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Journal of Organometallic Chemistry 552 (1998) 313–317

Journal of Organometallic Chemistry

Ethylene polymerization by zirconocene compounds having ether bonds

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Received 5 August 1997; received in revised form 6 October 1997

Abstract

Zirconocene compounds having ether bonds at the substituent of cyclopentadienyl ligand, $[\eta^5\text{-}C_5H_4(CH_2)_n OCH_2CH_2OCH_2CH_3]_2ZrCl_2$ ($n = 2, 4, 6, 8$) and $[\eta^5\text{-}C_5H_4CH_2CH_2OCH_2CH_3]_2ZrCl_2$, were prepared and tested for ethylene polymerization catalysts with methylaluminoxane as a cocatalyst. The presence of oxygen atom close to the metal center drastically reduced the polymerization activity. It increased as the distance between zirconium and oxygen atom increased and showed a maximum when n was 6. © 1998 Elsevier Science S.A.

Keywords: Zirconium; Metallocene; Polyethylene; Polymerization

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1. Introduction

The metallocene compounds activated by methylaluminoxane (MAO) or boron complexes have been widely investigated as a new generation catalyst for polyolefins [1–3]. The metallocene catalyst produces the polymers with narrow molecular weight distribution and uniform comonomer incorporation because it is a single site catalyst. The tactility can be controlled by the molecular geometry of catalyst in the case of α-olefin polymerization [4].

A metallocene catalyst is homogeneous in itself but, depending on process requirements, it may be heterogenized on inert materials such as silica. In those cases, the catalyst may be anchored on the solid surface through siloxane bond [5–7], which is formed by the reaction between the hydroxyl group of support materials and the substituent of metallocene catalyst (Fig. 1).

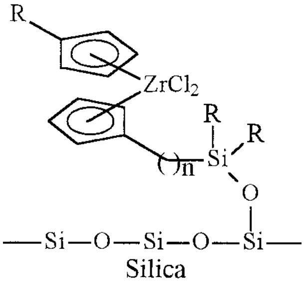

Fig. 1. Anchoring the zirconocene on silica.

However, the presence of siloxane or ether bonds in the cyclopentadienyl ligand reduces the polymerization activity. Several siloxane-bridged zirconocene compounds were prepared [8–11] and their activities were tested [8,12–14]. Song et al. [8] reported that the disiloxane-bridged bis(indenyl)metallocenes showed just 10^{-2}–10^{-4} order of the activity of conventional bridged or non-bridged metallocene compounds. The activities were reduced by the factor of 1/20–1/100 when the hydrogen atom was replaced by the methoxy group in the six-membered ring of the indenyl or fluorenyl ligand [15–18].

We thought that the activity might be closely related to the distance between the oxygen and the metal center and prepared several zirconocene compounds having oxygen atoms to elucidate the effect of distance.

2. Result and discussion

2.1. Synthesis of zirconocene dichloride, **3a–3d** and **5**

Our model compounds were easily synthesized (Scheme 1). Cyclopentadiene compounds having ether

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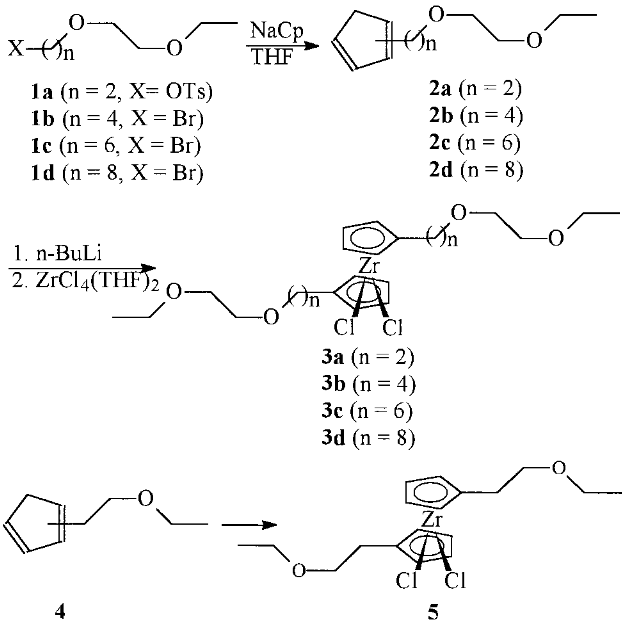

Scheme 1.

bonds, **2a–2d**, were prepared by the reaction of sodium cyclopentadienylide with the corresponding bromide or tosylated compounds, **1a–1d**. Bromide compounds, **1b–1d**, were prepared from α,ω-dibromide compounds by the Williamson ether synthesis. Metallation was conducted by conventional ways with good yields. Because **3a** is oily, it can not be purified by recrystallization. However, **3b–3d** were deposited and purified as solid in pentane at −30°C although they were also oily at room temperature. **5** was synthesized instead of **3a**. It could be also purified by recrystallization in hexane at −30°C. The melting point of **5** was 74–75°C.

