3OCH_2CH_2Br$ (**2L3**) [26], $C_6H_5OCH_2CH_2CH_2CH_2CH_2CH_2Br$ (**3L3**) [27], and $Me_2C_6H_3OCH_2CH_2CH_2CH_2CH_2CH_2Br$ (**4L3**) [28] were reported previously; however, they were achieved in a different way and with different results including yields and spectroscopic data.

2.3.1. Synthesis of $C_6H_5OCH_2CH_2OH$ (**1L1**)

A mixture of phenol (9.41 g, 100 mmol) and NaOH (8.00 g, 200 mmol) in water (40 mL) was stirred for 10 min. 2-Chloroethanol (8.53 g, 106 mmol) was added dropwise and refluxed for 40 h. The aqueous layer was extracted three times with dichloromethane (3 × 40 mL), and the combined organic portions were washed with H_2O (3 × 30 mL). The resulting residue was dried over $MgSO_4$ and filtered. The removal of solvent at reduced pressure gave the desired product **1L1** as colorless oil (7.33 g, yield = 53.1%).

^1H NMR ($CDCl_3$, 300.13 MHz, ppm): δ 7.28 (t, *J* = 7.9 Hz, 2H, Ar*H*), 6.99–6.90 (m, 3H, Ar*H*), 4.05 (t, *J* = 4.5 Hz, 2H, OCH_2CH_2OH), 3.93 (t, *J* = 4.5 Hz, 2H, OCH_2CH_2OH), 2.75 (s, 1H, O*H*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.46 MHz, ppm): δ 158.5, 129.4, 121.0, 114.4 (Ar), 69.97 (OCH_2CH_2OH), 61.22 (OCH_2CH_2OH).

HRMS Exact mass calculated for $C_8H_{10}NaO_2$ $[M+Na]^+$: 161.0578, found: 161.0573.

2.3.2. Synthesis of $Me_2C_6H_3OCH_2CH_2OH$ (**2L1**)

A yellow solid **2L1** was prepared in a yield of 51.4% (8.54 g) by the reaction between 2,6-dimethylphenol (12.2 g, 100 mmol), NaOH (8.00 g, 200 mmol), and 2-chloroethanol (8.53 g, 106 mmol) in a manner analogous to the procedure for **1L1**.

^1H NMR ($CDCl_3$, 300.13 MHz, ppm): δ 7.02–6.90 (m, 3H, Ar*H*), 3.94 (t, *J* = 4.5 Hz, 2H, OCH2CH2OH), 3.89 (t, *J* = 4.5 Hz, 2H, OCH_2CH_2OH), 2.38 (s, 1H, –O*H*), 2.28 (s, 6H, Ar*Me*$_2$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.46 MHz, ppm): δ 155.2, 130.8, 128.9, 124.0 (Ar), 72.89 (OCH_2CH_2OH), 62.31 (OCH_2CH_2OH), 16.19 (Ar*Me*$_2$).

HRMS Exact mass calculated for $C_{10}H_{14}NaO_2$ $[M+Na]^+$: 189.0891, found: 189.0886.

2.3.3. Synthesis of $C_6H_5OCH_2CH_2CH_2CH_2CH_2CH_2OH$ (**3L1**)

A light yellow oil **3L1** was prepared in a yield of 86.1% (16.7 g) by the reaction between phenol (9.41 g, 100 mmol), NaOH (8.00 g, 200 mmol), and 6-chloro-1-hexanol (14.3 g, 105 mmol) in a manner analogous to the procedure for **1L1**.

^1H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 7.25 (m, 3H, Ar*H*), 6.88 (m, 2H, Ar*H*), 3.94 (t, *J* = 5.1 Hz, 2H, $ArOCH_2$), 3.40 (t, *J* = 5.4 Hz, 2H, CH_2OH), 1.90–1.48 (m, 8H, $–CH_2–$), 1.52 (s, 1H, O*H*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.63 MHz, ppm): δ 158.0, 128.4, 119.5, 113.5 (Ar), 66.59 ($ArOCH_2$), 32.72 (CH_2OH), 31.69, 28.11, 26.92, 24.31 ($–CH_2–$).

HRMS Exact mass calculated for $C_{12}H_{19}O_2$ $[M+H]^+$: 195.1385, found: 195.1380.

2.3.4. Synthesis of $Me_2C_6H_3OCH_2CH_2CH_2CH_2CH_2CH_2OH$ (**4L1**)

A yellow oil **4L1** was prepared in a yield of 73.9% (16.4 g) by the reaction between 2,6-dimethylphenol (12.2 g, 100 mmol), NaOH (8.00 g, 200 mmol), and 6-chloro-1-hexanol (14.3 g, 105 mmol) in a manner analogous to the procedure for **1L1**.

^1H NMR ($CDCl_3$, 300.13 MHz, ppm): δ 6.99 (d, *J* = 7.2 Hz, 2H, Ar*H*), 6.89 (t, *J* = 7.4 Hz, 1H, Ar*H*), 3.74 (t, *J* = 6.5 Hz, 2H, $ArOCH_2$), 3.65 (t, *J* = 6.5 Hz, 2H, CH_2OH), 2.25 (s, 6H, Ar*Me*$_2$), 1.82–1.43 (m, 8H, $–CH_2–$), 1.23 (s, 1H, O*H*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.46 MHz, ppm): δ 151.5, 130.9, 128.7, 123.6 (Ar), 72.09 ($ArOCH_2$), 62.93 (CH_2OH), 32.70, 30.38, 25.98, 25.69 ($–CH_2–$), 16.25 (Ar*Me*$_2$).

HRMS Exact mass calculated for $C_{14}H_{23}O_2$ $[M+H]^+$: 223.1698, found: 223.1693.

2.3.5. Synthesis of $C_6H_5OCH_2CH_2OSO_2Me$ (**1L2**)

Triethylamine (6.00 mL, 43.0 mmol) was added to **1L1** (5.53 g, 40.0 mmol) in dichloromethane (30 mL) at 0 °C and stirred for 10 min. Methanesulfonyl chloride (3.70 mL, 47.8 mmol) was then added dropwise via cannula at 0 °C. The reaction mixture was warmed to room temperature and stirred for 3 h. The reaction was stopped by the addition of water (50 mL) and the organic portion was separated. The aqueous layer was extracted three times with dichloromethane (3 × 50 mL) and the combined organic portions were dried over $MgSO_4$ and filtered. The removal of solvent at reduced pressure gave the desired product **1L2** (8.24 g, yield = 95.3%) as a yellow oil.

