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Ethylene homopolymerization and ethylene/1-hexene copolymerization catalysed by mixed salicylaldiminato cyclopentadienyl zirconium complexes

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1. Introduction

Since the discovery of the metallocene–methylaluminoxane (MAO) catalytic system in the middle of 1970's [1], the group 4 metallocene catalysts have attracted considerable attention due to their high catalytic activities for olefin polymerizations [2,3]. Changes in the ligand skeleton of catalysts provided an access to obtain more novel polymeric materials. It means that the microstructure and physical characters of polyolefins can be controlled by modification of the ligand substituents of metallocene, so it is possible to get tailor-made polymers [4].

With the rapid development of metallocene catalysts, a good many of non-metallocene complexes [5,6] have been synthesized to avoid the growing patent minefield in group 4 cyclopentadienyl structures. Group 4 metal complexes with bidentate N,O [7,8], N,N [9,10] chelate ligands behave as a versatile class of olefin polymerization catalysts, capable of producing new polyolefin architectures [11]. Since Grubbs synthesized the first salicylaldiminato nickel complex [12], phenoxyimine ligand complexes including bis(salicylaldiminato) complexes [13,14], momo(salicylaldiminato) complexes [15,16] and binuclear salicylaldiminato complexes [17] and so on have been widely investigated. Especially bis(salicylaldiminato) complexes of group 4 metal have attracted more attention for efficient ethylene polymerization catalytic activities [18,19], as well as their excellent copolymerization ability of ethylene with α -olefin [20–23].

ABSTRACT

Three new mixed salicylaldiminato cyclopentadienyl zirconium complexes Cp'[2-Bu^t-6-(C₆H₁₁NCH) C₆H₃O]ZrCl₂ (Cp' = ⁿBuC₅H₄ (**3a**), ^tBuC₅H₄ (**3b**) and Me₄C₅H (**3c**)) were prepared and the structure of complex **3c** was confirmed by X-ray diffraction analysis. All of the three complexes showed high activities for ethylene homopolymerization with the activation of methylaluminoxane, and **3a** showed the highest activity up to 1.15×10^6 g PE/mol Zr h for ethylene homopolymerization at 70 °C. The ¹³C NMR spectrum showed that the obtained polymer is linear polyethylene. Complexes **3a–c** also catalysed ethylene/1-hexene copolymerization with high activities from 6.29×10^5 to 12.3×10^5 g Copolymer/mol Zr h and with 0.89–1.39% 1-hexene incorporation level. In addition, the influence of the substituted alkyl on Cp on the catalytic behavior of corresponding zirconium complexes was discussed.

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Considering the different catalytic behavior of metallocenes and salicylaldiminato complexes, several mixed salicylaldiminato cyclopentadienyl complexes of group 4 metal [24] were prepared and expected to exhibit the characters of both cyclopentadienyl ligand and chelating salicylaldiminato ligand. Lancaster and his coworkers concentrated on complexes with mixed cyclopentadienyl and various salicylaldiminato ligands, which showed satisfactory activities in ethylene polymerization. In order to investigate the influence of the different bulky alkyl groups on cyclopentadienyl on the catalytic behavior of resultant metal complexes, we synthesized three new mixed alkyl-substituted cyclopentadienyl salicylaldiminato zirconium complexes **3a-c** (Scheme 1). Their catalytic behavior for homopolymerization of ethylene and copolymerization of ethylene/1-hexene was further investigated and compared with that of the analogous zirconium complex with unsubstituted cyclopentadienyl ligand, Cp[2-Bu^t-6-(C₆H₁₁NCH)C₆H₃O]ZrCl₂ (**3d**) [24].

2. Experimental

2.1. General procedures

All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques unless otherwise indicated. Toluene, diethyl ether (Et_2O) and tetrahydrofuran (THF) were refluxed over sodium benzophenone. Dichloromethane (CH_2Cl_2) was refluxed over CaH_2 . Chloroform-*d* and 1-hexene were dried over calcium hydride under argon and stored in the presence of activated 4 Å molecular sieves. *n*-BuLi (2.5 M in *n*-hexane) were





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Scheme 1. Synthetic route of complexes 3a-c.

purchased from Chemetall GmbH. The co-catalyst methylaluminoxane (MAO, 1.53 M in toluene) was purchased from Witco GmbH. Polymer grade ethylene was directly used for polymerization. Phenoxyimine **1** [24,25], Cp'SiMe₃ (Cp' = n BuC₅H₄, t BuC₅H₄ and Me₄C₅H) [26,27] were synthesized according to the published procedures.