*2.2. Characterization of **3b–3d** and **5***

3b–3d and **5** were characterized by ^{1}H NMR, ^{13}C NMR, IR spectroscopy, and elemental analysis. The ^{1}H NMR spectra of **3b–3d** showed four cyclopentadienyl protons in 6.3 and 6.2 ppm as two triplets, eight etheral CH_2 protons in 3.6–3.4 ppm, two CH_2 protons near cyclopentadienyl ring in 2.6 ppm as a triplet, terminal CH_3 protons in 1.2 ppm as a triplet and the rest CH_2 protons in 1.7–1.4 ppm. The ^{1}H NMR spectra of **3a** and **5** showed similar patterns to those of **3b–3d** except the four cyclopentadienyl ring protons. The ring protons of **3a** and **5** were seen as singlet and pseudosinglet instead of two triplets. The ^{13}C NMR spectra showed three-ring carbons in 135–110 ppm, four etheral carbon in 72–65 ppm and the other carbons in 31–15 ppm. The IR spectra showed strong band near 1100 cm^{-1} corresponding to the ether bonds.

2.3. Ethylene polymerization studies

3a–3d and **5** were tested for ethylene polymerization catalysts. Bis(*n*-butylcyclopentadienyl)zirconium dichloride which has been known to show good activity was also utilized for comparison [19]. Polymerization was conducted in a 500-ml glass reactor at 80°C under 40 psig of ethylene pressure for 15 min with hexane as diluent. MAO was used as cocatalyst and Al/Zr ratio was 5000.

The activity was closely related to the distance between the zirconium and oxygen atom (Table 1). **3a** and **5** produced trace amount of polyethylene. However, the activity increased as the distance between the zirconium and oxygen atom increased. The activity of compound **3c** was about 2/3 of that of bis(*n*-butylcyclopentadienyl)zirconium dichloride. When the distance increased further, the activity decreased.

The metallocene catalysts having oxygen atoms were reported to produce polyethylene having low molecular weight and somewhat broader molecular weight distribution [15–18]. In the current investigation, however, **3b–3d** produced the polyethylene of similar molecular weight to that of the bis(*n*-butylcyclopentadienyl) zirconium dichloride. As the chain length increased, the molecular weight somewhat increased. Unexpectedly, **5** gave a high molecular weight polyethylene. Molecular weight distributions were also somewhat broader in our case.

Activity reduction due to oxygen atom has been explained by two factors—the inductive effect [15–18] and the σ-donation of oxygen to zirconium center [8]. In the present case, the inductive effect may be negligible because it diminishes when the functional group is located beyond a few methylene groups. The activity reduction may be illustrated by the σ-donated conformation (Fig. 2). These conformations were known to be inactive for the polymerization [8].

For **3a** and **5**, the inactive conformation may be easily formed because the oxygen atom is very close to the zirconium center. As the distance between the zirconium and oxygen atom increases, the formation of the inactive conformation become more unfavorable. Be-

Table 1
Ethylene polymerization results ($T_p = 80$°C; $t = 15$ min; $p(C_2H_4) =$ 40 psig, zirconocene $= 0.5 \times 10^{-6}$ mol; mole ratio Al/Zr = 5000)

Zirconocene	Yield (g)	Activity[a]	MW ($\times 10^3$)	M_w/M_n
3a	Trace			
5	0.32	2.56	892	3.18
3b	1.15	9.20	258	3.04
3c	3.95	31.6	348	3.15
3d	1.50	12.0	457	3.24
$(n\text{-BuCp})_2ZrCl_2$[b]	6.00	48.0	444	2.56

[a] Activity in 10^3 kg PE/(mol Zr h).
[b] Bis(*n*-butylcyclopentadienyl)zirconium dichloride.

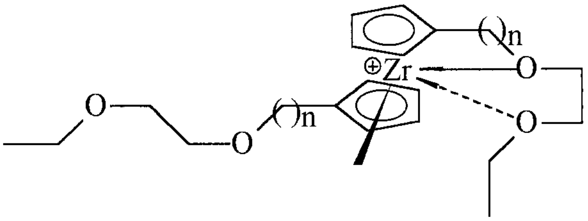

Fig. 2. Inactive conformation.

cause the medium rings, 8–11 membered rings, have large ring strain energy [20], the formation of inactive conformation may be most unfavorable for **3c**. Hence, the activity was maximum for **3c**.