^1H NMR ($CDCl_3$, 300.13 MHz, ppm): δ 7.28 (t, *J* = 7.9 Hz, 2H, Ar*H*), 7.00–6.87 (m, 3H, Ar*H*), 4.54 (m, 2H, $OCH_2CH_2OSO_2Me$), 4.21 (m, 2H, $OCH_2CH_2OSO_2Me$), 3.06 (s, 3H, S*Me*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.46 MHz, ppm): δ 157.8, 129.5, 121.5, 114.4 (Ar), 68.11 ($OCH_2CH_2OSO_2Me$), 65.58 ($OCH_2CH_2OSO_2Me$), 37.59 (S*Me*).

HRMS Exact mass calculated for $C_9H_{12}O_4SNa$ $[M+Na]^+$: 239.0354, found: 239.0347.

2.3.6. Synthesis of $Me_2C_6H_3OCH_2CH_2OSO_2Me$ (**2L2**)

A yellow oil **2L2** was prepared in a yield of 88.0% (8.60 g) by the reaction between **2L1** (6.65 g, 40.0 mmol), triethylamine (6.00 mL, 43.0 mmol), and methanesulfonyl chloride (3.70 mL, 47.8 mmol) in a manner analogous to the procedure for **1L2**.

^{1}H NMR ($CDCl_3$, 300.13 MHz, ppm): δ 7.02–6.92 (m, 3H, Ar*H*), 4.52 (t, *J* = 4.2 Hz, 2H, $OCH_2CH_2OSO_2Me$), 4.02 (t, 2H, *J* = 4.2 Hz, $OCH_2CH_2OSO_2Me$), 3.08 (s, 3H, S*Me*), 2.28 (s, 6H, ArMe_2).

^{13}C{^{1}H} NMR ($CDCl_3$, 75.46 MHz, ppm): δ 154.7, 130.5, 128.8, 124.2 (Ar), 69.16 ($OCH_2CH_2OSO_2Me$), 68.88 ($OCH_2CH_2OSO_2Me$), 37.40 (S*Me*), 16.01 (ArMe_2).

HRMS Exact mass calculated for $C_{11}H_{16}O_4SNa$ [M+Na]$^+$: 267.0667, found: 267.0661.

2.3.7. Synthesis of $C_6H_5OCH_2CH_2CH_2CH_2CH_2CH_2OSO_2Me$ (***3L2***)

A yellow oil **3L2** was prepared in a yield of 94.5% (10.3 g) by the reaction between **3L1** (7.77 g, 40.0 mmol), triethylamine (6.00 mL, 43.0 mmol), and methanesulfonyl chloride (3.70 mL, 47.8 mmol) in a manner analogous to the procedure for **1L2**.

^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 7.25 (m, 2H, Ar*H*), 6.87 (m, 3H, Ar*H*), 4.21 (t, *J* = 6.5 Hz, 2H, $ArOCH_2$), 3.93 (t, *J* = 6.4 Hz, 2H, CH_2OSO_2Me), 2.97 (s, 3H, S*Me*), 1.80–1.45 (m, 8H, –CH_2–).

^{13}C{^{1}H} NMR ($CDCl_3$, 100.63 MHz, ppm): δ 158.9, 129.3, 120.4, 114.3 (Ar), 69.92 (CH_2O), 67.36 ($ArOCH_2$), 37.17 (S*Me*), 28.94, 28.93, 25.45, 25.10 (–CH_2–).

HRMS Exact mass calculated for $C_{13}H_{21}SO_4$ [M+H]$^+$: 273.1161, found: 273.1155.

2.3.8. Synthesis of $Me_2C_6H_3OCH_2CH_2CH_2CH_2CH_2CH_2OSO_2Me$ (***4L2***)

A yellow oil **4L2** was prepared in a yield of 93.3% (11.2 g) by the reaction between **4L1** (8.89 g, 40.0 mmol), triethylamine (6.00 mL, 43.0 mmol), and methanesulfonyl chloride (3.70 mL, 47.8 mmol) in a manner analogous to the procedure for **1L2**.

^{1}H NMR ($CDCl_3$, 300.13 MHz, ppm): δ 7.00 (d, *J* = 7.6 Hz, 2H, Ar*H*), 6.91 (t, *J* = 6.6 Hz, 1H, Ar*H*), 4.23 (t, *J* = 6.5 Hz, 2H, $ArOCH_2$), 3.74 (t, *J* = 6.4 Hz, 2H, CH_2OSO_2Me), 2.99 (s, 3H, S*Me*), 2.25 (s, 6H, ArMe_2), 1.82–1.49 (m, 8H, –CH_2–).

^{13}C{^{1}H} NMR ($CDCl_3$, 75.46 MHz, ppm): δ 155.9, 130.8, 128.7, 123.6 (Ar), 71.80 ($ArOCH_2$), 69.96 (CH_2O), 37.30 (S*Me*), 30.17, 29.06, 25.63, 25.38 (–CH_2–), 16.20 (ArMe_2).

HRMS Exact mass calculated for $C_{15}H_{25}O_4S$ [M+H]$^+$: 301.1474, found: 301.1469.

2.3.9. Synthesis of $C_6H_5OCH_2CH_2Br$ (***1L3***)

1L2 (6.49 g, 30.0 mmol) in acetone (20 mL) was added dropwise to LiBr (13.0 g, 150 mmol) in 100 mL acetone at room temperature. After stirring for 24 h, a reaction was stopped by the addition of water (50 mL) and the organic portion was separated. The aqueous layer was extracted three times with diethyl ether (3 × 50 mL) and the combined organic portions were dried over $MgSO_4$. Filtration followed by evaporation gave the desired product **1L3** (4.08 g, yield = 67.6%) as a yellow oil.