¹H NMR spectra were recorded on Bruker ADVANCE-500 spectrometers with CDCl₃ as solvent. Chemical shifts for ¹H NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane (TMS). Elemental analyses were carried out on an EA-1106 type analyzer. ¹³C NMR spectra of polymers were recorded on a Bruker ADVANCE-500 spectrometer with 1,2-dichlorobenzene-*d* at 100 °C. Intrinsic viscosity was determined in decahydronaphthalene at 135 °C and viscosity average molecular weights of PEs were calculated according to the equation [28]:

$$[\eta] (dL/g) = 6.77 \times 10^{-4} M_{\rm p}^{0.67}$$

The gel permeation chromatography (GPC) performed on a Waters 150 ALC/GPC system in a 1,2-dichlorobenzene solution at 135 °C was used to determine the weight-average molecular weights (M_w) and the molecular weight distribution (M_w/M_n) of the polymer.

2.2. Synthesis

2.2.1. $(Me_4C_5H)ZrCl_3 \cdot DME$ (**2c**)

These complexes were prepared by the procedure according to the method of CpZrCl₃·DME reported by Lund and Livinghouse [29]. A typical route was given for **2c**. To a suspension of ZrCl₄ (1.84 g, 7.88 mmol) in 50 mL of CH₂Cl₂ was added Me₂S (1.5 mL, 20.4 mmol) at 0 °C. Then the mixture was warmed to room temperature and stirred for 2 h. Filtrating the solution of ZrCl₄·2Me₂S, (Me₄C₅H)SiMe₃ [26] (1.53 g, 7.88 mmol) was added dropwise to the filtrate and the mixture was stirred overnight. DME (30 mL) was added and stirred for 2 h, the solvent was then removed in vacuo. The resulted yellow solid was recrystallized with DME to afford **2c** as a yellow crystal (1.97 g, 61.1% yield). ¹H NMR (500 MHz, 298 K, CDCl₃): δ 5.63 (s, 1H, Me₄C₅H), 4.02 (s, 4H, OCH₂CH₂O), 3.77 (s, 6H, CH₃O), 2.16 (s, 6H, (CH₃)₄Cp), 2.07 (s, 6H, (CH₃)₄Cp).

2.2.2. $(^{n}BuC_{5}H_{4})ZrCl_{3} \cdot DME$ (**2a**)

Following the above procedure, **2a** was isolated as a colorless crystal in 74.0% yield. ¹H NMR (500 MHz, 298 K, CDCl₃): δ 6.51 (s, 2H, ^{*n*}BuC₅H₄), 6.42 (s, 2H, ^{*n*}BuC₅H₄), 4.11 (s, 4H, OCH₂CH₂O), 3.89 (s, 6H, CH₃O), 2.84 (t, 2H, *J* = 7.7, CH₂Cp), 1.60 (m, 2H, CH₂CH₂Cp), 1.37 (m, 2H, CH₃CH₂), 0.93 (t, 3H, *J* = 7.7, CH₃CH₂).

2.2.3. (${}^{t}BuC_{5}H_{4}$)ZrCl₃·DME (**2b**)

Following the above procedure, **2b** was isolated as a colorless crystal in 45.7% yield. ¹H NMR (500 MHz, 298 K, CDCl₃): δ 6.56 (s, 2H, ^tBuC₅H₄), 6.49 (s, 2H, ^tBuC₅H₄), 3.97 (s, 4H, OCH₂CH₂O), 3.76 (s, 6H, CH₃O), 1.41 (s, 9H, ^tBuCp).

2.2.4. $[{}^{n}BuC_{5}H_{4}][2-Bu^{t}-6-(C_{6}H_{11}NCH)C_{6}H_{3}O]ZrCl_{2}$ (3a)