In conclusion, we have demonstrated that the activity of the zirconocene compounds having ether bonds is strongly related to the distance between the zirconium and oxygen atom. The activity was maximum when the σ-donated conformation was most unfavorable. This result may be informative to the heterogenation of the metallocene catalyst on silica.

3. Experimental

3.1. General comments

All manipulations were performed under an inert atmosphere (dinitrogen or argon) using standard Schrenk technique or a VAC glove box. Hexane, toluene and pentane were purified by distillation over Na/K alloys under argon. Anhydrous DMF, THF and starting chemicals were purchased from Aldrich and used without further purification. Bis(n-butylcyclopentadienyl) zirconium dichloride was purchased from Boulder Scientific. Methylaluminoxane (MAO) was purchased as a solution in toluene from Akzo (6.4 wt.% of Al, MMAO type 4). Ethylene was purchased from Matheson as high purity grade, 99.9% and dried by passing through the columns of activated molecular sieves and copper. Column chromatography was done on silica gel 60 from Merk (230–400 mesh). NMR spectra were obtained on a Bruker ARX-300 or Jeol GSX-270 or Jeol GSX-500 spectrometer. IR spectra were recorded on a BIO-RAD FTA-60A instrument. Elemental analyses were carried out on a Perkin-Elmer 2400 CHN micoanalyzer. Gel permeation chromatograms (GPC) were obtained at 140°C in trichlorobenzene using Waters Model 150-C + GPC and the data were analyzed using polystyrene analyzing curve.

3.2. Synthesis of *1b–1d*

To the dispersion of NaH (2.0 g, dispersed in mineral oil as 60 wt.%, 50 mmol) in anhydrous DMF (40 ml) at −20°C was added dropwise 2-ethoxyethanol (4.9 ml, 50 mmol). The mixture was stirred for 2 h at room temperature. To the mixture was added slowly 1,4-dibromobutane (12 ml, 100 mmol) by syringe at −20°C. After stirring overnight, the mixture was poured into a separator funnel containing hexane (150 ml) and water (100 ml). The organic phase was separated and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel with hexane and diethyl ether (v/v, 10/1) to give monosubstituted product (**1b**) as a major product.

1c–1d were prepared from the corresponding dibromide compounds according to the same procedure. Yields were as follows; **1b**, 21%; **1c**, 32%; **1d**, 40%. The spectral data for these compounds are summarized below.

1-Bromo-4-(2-ethoxyethoxy)-butane (**1b**): Anal. Found: C, 42.75; H, 7.79. $C_8H_{17}O_2Br_1$ Calc.: C, 42.68; H, 7.63%. IR (neat): [ν/cm^{-1}] 2928 s, 2861 s, 1114 s. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.57 (s, 4 H), 3.53 (q, $J = 7.0$ Hz, 2 H), 3.50 (t, $J = 6.3$ Hz, 2 H), 3.44 (t, $J = 6.8$ Hz, 2 H), 1.94 (quintet, $J = 7.0$ Hz, 2 H), 1.73 (quintet, $J = 7.0$ Hz, 2 H), 1.21 (t, $J = 7.0$ Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 70.02, 69.98, 69.6, 66.4, 33.4, 29.5, 28.0, 14.9.

1-Bromo-6-(2-ethoxyethoxy)-hexane (**1c**): Anal. Found: C, 47.65; H, 7.99. $C_{10}H_{21}O_2Br_1$ Calc.: C, 47.43; H, 8.38%. IR (neat): [ν/cm^{-1}] 2934 s, 2867 s, 1115 s. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.57 (s, 4 H), 3.53 (q, $J = 7.0$ Hz, 2 H), 3.46 (t, $J = 6.6$ Hz, 2 H), 3.40 (t, $J = 6.8$ Hz, 2 H), 1.86 (quintet, $J = 7.0$ Hz, 2 H), 1.60 (quintet, $J = 7.0$ Hz, 2 H), 1.50–1.30 (m, 4 H), 1.21 (t, $J = 7.0$ Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 71.1, 70.0, 69.7, 66.5, 33.6, 32.6, 29.3, 27.8, 25.4, 15.0.