^{1}H NMR ($CDCl_3$, 300.13 MHz, ppm): δ 7.28 (t, *J* = 7.9 Hz, 2H, Ar*H*), 7.00–6.89 (m, 3H, Ar*H*), 4.28 (t, *J* = 4.5 Hz, 2H, OCH_2CH_2Br), 3.62 (t, *J* = 4.5 Hz, 2H, OCH_2CH_2Br).

^{13}C{^{1}H} NMR ($CDCl_3$, 75.46 MHz, ppm): δ 158.1, 129.6, 121.4, 114.7 (Ar), 67.77 (OCH_2CH_2), 29.11 (OCH_2CH_2Br).

HRMS Exact mass calculated for C_8H_9BrNaO [M+Na]$^+$: 222.9734, found: 222.9729.

2.3.10. Synthesis of $Me_2C_6H_3OCH_2CH_2Br$ (***2L3***)

A yellow oil **2L3** was prepared in a yield of 74.2% (5.10 g) by the reaction between **2L2** (7.32 g, 30.0 mmol) and LiBr (13.0 g, 150 mmol) in a manner analogous to the procedure for **1L3**.

^{1}H NMR ($CDCl_3$, 300.13 MHz, ppm): δ 7.04–6.96 (m, 3H, Ar*H*), 4.10 (t, *J* = 6.2 Hz, 2H, OCH_2CH_2Br), 3.67 (t, *J* = 6.2 Hz, 2H, OCH_2CH_2Br), 2.32 (s, 6H, ArMe_2).

^{13}C{^{1}H} NMR ($CDCl_3$, 75.46 MHz, ppm): δ 155.0, 130.7, 128.9, 124.1 (Ar), 71.39 (OCH_2CH_2Br), 30.15 (OCH_2CH_2Br), 16.29 (ArMe_2).

HRMS Exact mass calculated for $C_{10}H_{14}BrO$ [M+H]$^+$: 229.0228, found: 229.0222.

2.3.11. Synthesis of $C_6H_5OCH_2CH_2CH_2CH_2CH_2CH_2Br$ (***3L3***)

A yellow oil **3L3** was prepared in a yield of 76.3% (5.89 g) by the reaction between **3L2** (8.17 g, 30.0 mmol) and LiBr (13.0 g, 150 mmol) in a manner analogous to the procedure for **1L3**.

^{1}H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 7.25 (m, 2H, Ar*H*), 6.89 (m, 3H, Ar*H*), 3.93 (t, *J* = 5.1 Hz, 2H, $ArOCH_2$), 3.63 (t, *J* = 5.2 Hz, 2H, CH_2Br), 1.79 – 1.39 (m, 8H, –CH_2–).

^{13}C{^{1}H} NMR ($CDCl_3$, 100.63 MHz, ppm): δ 159.0, 129.4, 120.5, 114.4 (Ar), 67.66 ($ArOCH_2$), 62.80 (CH_2Br), 32.62, 29.21, 25.86, 25.50 (–CH_2–).

HRMS Exact mass calculated for $C_{12}H_{18}BrO$ [M+H]$^+$: 257.0541, found: 257.0536.

2.3.12. Synthesis of $Me_2C_6H_3OCH_2CH_2CH_2CH_2CH_2CH_2Br$ (***4L3***)

A yellow oil **4L3** was prepared in a yield of 79.2% (6.78 g) by the reaction between **4L2** (9.01 g, 30 mmol) and LiBr (13.0 g, 150 mmol) in a manner analogous to the procedure for **1L3**.

^{1}H NMR ($CDCl_3$, 300.13 MHz, ppm): δ 7.00 (d, *J* = 7.6 Hz, 2H, Ar*H*), 6.92 (t, *J* = 7.4 Hz, 1H, Ar*H*), 3.75 (t, *J* = 6.5 Hz, 2H, $ArOCH_2$), 3.42 (t, *J* = 6.4 Hz, 2H, CH_2Br), 2.26 (s, 6H, ArMe_2), 1.93–1.52 (m, 8H, –CH_2–).

^{13}C{^{1}H} NMR ($CDCl_3$, 75.46 MHz, ppm): δ 155.9, 130.9, 128.7, 123.6 (Ar), 71.89 ($ArOCH_2$), 33.85 (CH_2Br), 32.73, 30.23, 28.07, 25.39 (–CH_2–), 16.25 (ArMe_2).

HRMS Exact mass calculated for $C_{14}H_{22}BrO$ [M+H]$^+$: 285.0854, found: 285.0848.

2.3.13. In situ generation of $C_6H_5OCH_2CH_2Cp$ (***1L4***)

A solution of LiCp (1.58 g, 21.9 mmol) in THF (20 mL) was added dropwise to solution of **1L3** (4.03 g, 20.0 mmol) in THF (30 mL) at −60 °C. The reaction mixture was then warmed to room temperature and stirred for 12 h. The reaction was stopped by the addition of 30 mL saturated aqueous NH_4Cl and the organic portion was separated. The mixture was extracted with diethyl ether (2 × 50 mL) and the combined organic portions were dried over $MgSO_4$, filtered, and evaporated to dryness. Colorless oil **1L4** was obtained and used without further purification (1.31 g, 35.2%).

2.3.14. In situ generation of $Me_2C_6H_3OCH_2CH_2Cp$ (***2L4***)

Pale yellow oil **2L4** was prepared in a yield of 51.3% (2.20 g) by the reaction between **2L3** (4.58 g, 20.0 mmol) and LiCp (1.58 g, 21.9 mmol) in a manner analogous to the procedure for **1L4**.

2.3.15. In situ generation of $C_6H_5OCH_2CH_2CH_2CH_2CH_2CH_2Cp$ (***3L4***)

Pale yellow oil **3L4** was prepared in a yield of 92.8% (4.50 g) by the reaction between **3L3** (5.14 g, 20.0 mmol) and LiCp (1.58 g, 21.9 mmol) in a manner analogous to the procedure for **1L4**.

2.3.16. In situ generation of $Me_2C_6H_3OCH_2CH_2CH_2CH_2CH_2CH_2Cp$ (***4L4***)

Pale yellow oil **4L4** was prepared in a yield of 83.6% (4.52 g) by the reaction between **4L3** (5.69 g, 20.0 mmol) and LiCp (1.58 g, 21.9 mmol) in a manner analogous to the procedure for **1L4**.

