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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**.