1-Bromo-8-(2-ethoxyethoxy)-octane (**1d**): Anal. Found: C, 51.59; H, 9.05. $C_{12}H_{25}O_2Br_1$ Calc.: C, 51.24; H, 8.98%. IR (neat): [ν/cm^{-1}] 2933 s, 2864 s, 1113 s. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.57 (s, 4 H), 3.53 (q, $J = 7.0$ Hz, 2 H), 3.45 (t, $J = 6.9$ Hz, 2 H), 3.39 (t, $J = 6.8$ Hz, 2 H), 1.84 (quintet, $J = 7.0$ Hz, 2 H), 1.70–1.50 (m, 2 H), 1.50–1.25 (m, 8H), 1.21 (t, $J = 7.0$ Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 71.4, 70.0, 69.8, 66.5, 33.9, 32.7, 29.4, 29.2, 28.6, 28.0, 25.9, 15.1.

3.3. Synthesis of *2a–d* and *4*

To the solution of tosylated compound **1a** (7.04 g, 24.4 mmol, prepared from the alcohol and p-TsCl [21]) in THF (50 ml) was added dropwise the NaCp solution in THF (15 ml, 2.0 M, 30 mmol) at −20°C. The mixture was stirred for 5 h. The reaction mixture was poured into a separator funnel containing hexane (15 ml) and water (150 ml). The organic phase was separated and dried over anhydrous $MgSO_4$. After the solvent was removed, the residue was chromatographed on silica gel with hexane and diethyl ether (v/v, 5/1) to give the product (**2a**).

2b–2d were prepared from the corresponding bromide according to the same procedure. **4** was prepared according to the literature methods [22]. The cyclopentadiene compounds were always mixture of inseparable isomers. Yields were as follows; **2a**, 70%, **2b**, 69%; **2c**, 61%; **2d**, 71%. The ^{1}H NMR spectral data for these compounds are summarized below.

Compound **2a**: ^{1}H NMR (270 MHz, $CDCl_3$): δ 6.50–6.00 (m, 3 H), 3.75–3.40 (m, 8 H), 2.95 (s, 1 H), 2.92 (s, 1 H), 2.80–2.60 (m, 2 H), 1.21 (t, $J = 7.0$ Hz, 3 H).

Compound **2b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.45–5.95 (m, 3 H), 3.57 (s, 4 H), 3.60–3.40 (m, 4 H), 2.94 (s, 1 H), 2.87 (s, 1 H), 2.45–2.25 (m, 2 H), 1.70–1.50 (m, 4 H), 1.21 (t, $J = 7.0$ Hz, 3 H).

Compound **2c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.45–5.95 (m, 3 H), 3.58 (s, 4 H), 3.56 (q, $J = 7.0$ Hz, 2 H), 3.46 (t, $J = 6.8$ Hz, 2 H), 2.93 (s, 1 H), 2.86 (s, 1 H), 2.45–2.25 (m, 2 H), 1.70–1.45 (m, 4 H), 1.45–1.25 (m, 4 H), 1.20 (t, $J = 7.0$ Hz, 3 H).

Compound **2d**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.45–5.95 (m, 3H), 3.57 (s, 4 H), 3.53 (q, $J = 7.0$ Hz, 2 H), 3.45 (t, $J = 6.8$, 2 H), 2.94 (s, 1 H), 2.87 (s, 1 H), 2.40–2.25 (m, 2 H), 1.60–1.40 (m, 4 H), 1.40–1.20 (m, 8 H), 1.21 (t, $J = 7.0$ Hz, 3 H).

3.4. Synthesis of *3a–d* and *5*

To **2a** (2.86 g, 17.0 mmol) in THF (25 ml) was added *n*-BuLi (6.8 ml, 17 mmol, 2.5 M in hexane) at −78°C. The mixture was slowly warmed to room temperature and stirred overnight. The THF solution was transferred by cannula to the slurry of $ZrCl_4(THF)_2$ [23] in toluene (50 ml) at room temperature. After the mixture was stirred for 3 days at 55°C, all volatiles were removed under vacuum. The product was extracted by hot pentane (200 ml). The hot pentane solution was filtered and stored in refrigerator (−30°C) for a week. The crude product was not purified by recrystallization because it was deposited as oil.

3b–3d and **5** were prepared from the corresponding cyclopentadiene compounds according to the same procedure. After several repeated recrystallizations in pentane, the analytically pure compounds were obtained. **3b–3d** were oily at room temperature. The synthetic yields were as follows; **3a**, about 35%; **3b**, 45%; **3c**, 65%; **3d**, 55%; **5**, 51%. The spectral data for these compounds are summarized below.

Compound **3a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.33 (s, 4 H), 3.67 (t, $J = 6.4$ Hz, 2 H), 3.60–3.55 (m, 4 H), 3.52 (q, $J = 7.0$ Hz, 2 H), 2.92 (t, $J = 6.4$ Hz, 2 H), 1.22 (t, $J = 7.0$ Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.4, 117.3, 112.7, 71.6, 71.0, 69.7, 66.5, 30.3, 15.1.