2.3.17. Synthesis of $(C_6H_5OCH_2CH_2Cp)_2ZrCl_2$ (***1***)

(Route 1) A solution of **1L4** (0.933 g, 5.01 mmol) in diethyl ether (20 mL) was treated with *n*-butyllithium (5.25 mmol, 2.1 mL of 2.5 M solution in hexane) at −78 °C. The reaction mixture was then warmed to room temperature and stirred overnight. All volatiles were removed and the remaining ivory solid was dried under vacuum after washed twice with *n*-hexane. Into a precooled flask containing $ZrCl_4$ (0.466 g, 2.00 mmol) and lithiated **1L4** (0.773 g, 4.02 mmol) powders was added diethyl ether (40 mL) at −78 °C with vigorous stirring. The reaction mixture was warmed to room temperature over 2 h and stirred overnight at this temperature. The yellow solution was filtered through Celite and concentrated to about 10 mL. Overnight cooling at −20 °C after the addition of 10 mL of *n*-hexane afforded 0.366 g (34.4%) of yellow crystals of **1**.

(Route 2) $Zr(NMeEt)_4$ (0.809 g, 2.50 mmol) in hexane (10 mL) was added dropwise via cannula with vigorous stirring to a flask precooled at −78 °C containing freshly obtained **1L4** (0.933 g, 5.01 mmol) in hexane (10 mL). The reaction mixture was allowed to warm slowly to room temperature over 2 h. After 12 h stirring, all volatiles were evaporated under the reduced pressure, leaving yellow oil, to which methylene chloride (20 mL) was added. Me_3SiCl (1.36 g, 12.5 mmol) was added slowly via syringe at 0 °C with vigorous stirring. The reaction mixture was slowly allowed to warm to room temperature over 20 min and then stirred for 12 h. The solvent evaporated to afford the desired product **1** as a deep yellow solid. (1.14 g, yield = 85.5%).

^1H NMR ($CDCl_3$, 300.13 MHz, ppm): δ 7.26 (t, *J* = 7.6 Hz, 4H, Ar*H*), 6.95–6.86 (m, 6H, Ar*H*), 6.33 (s, 8H, Cp-*H*), 4.15 (t, *J* = 6.1 Hz, 4H, OCH_2CH_2OCp), 3.12 (t, *J* = 6.1 Hz, 4H, OCH_2CH_2Cp).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.46 MHz, ppm): δ 158.6, 131.0, 129.5, 120.8, 117.7, 114.5, 112.2 (Ar, Cp), 67.37 (OCH_2CH_2Cp), 30.15 (OCH_2CH_2Cp).

Elemental *Anal.* Calc. for $C_{26}H_{26}Cl_2O_2Zr$: C, 58.63; H, 4.92. Found: C, 58.58; H, 5.01%.

2.3.18. Synthesis of $(Me_2C_6H_3OCH_2CH_2Cp)_2ZrCl_2$ (**2**)

A deep yellow solid **2** was prepared in a yield of 71.9% (2.11 g) by the reaction between $Zr(NMeEt)_4$ (1.62 g, 5.00 mmol), **2L4** (2.14 g, 10.0 mmol), and Me_3SiCl (2.72 g, 25.0 mmol) in a manner analogous to the synthetic route 2 for **1**.

^1H NMR ($CDCl_3$, 300.13 MHz, ppm): δ 6.98–6.89 (m, 6H, Ar*H*), 6.37 (s, 8H, Cp-*H*), 3.92 (t, *J* = 6.3 Hz, 4H, OCH_2CH_2OCp), 3.13 (t, *J* = 6.3 Hz, 4H, OCH_2CH_2Cp), 2.15 (s, 12H, Ar*Me*$_2$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.46 MHz, ppm): δ 155.6, 131.5, 130.9, 128.8, 123.8, 117.7, 112.3 (Ar, Cp), 71.55 (OCH_2CH_2Cp), 31.39 (OCH_2CH_2Cp), 16.24 (Ar*Me*$_2$).

Elemental *Anal.* Calc. for $C_{30}H_{34}Cl_2O_2Zr$: C, 61.21; H, 5.82. Found: C, 61.33; H, 5.94%.

2.3.19. Synthesis of $(C_6H_5OCH_2CH_2CH_2CH_2CH_2CH_2Cp)_2ZrCl_2$ (**3**)

A deep yellow solid **3** was prepared in a yield of 70.1% (2.26 g) by the reaction between $Zr(NMeEt)_4$ (1.62 g, 5.00 mmol), **3L4** (2.42 g, 10.0 mmol), and Me_3SiCl (2.72 g, 25.0 mmol) in a manner analogous to the synthetic route 2 for **1**.

^1H NMR ($CDCl_3$, 400.15 MHz, ppm): δ 7.25 (m, 5H, Ar*H*), 6.89 (m, 5H, Ar*H*), 6.26 (t, *J* = 2.1 Hz, 3H, Cp-*H*), 6.18 (t, *J* = 2.1 Hz, 3H, Cp-*H*), 3.92 (t, *J* = 5.2 Hz, 4H, $ArOCH_2$), 2.62 (t, *J* = 6.2 Hz, 4H, CH_2-Cp), 1.77–1.36 (m, 16H, $-CH_2-$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.63 MHz, ppm): δ 158.1, 134.0, 128.4, 119.5, 115.7, 113.5, 111.2, (Ar and Cp), 66.70 ($ArOCH_2$), 29.54 (CH_2-Cp), 29.07, 28.19, 28.01, 24.79 ($-CH_2-$).

Elemental *Anal.* Calc. for $C_{34}H_{42}Cl_2O_2Zr$: C, 63.33; H, 6.57. Found: C, 63.49; H, 6.38%.

2.3.20. Synthesis of $(Me_2C_6H_3OCH_2CH_2CH_2CH_2CH_2CH_2Cp)_2ZrCl_2$ (**4**)

The desired product **4** as an orange-yellow solid was prepared from $Zr(NMeEt)_4$ (0.186 g, 0.575 mmol), **4L4** (0.311 g, 1.15 mmol), and Me_3SiCl (0.313 g, 2.88 mmol) in a yield of 84.3% (0.340 g) in a manner analogous to the synthetic route 2 for **1**.