The lithium salt of **1** was prepared by the dropwise addition of 2.5 M butyllithium (1.10 mL, 2.75 mmol) to a solution of 1 (0.71 g, 2.74 mmol) in THF (50 mL) at -78 °C for 30 min. Then the solution of **1Li** was added to a mixture of $({}^{n}BuC_{5}H_{4})ZrCl_{3}$ ·DME (1.12 g, 2.74 mmol) and THF (20 mL) at -78 °C. The yellow solution was allowed to stir at this temperature and then at room temperature overnight. After removing the solvent under reduced pressure, the remainder was recrystallized with CH₂Cl₂ and light petroleum at -10 °C. Complex 3a was obtained as a yellow crystal (0.54 g, 36.9% yield). ¹H NMR (500 MHz, 298 K, CDCl₃): δ 8.46 (s, 1H, HC=N), 7.54 (dd, 1H, J = 7.7, 1.6 Hz, Ar), 7.27 (dd, 1H, J = 7.7, 1.6 Hz, Ar), 6.94 (t, 1H, J = 7.7 Hz, Ar), 6.38–6.23 (br, 4H, C₅H₄), 4.38 (m, 1H, N-CH), 2.78 (m, 2H, CH₂C₅H₄), 2.30-1.26 (br, 10H, cyclohexyl CH₂), 1.55 (m, 2H, -CH₂CH₂C₅H₄), 1.44 (s, 9H, ^tBu), 1.31 (m, 2H, CH₃CH₂), 0.89 (t, 3H, CH₃CH₂). Anal. Calc. for C₂₆H₃₇Cl₂NOZr: C, 57.65; H, 6.88; N, 2.59. Found: C, 57.03; H, 7.33; N, 2.05%.

2.2.5. $[{}^{t}BuC_{5}H_{4}]/2-Bu^{t}-6-(C_{6}H_{11}NCH)C_{6}H_{3}O/2rCl_{2}$ (**3b**)

Following the procedure described for **3a**, **1** (1.03 g, 3.97 mmol), 2.5 M butyllithium (1.59 mL, 3.98 mmol), and (${}^{t}BuC_{5}H_{4}$)ZrCl₃·DME (1.63 g, 3.98 mmol) gave **3b** as a brown crystal (1.10 g, 51.2% yield). ¹H NMR (500 MHz, 298 K, CDCl₃): δ 8.49 (s, 1H, *HC*=N), 7.55 (dd, 1H, *J* = 7.7, 1.7 Hz, *Ar*), 7.28 (dd, 1H, *J* = 7.7, 1.7 Hz, *Ar*), 6.96 (t, 1H, *J* = 7.7 Hz, *Ar*), 6.82–5.88 (br, 4H, C₅H₄), 4.21 (m, 1H, N–CH), 2.28–1.23 (br, 10H, cyclohexyl CH₂), 1.47 (s, 9H, ${}^{t}BuC_{5}H_{4}$), 1.44 (s, 9H, ${}^{t}BuPh$). *Anal.* Calc. for C₂₆H₃₇Cl₂NOZr: C, 57.65; H, 6.88; N, 2.59. Found: C, 57.47; H, 6.87; N, 2.38%.

2.2.6. $[Me_4C_5H][2-Bu^t-6-(C_6H_{11}NCH)C_6H_3O]ZrCl_2$ (**3***c*)

Following the procedure described for **3a**, **1** (1.15 g, 4.43 mmol), 2.5 M butyllithium (1.78 mL, 4.45 mmol), and (Me₄C₅H)ZrCl₃·DME (1.82 g, 4.45 mmol) gave **3c** as a yellow crystal (1.6 g, 66.7% yield). ¹H NMR (500 MHz, 298 K, CDCl₃): δ 8.50 (s, 1H, HC=N), 7.53 (dd, 1H, *J* = 7.7, 1.7 Hz, *Ar*), 7.26 (dd, 1H, *J* = 7.7, 1.7 Hz, *Ar*), 6.93 (t, 1H, *J* = 7.7 Hz, *Ar*), 5.83 (s, 1H, Me₄C₅H), 4.01 (m, 1H, N–CH), 2.36–1.16 (br, 10H, cyclohexyl CH₂), 2.33 (s, 3H, CH₃C₅H), 2.29 (s, 3H, CH₃C₅H), 2.22 (s, 3H, CH₃C₅H), 1.65 (s, 3H, CH₃C₅H), 1.45 (s, 9H, ^{*i*}Bu). Anal. Calc. for C₂₆H₃₇Cl₂NOZr: C, 57.65; H, 6.88; N, 2.59. Found: C, 57.45; H, 6.71; N, 2.38%.