Compound **3b**: Anal. Found: C, 54.10; H, 7.50. $C_{26}H_{42}O_4Cl_2Zr_1$ Calc.: C, 53.77; H, 7.30%. IR (neat): [ν/cm^{-1}] 3096 s, 2933 s, 2855 s, 1110 s, 816 s. ^{1}H NMR (270 MHz, $CDCl_3$): δ 6.28 (t, $J = 2.7$ Hz, 2 H), 6.20 (t, $J = 2.7$ Hz, 2 H), 3.57 (s, 4 H), 3.52 (q, $J = 7.0$ Hz, 2 H), 3.47 (brs, 2 H), 2.62 (brs, 2 H), 1.70–1.55 (m, 4 H), 1.21 (t, $J = 7.0$ Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.6, 116.6, 112.1, 70.9, 70.1, 69.7, 66.5, 29.8, 29.1, 27.1, 15.1.

Compound **3c**: Anal. Found: C, 56.33; H, 7.59. $C_{30}H_{50}O_4Cl_2Zr_1$ Calc.: C, 56.57; H, 7.93%. IR (neat): [ν/cm^{-1}] 3096 s, 2935 s, 2865 s, 1107 s, 810 s. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.28 (t, $J = 2.7$ Hz, 2 H), 6.19 (t, $J = 2.7$ Hz, 2 H), 3.57 (s, 4 H), 3.53 (q, $J = 7.0$ Hz, 2 H), 3.45 (t, $J = 6.8$ Hz, 2 H), 2.61 (t, $J = 7.7$ Hz, 2 H), 1.65–1.45 (m, 4 H), 1.45–1.25 (m, 4 H), 1.21 (t, $J = 7.0$ Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.9, 116.5, 112.2, 71.2, 70.0, 69.7, 66.5, 30.5, 30.0, 29.4, 29.0, 25.7, 15.1.

Compound **3d**: Anal. Found: C, 58.60; H, 8.20. $C_{34}H_{58}O_4Cl_2Zr_1$ Calc.: C, 58.93; H, 8.45%. IR (neat): [ν/cm^{-1}] 3095 s, 2929 s, 2857 s, 1116 s, 815 s. ^{1}H NMR (270 MHz, $CDCl_3$): δ 6.28 (t, $J = 2.7$ Hz, 2 H), 6.19 (t, $J = 2.7$ Hz, 2 H), 3.57 (s, 4 H), 3.53 (q, $J = 7.0$ Hz, 2 H), 3.45 (t, $J = 6.8$ Hz, 2 H), 2.61 (t, $J = 7.7$ Hz, 2 H), 1.65–1.40 (m, 4 H), 1.40–1.20 (m, 8 H), 1.21 (t, $J = 7.0$ Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.9, 116.4, 112.2, 71.3, 69.9, 69.7, 66.4, 30.4, 30.0, 29.4, 29.16, 29.09, 29.05, 25.9, 15.0.

Compound **5**: M.p. 84–85°C. Anal. Found: C, 49.89; H, 6.12. $C_{18}H_{26}O_2Cl_2Zr_1$ Calc.: C, 49.52; H, 6.02%. IR (KBr): [ν/cm^{-1}] 3098 s, 2973 s, 2870 s, 1097 s, 829 s. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.32 (brs, 4 H), 3.62 (t, $J = 6.4$ Hz, 2 H), 3.49 (q, $J = 7.0$ H, 2 H), 2.91 (t, $J = 6.4$ Hz, 2 H), 1.19 (t, $J = 7.0$ Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 131.5, 117.4, 112.5, 70.1, 66.1, 30.6, 15.2.

3.5. Ethylene polymerization

To a 500-ml glass reactor dried by evacuation at 80°C for 1 h was successively added hexane (200 ml), MAO (1.2 ml, 2.5 mmol Al, 6.4 wt.% in toluene) and zirconocene compound (0.5 μmol) which had been diluted in hexane before. The reactor was immersed into oil bath (80°C) and stood for 5 min. Stirring was started and ethylene was fed continuously under the pressure of 40 psig for 15 min. The reaction was stopped by addition of MeOH. Concentrated HCl was added, and the suspension was stirred overnight. After filtration, the polymer was dried under vacuum at 80°C. The molecular weight distribution was measured by GPC on linear columns composed of Styrageal HT2 (100–10,000), HT4 (5000–600,000), HT6E (5000–10^7) and HMW7 (500,000–10^8) at 140°C with 1,2,4-trichlorobenzene.

The yields and molecular weights and molecular weight distributions (M_w/M_n) of the polymers were in Table 1.

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