^1H NMR ($CDCl_3$, 300.13 MHz, ppm): δ 6.99 (d, *J* = 7.5 Hz, 4H, Ar*H*), 6.88 (t, *J* = 4.1 Hz, 2H, Ar*H*), 6.28 (t, *J* = 2.6 Hz, 4H, Cp-*H*), 6.19 (t, *J* = 2.6 Hz, 4H, Cp-*H*), 3.72 (t, *J* = 6.5 Hz, 4H, $ArOCH_2$), 2.64 (t, *J* = 7.7 Hz, 4H, CH_2Cp), 2.24 (s, 12H, Ar*Me*$_2$), 1.79–1.23 (m, 16H, $-CH_2-$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.46 MHz, ppm): δ 156.0, 135.0, 130.9, 128.7, 123.6, 116.7, 112.2, (Ar and Cp), 72.09 ($ArOCH_2$), 30.60 (CH_2-Cp), 30.33, 30.13, 29.23, 25.93 ($-CH_2-$), 16.27 (Ar*Me*$_2$).

Elemental *Anal.* Calc. for $C_{38}H_{50}Cl_2O_2Zr$: C, 65.12; H, 7.19. Found: C, 65.38; H, 7.42%.

2.4. X-ray structure determination of **4**

Crystallographic assessment of **4** was performed at ambient temperature using a Bruker APEXII CCD area detector diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. A single crystal of suitable size and quality was selected and mounted on a glass capillary using Paratone® oil and centered in the X-ray beam using a video camera. Multi-scan reflection data were collected with a frame width of 0.5° in *w* and θ and 5 s exposures per frame. Determination of cell parameters, data reduction, and empirical absorption corrections were conducted using the programs APEX2, SAINT and SADABS, respectively [29]. The structure of **4** was solved by direct methods and refined to convergence using full matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL program package [30]. The molecular structure of **4** (Fig. 2) was drawn using the program DIAMOND [31]. Details of the crystallographic data and parameters are listed in Table 1.

2.5. Ethylene polymerization

Ethylene was polymerized in 250 mL Schlenk flask. Toluene, the polymerization solvent, was distilled from sodium diphenylketyl under dinitrogen immediately before use. Toluene (50 mL), MAO (20 mmol or 10 mmol), and zirconium compounds (5 μmol or 10 μmol) were sequentially injected into the flask at the desired polymerization temperature. The mixtures were then saturated with 1 bar ethylene, which was kept constant. After 3 min or 1 h, polymerizations were terminated by venting the ethylene gas and quenching with a small volume of MeOH. The polymer was isolated by filtration, sequentially washed with MeOH, 10% HCl in MeOH, and then dried *in vacuo* at 50 °C for 12 h.

3. Results and discussion

The aim of this work is the synthesis, characterization, and the comparison of ethylene polymerization behaviors of novel zirconium complexes with pendant aryloxy groups attached to the metallocene moiety by $-CH_2CH_2-$ and $-CH_2CH_2CH_2CH_2CH_2CH_2-$ spacers. The final products synthesized were bis[(2-phenoxyethyl)cyclopentadienyl]zirconium dichloride (**1**), bis[{2-(2,6-dimethylphenoxy)ethyl}cyclopentadienyl]zirconium dichloride (**2**), bis[(6-phenoxyhexyl)cyclopentadienyl]zirconium dichloride (**3**), and bis[{6-(2,6-dimethylphenoxy)hexyl}cyclopentadienyl]zirconium dichloride (**4**) (See Fig. 1). The synthetic routes to complexes **1**–**4** are outlined in Scheme 1. To introduce two different ancillary groups such as Cp ring and aryloxy group at the ends of the ethyl or hexyl spacer, a set of stepwise reactions was performed.

The preparation of 2-phenoxyethan-1-ol (**1L1**) was achieved by the reaction of phenol, 2-chloroethanol, and NaOH in water. Suitable workup gave **1L1** as colorless oil in 53.1% yield and the subsequential reaction between **1L1** and MsCl in the presence of NEt_3 afforded 2-phenoxyethyl methanesulfonate (**1L2**) in 95.3% yield after aqueous workup. Excess NEt_3 was necessary for the successful synthesis of compound **1L2**, which was treated with LiBr in acetone to give (2-bromoethoxy)benzene (**1L3**) as a yellow oil in 67.6% yield. **1L3** was a critical intermediate in the synthesis of the desired ligand **1L4**; an attempt at the direct nucleophilic substitution of **1L2** with LiCp to prepare **1L4** yielded only the starting materials after workup (Scheme 1). Compound **1L4** formed in 35.2% yield when compound **1L3** reacted with lithium cyclopentadienylide in THF. It was used without further purification and easily decom-

Table 1
Crystallographic data and parameters for compound **4**.

	4
Empirical formula	$C_{38}H_{50}O_2Cl_2Zr$
Formula weight	700.90
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	15.338(3)
b (Å)	18.181(3)
c (Å)	13.854(2)
α (°)	90
β (°)	110.189(8)
γ (°)	90
V (Å^3)	3626.1(10)
Z	4
D_{calc} (g/cm^3)	1.284
μ (mm^{-1})	0.481
$F(000)$	1472
Index ranges	$-21 \leqslant h \leqslant 22$, $-25 \leqslant k \leqslant 27$, $-20 \leqslant l \leqslant 20$
θ range (°)	$1.41 \leqslant \theta \leqslant 32.02$
Reflections collected	52011
Independent reflections	12225
Number of observed reflections ($I > 2\sigma(I)$)	6206
Number of parameters refined	392
GOF ($I > 2\sigma(I)$)	0.998
R_1 (all data)	0.1196
$R_1(I > 2\sigma(I))$ [a]	0.0462
wR_2 (all data)	0.1380
$wR_2(I > 2\sigma(I))$ [a]	0.1061
Largest difference in peak and hole (e Å^{-3})	0.695 and −0.522

[a] $R_1 = \sum||Fo| - |F_c||/\sum|F_o|$ and $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