2.3. X-ray diffraction measurements

Single crystal of complex **3c** suitable for X-ray diffraction measurement was obtained by slowly cooling a saturated dichloromethane and light petroleum solution to -10 °C. The crystallographic data for complex **3c** was collected on a Bruker AXSD8 diffractometer with graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. All data were collected at 20 °C using the ω -scan techniques. The structure of **3c** was solved by direct method and refined using Fourier techniques. An absorption correction based on sADABS was applied [30]. All non-hydrogen atoms were refined by full-matrix least-squares on F^2 using the SHELXTL program package [31]. Hydrogen atoms were located and refined by the geometry method. The cell refinement, data collection, and reduction were done by Bruker SAINT [32]. The structure determination and refinement were performed by SHELXS-97 [33] and SHELXL-97 [34], respectively. The crystal and refinement data are collected in Tables 1 and 2.

2.4. Polymerization procedure

2.4.1. Ethylene polymerization

A 100 mL autoclave, equipped with a magnetic stirrer, was heated at 100 °C under vacuum for 30 min and then cooled to the desired temperature by immerging it into a thermostatically heated bath, then filled with ethylene. Proper amount of MAO solution and toluene were added to the autoclave and the mixture was saturated with ethylene for 15 min at the desired temperature. After that proper amount of toluene solution of zirconium complex was injected to the autoclave and the reactor was pressurized with ethylene to reach the required value to start the polymerization. The ethylene pressure was kept constant during the polymerization. The reaction mixture was stirred vigorously for a certain time and the ethylene pressure in the autoclave was slowly vented. Then the reaction was quenched with 3% HCl in ethanol (50 mL). The contents of the reactor were transferred to a beaker and then filtrated. The collected polymer was washed to neutral with ethanol and then dried overnight in a vacuum oven at 60 °C to constant weight.

2.4.2. Ethylene/1-hexene copolymerization

A 100 mL autoclave, equipped with a magnetic stirrer, was heated at 100 °C under vacuum for 30 min and then cooled to the desired temperature by immerging into a thermostatically heated bath, then filled with ethylene. Proper amount of MAO solution, 1-hexene and toluene were added to the autoclave and the mixture was saturated with ethylene for 15 min at the desired temperature. After that proper amount of toluene solution of zirconium complex was injected to the autoclave and the reactor was pressurized with ethylene to reach the required value to start the

Table 1

Crystal data and structure refinement details for 3c.

	3c
Empirical formula	C ₂₆ H ₃₇ Cl ₂ NOZr
Formula weight	541.69
T (K)	293(2)
Wavelength (Å)	0.71073
Crystal size (mm ³)	$0.429 \times 0.347 \times 0.301$
Crystal system	monoclinic
Space group	C2/c
a (Å)	25.305(4)
b (Å)	13.9834(19)
c (Å)	16.282(2)
α (°)	90.00
β(°)	110.381(2)
γ (°)	90.00
Volume (Å ³)	5400.7(13)
Ζ	8
Calculated density (Mg/m ³)	1.332
Absorption coefficient (mm ⁻¹)	0.662
F (0 0 0)	2256
θ Range for data collection (°)	1.74-27.00
Limiting indices	$-32 \leqslant h \leqslant 22, -15 \leqslant k \leqslant 17, -20 \leqslant l \leqslant 20$
Reflections collected/unique	15 678/5887 [<i>R</i> _{int} = 0.0915]
Maximum and minimum transmission	1.00000 and 0.75145
Data/restrains/parameters	5887/0/287
Goodness-of-fit (GOF) on F^2	0.934
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0403, wR_2 = 0.0977$
R indices (all data)	$R_1 = 0.0511$, $wR_2 = 0.1009$
Largest difference in peak/hole ($e Å^{-3}$)	1.190 and -0.642

Table 2

Selected structural parameters for complex 3c.

Distances (Å)			
Zr-C(18)	2.464(3)	Zr-O(1)	1.9908
Zr-C(19)	2.553(3)	Zr-Cl(1)	2.4332
Zr-C(20)	2.555(3)	Zr-Cl(2)	2.4713
Zr-C(21)	2.507(3)	C(1)-N(1)	1.284(3)
Zr-C(22)	2.470(3)	C(8)-N(1)	1.499(3)
Zr-N(1)	2.348(2)	C(7)-O(1)	1.339(3)
Angles (°)			
O(1)-Zr-N(1)	76.84(7)	N(1)-Zr-C(18)	75.86(9)
Cl(1)-Zr-Cl(2)	87.06(3)	Cl(1)-Zr-C(18)	107.73(7)
O(1)-Zr-C(18)	112.06(9)	Cl(2)-Zr-C(19)	112.97(8)
C(7)–O(1)–Zr	146.41(15)	C(8)-N(1)-Zr	118.60(16)

polymerization. The ethylene pressure was kept constant during the polymerization. The reaction mixture was stirred vigorously for a certain time and the ethylene pressure in the autoclave was slowly vented. Then the reaction was quenched with 3% HCl in ethanol (50 mL). The collected polymer was washed to neutral with ethanol and then dried overnight in a vacuum oven at 60 °C to constant weight.