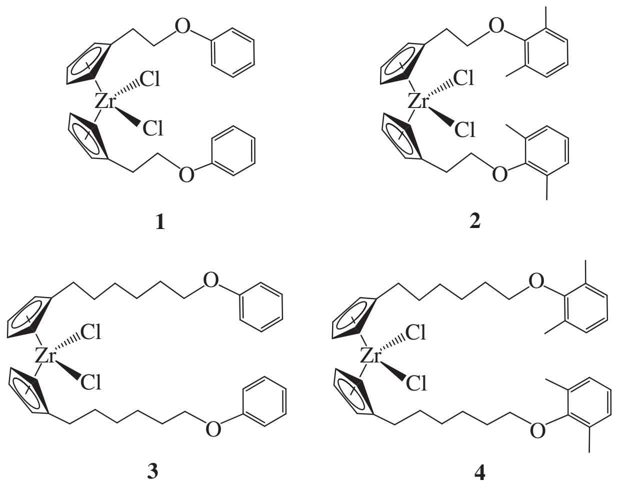
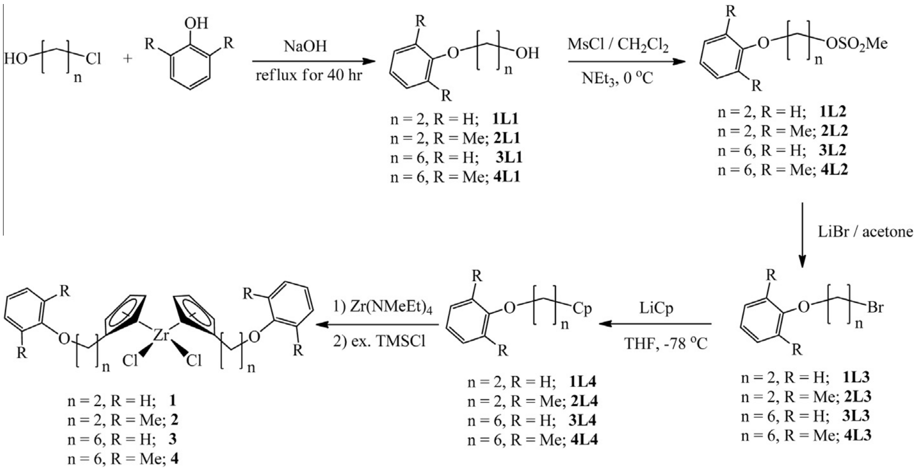


Fig. 1. Sketches of the synthesized complexes.

posed even at room temperature through an intramolecular Diels–Alder reaction. Straightforward metallation of **1L4** with $Zr(NMeEt)_4$ followed by the treatment of trimethylsilyl chloride gave bis[(2-phenoxyethyl)cyclopentadienyl]zirconium dichloride (**1**) as a deep yellow crystalline solid in 85.5% yield. The reaction between two equivalents lithiated **1L4** and $ZrCl_4$ also gave the desired product **1** with a poor yield of 34.4%, suggesting that the mild reaction conditions of amine elimination were required. Complexes **2**–**4** were prepared in a manner analogous to the multistep synthetic route for **1** via amine elimination process. Like other zirconocene dichlorides, complexes **1**–**4** were comparably stable in air and were freely soluble in polar organic solvents and toluene but insoluble in hydrocarbon solvents such as *n*-hexane and *n*-pentane. All compounds were fully characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and HR-mass spectrometry or elemental analysis. The NMR spectra are in accord with the suggested structures and all proton and carbon chemical shifts appeared in the expected ranges. The NMR signals were sharp and variable-temperature studies showed no evidence of inter- or intra-molecular ligand exchange at ambient temperature.

Recrystallization from dichloromethane/diethyl ether at −20 °C gave **4** as an orange-yellow crystalline solid suitable for X-ray diffraction analysis, which assessed its solid-state structure (Fig. 2). Tables 1 and 2 list detailed crystallographic data and selected interatomic distances and angles, respectively. The zirconium complex **4** crystallized in the space group $P2_1/c$ and different views of the structure (Fig. 2(a)–(c)) show that chlorine atoms and the centroids of the Cp ring formed a considerably distorted *pseudo*-tetrahedral coordination geometry around the zirconium with angles ranging from 95.15° (Cl1–Zr–Cl2) to 131.61° (C_{cent1}–Zr–C_{cent2}). The Cp rings were slightly staggered, with side chains arranged at the open side of the stacking. The structure of **4** showed that the complex's aryloxy groups were far from the zirconium center, with neither intra- nor inter-molecular interactions occurring between the O atom and the Zr center. The plane perpendicular to the Cl1–Zr–Cl2 plane and bisecting the Cl1–Zr–Cl2 angle was σ-symmetric; the C_2 symmetric axis bisected the Cl1–Zr–Cl2 angle, giving **4** a *pseudo*-C_{2v} symmetry. The bond distance data (Table 2) show that the Cp' ring formed largely uniform Zr–C_{Cp} distances, averaging 2.504 Å with a small standard deviation of 0.020 Å, indicating that two Cp' rings were bonded to the Zr atom in the usual η^5 fashion. Zr–C_{cent1} and Zr–C_{cent2} lengths were 2.196 and 2.202 Å, respectively. The C_{cent1}–Zr–C_{cent2} angle (131.61(5)°) was found to be similar to that of other zirconocene complexes [32]. A similar trend was shown by the Cl1–Zr–Cl2 angle (95.15(3)°). The substituents of the Cp ligand were oriented in the lateral sector in opposite directions to each other. The Zr–Cl bond lengths were 2.4506(8) Å and 2.4554(9) Å. An acute dihedral angle of 51.13(6)° was found between the two π-ring planes.



Scheme 1. Synthetic routes to **1**–**4**.

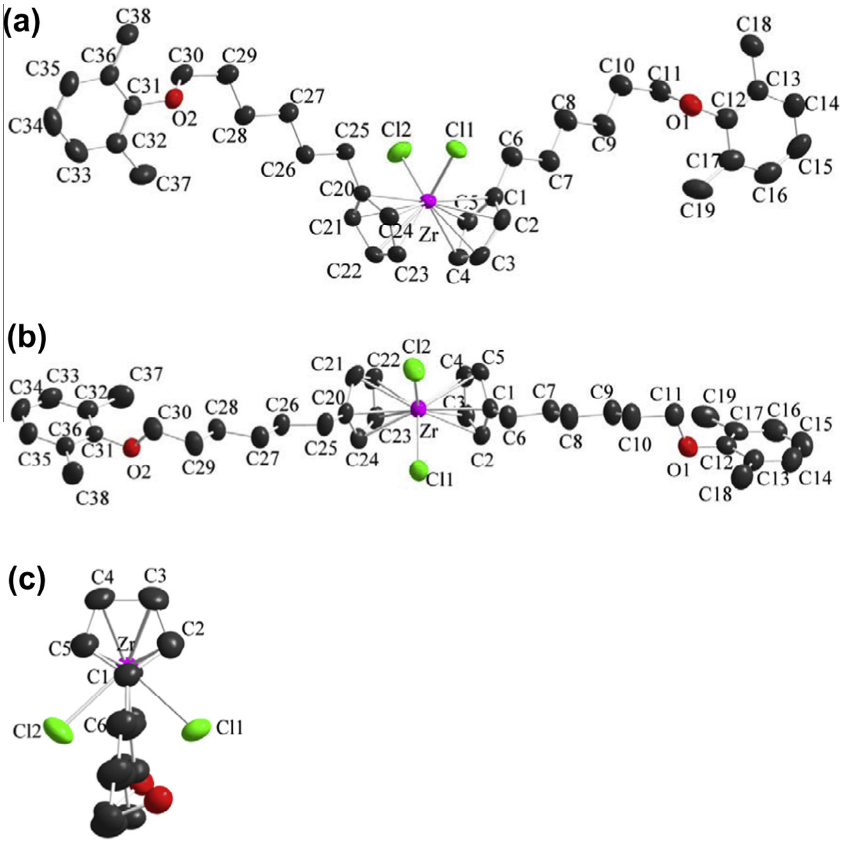


Fig. 2. X-ray molecular structure of compound **4** with 50% thermal ellipsoids. H atoms are omitted for clarity. (a) Side view. (b) Front view. (c) Top view (Aryl rings are omitted for clarity.).

Ethylene polymerization involving compounds **1**–**4** and MAO as a cocatalyst were performed at 50 °C (Table 3, entries 1–3, 6). To compare catalytic property with those of **1**–**4**, polymerization with Cp_2ZrCl_2 was also performed under similar condition (Table 3, entry 9). The polymerization results at 50 °C show that the catalytic activity was closely related to the distance between Cp ring and aryloxy groups in complexes **1**–**4**. Even though the doubled concentration of catalyst (10 μmol) and elongated polymerization time (1 h) were applied, **1** and **2** produced trace amount of polyethylene. The similar observations were reported in the literature for $[CH_3CH_2CH_2OCH_2CH_2O(CH_2)_2Cp]_2ZrCl_2$ [14] and $(3\text{-THF-}CH_2Cp)_2ZrCl_2$ [19]. This behavior can be explained by the possible formation of σ-donated complex with direct contacts between donor oxygen atoms of short ether linkage and the cationic zirconium center during the polymerization [33]. In contrast with these results, **3** and **4** with long spacers between Cp ring and aryloxy group behave as a highly active single-site catalyst. Complexes **3**, **4**, and Cp_2ZrCl_2 could catalyze ethylene polymerizations well at 50 °C within just 3 min. The activities of compounds **3** and **4** at 50 °C were about 87% and 48% of that of Cp_2ZrCl_2, respectively. This relatively small decrease of activity for **3** and **4** can be explained that the molecular structure in Fig. 2, where the aryoxy group is far

Table 2
Selected interatomic distances (Å) and angles (°) of compound **4**.

Distances			
Zr–Cl1	2.4506(8)	Zr–Cl2	2.4554(9)
Zr–C1	2.524(3)	Zr–C2	2.503(3)
Zr–C3	2.477(3)	Zr–C4	2.486(3)
Zr–C5	2.520(3)	Zr–C20	2.536(3)
Zr–C21	2.529(3)	Zr–C22	2.485(3)
Zr–C23	2.485(3)	Zr–C24	2.497(3)
Zr–C_{cent1}[a]	2.1961(13)	Zr–C_{cent2}[b]	2.2023(13)
C1–C2	1.420(4)	C2–C3	1.401(4)
C3–C4	1.406(4)	C4–C5	1.410(4)
C5–C1	1.409(4)	C20–C21	1.414(4)
C21–C22	1.407(4)	C22–C23	1.411(4)
C23–C24	1.402(4)	C24–C20	1.402(4)
C1–C6	1.513(4)	C20–C25	1.503(3)
Angles			
Cl1–Zr–Cl2	95.14(3)	C_{cent1}–Zr– C_{cent2}	131.61(5)
C_{cent1}–Zr–Cl1	105.70(4)	C_{cent1}–Zr–Cl2	106.82(5)
C_{cent2}–Zr–Cl1	105.88(4)	C_{cent2}–Zr–Cl2	105.80(4)
C_{cent1}–C1–C6	178.56(4)	C_{cent2}–C20–C25	179.03(5)
C1–C6–C7	112.20(4)	C20–C25–C26	111.77(5)
C11–O1–C12	114.5(2)	C30–O2–C31	114.3(2)

[a] C_{cent1} = centroid of C1, C2, C3, C4, and C5.
[b] C_{cent2} = centroid of C20, C21, C22, C23, and C24.

away from the metal center, is predominantly maintained in solution.

Generally, the metallocene catalysts containing oxygen atoms have been known to produce polyethylene with low molecular weight and somewhat broader molecular weight distribution [14]. Unexpectedly, **3** and **4** gave polyethylene with much higher molecular weight than that of Cp_2ZrCl_2. The introduction of long chain aryloxy group in Cp_2ZrCl_2 induces the small decrease in catalytic activity as well as a large increase in molecular weight. Molecular weight distributions were also somewhat broad in our systems. The resulting polyethylene's T_m and T_c are indicative of high-density polyethylene.

In order to further investigate the characteristics of catalyst for the polymerization reaction, the ethylene polymerizations for compounds **3**, **4**, and Cp_2ZrCl_2, which showed the good catalytic activity at 50 °C, were carried out at various temperatures under the fixed MAO concentration (Table 3, entries 3–11). Generally, the activity in the olefin polymerization using homogenous catalysts increases along with the raised polymerization temperature.

Table 3
Ethylene polymerization data for catalysts **1**–**4** and Cp_2ZrCl_2 in the presence of cocatalyst MAO.

Entry	Cat.	T_p (°C)	Polymer (g)	A[c]	T_m (°C)[d]	T_c (°C)[d]	M_w[e]	M_w/M_n[e]
1[a]	**1**	50	0.0215	2.2	134.3	114.2	–[f]	–[f]
2[a]	**2**	50	0.0294	2.9	133.3	114.3	–[f]	–[f]
3[b]	**3**	50	0.514	2060	135.9	113.3	273,000	3.24
4[b]		70	0.673	2690	132.4	116.9	117,000	2.72
5[b]		90	0.746	2980	128.9	116.1	35,300	5.38
6[b]	**4**	50	0.285	1140	133.6	115.7	491,000	3.77
7[b]		70	0.515	2060	132.3	116.7	144,000	4.83
8[b]		90	0.665	2660	131.5	116.4	68,800	3.23
9[b]	Cp_2ZrCl_2	50	0.593	2370	136.2	117.6	148,000	3.02
10[b]		70	1.287	5150	133.2	119.0	36,400	2.89
11[b]		90	1.135	4540	129.7	116.3	21,400	3.56

[a] Polymerization Condition: [Zr] = 10 μmol, [MAO] = 20 mmol, [Al]/[Zr] = 2000, ethylene 1 bar, toluene 50 mL, 1 h.
[b] Polymerization Condition: [Zr] = 5 μmol, [MAO] = 10 mmol, [Al]/[Zr] = 2000, ethylene 1 bar, toluene 50 mL, 3 min.
[c] Activity = kg polymer/(mol Zr × hr × bar).
[d] Determined by DSC.
[e] Determined by GPC.
[f] Not determined.

The data given in Table 3 and Fig. 3(a) clearly indicate that the catalytic activity of **3**/MAO and **4**/MAO systems towards synthesis of polyethylene increases as temperature rose from 50 to 90 °C. Both systems showed that activity increased sharply with heating to 70 °C and then increased smoothly with further heating to 90 °C. However, Cp_2ZrCl_2 showed the maximum activity in 70 °C. Complexes **3**, **4**, and Cp_2ZrCl_2 yielded high-density polyethylene with M_w of 35300–273000, 68000–491000, and 21400–148000, respectively (Table 3, entries 3–11). As shown in Fig. 3(b), the temperature of the polymerization significantly affected the polymers' molecular weights, consistently decreasing them at higher temperature. A similar trend of lowering polyethylene's T_m with increasing temperature was observed. Interestingly, **4**/MAO produced polyethylene with a very high molecular weight of 491000 at 50 °C (Table 3, entry 6). The produced polyethylene showed a slightly higher M_w/M_n of 2.72–5.38 (Table 3, entries 3–8) than that formed using other zirconocenes [3–6], suggesting that chain transfer reactions occurred due to the coordination of oxygen atoms of the pendant groups of **3** or **4** with the Al centers of MAO. Furthermore, **3**/MAO system showed better catalytic activity than **4**/MAO system; however, **4**/MAO system produced polyethylene with higher molecular weight.

In summary, bis[(2-phenoxyethyl)cyclopentadienyl]zirconium dichloride (**1**), bis[{2-(2,6-dimethylphenoxy)ethyl}cyclopentadienyl]zirconium dichloride (**2**), bis[(6-phenoxyhexamethylene)cyclopentadienyl]zirconium dichloride (**3**), and bis[{6-(2,6-dimethylphenoxy)hexamethylene}cyclopentadienyl]zirconium dichloride (**4**) were prepared in five steps from inexpensive, commercially available materials. They are zirconium complexes containing Cp ring and aryloxy group linked by $-CH_2CH_2-$ or $-CH_2CH_2CH_2CH_2CH_2CH_2-$ spacers. In the presence of MAO cocatalyst, complexes **1** and **2** showed very low catalytic activity towards

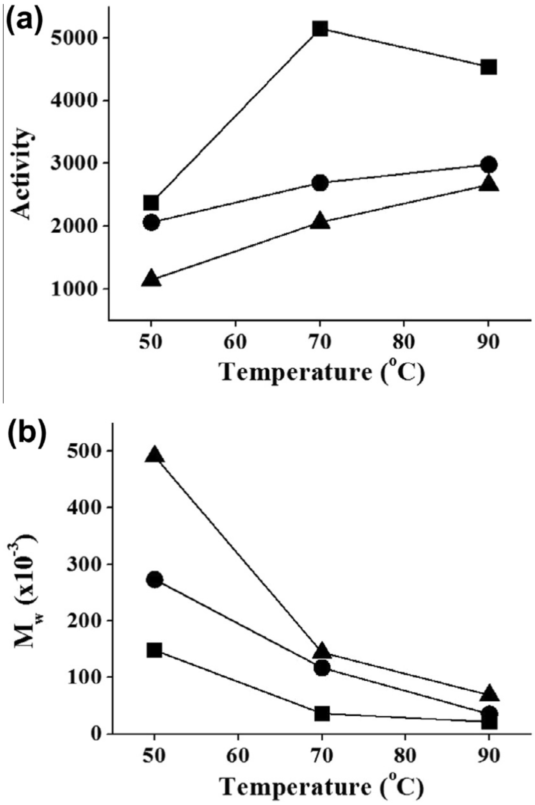


Fig. 3. (a) Catalytic activities and (b) M_w of polyethylene vs. polymerization temperature for complexes **3** (●), **4** (▲), and Cp_2ZrCl_2 (■).

the polymerization of ethylene; however, complexes **3** and **4** were proven to be good catalysts for polyethylene over a range of temperatures comparable to Cp_2ZrCl_2. Polymerization at 50 °C using **4**/MAO system resulted in producing polyethylenes with the highest molecular weight of 491,000.

Acknowledgments

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Appendix A. Supplementary data

CCDC 856703 contains the supplementary crystallographic data for **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.08.066.

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