3. Results and discussion

3.1. Synthesis of the complexes **3a-c**

Three new complexes **3a–c** were prepared via the route described in Scheme 1. Salicylaldehyde derivative [25] and substituted half-metallocenes (Cp'ZrCl₃·DME, **2a–c**) [29] were prepared according to established procedures. The salicylaldimine **1** [24,25] was obtained as a yellow solid by the reaction of cyclohexylamine with the salicylaldehyde derivative and recrystallized by ethanol. The desired mono(salicylaldiminato) cyclopentadienyl zirconium complexes **3a–c** were synthesized by the reaction of the lithium salt of the salicylaldimine **1** with one equivalent of the corresponding Cp'ZrCl₃·DME in moderate yields (37–67%). All the new complexes were characterized by ¹H NMR spectroscopy and elemental analysis.

Additionally, the complex $Cp[2-Bu^t-6-(C_6H_{11}NCH)C_6H_3O]ZrCl_2$ (**3d**) was prepared to compare with complexes **3a–c**.

In the ¹H NMR spectra of **3a–c**, the chemical shift of =N–CH protons is observed at 4.01-4.24 ppm which is different from 3.23 ppm of ligand 1, denoting coordinative affect of N-Zr. The imino protons of complexes **3a–c** appearing at δ 8.43–8.50 ppm while the free imino proton at 8.37 ppm also indicates that the nitrogen atom is coordinated to the metal center. The chemical shift of imino protons have a tendency with **3a** < **3b** < **3c**, suggesting strong deshielding effect with increase of steric bulkiness of Cp' group. The chemical shifts of Cp protons of Cp'[2-Bu^t-6- $(C_6H_{11}NCH)C_6H_3O]ZrCl_2$ (**3a–c**) are also different from corresponding half-metallocene complexes Cp'ZrCl₃·DME (**2a-c**). In complex 3a with less bulky Cp moiety, the chemical shifts of Cp protons move from 6.51 to 6.42 ppm of **2a** to upfield. The same tendency is observed for the unsubstituted complex 3d. In contrast, the chemical shift of Cp proton in complex 3c moves from 5.63 ppm of **2c** to downfield.

3.2. X-ray diffraction of complex 3c

The structure of complex **3c** has been confirmed by single crystal X-ray diffraction (Fig. 1).

The crystal data for complex **3c** is collected in Table 1. Selected structural parameters are given in Table 2. In **3c**, the zirconium atom is five-coordinate with the Cp ligand in the apical site of a distorted square–pyramid. Similar to the titanium complex $[Cp\{2-Bu^t-6-(2,4,6-Me_3C_6H_2NCH)C_6H_3O\}TiCl_2]$ [24], the N,O – che-



Fig. 1. ORTEP diagram of the molecular structure of [Me₄C₅H][2-Bu^t-6-(C₆H₁₁NCH)C₆H₃O]ZrCl₂ (**3c**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

lating moiety which includes the -C=N group lies in the same plane with the phenyl ring and two of the atoms of the *tert*-butyl group (C(14) and C(16)), while the Cp ring is almost parallel with the phenoxide ring. The two torsion angles of Zr-N(1)-C(8)-C(9) and Zr-N(1)-C(8)-C(13) with values of -105.2(2) and 129.4(2), denote that there is steric repulsion between the cyclohexyl group and the Cp plane.

The Zr–O(1) length of 1.9908(18) which is shorter than the single Zr–O bond (2.244 Å) [35] indicate a partial double bond character due to oxygen π -donation [36]. The Zr–N(1) bond distance (2.348(2) Å) is slightly longer than that observed for (bis[N-(3-tert-butylsalicylidene)] cyclohexylaminato zirconium(IV) dichloride (2.309(6) Å) [37], which indicates less donating ability of imino nitrogen atom to the metal center. The Cl(1)–Zr–Cl(2) angle of 87.06(3)° is not only smaller than bis(phenoxyimine) zirconium complex (99.8(2)°) [37] but also smaller than the analogous mixed salicylaldiminato pentamethyl cyclopentadienyl zirconium complex (88.04(4)°) [38], which may be due to a strong steric repulsion between the Cl ligand and the salicyladimine.

3.3. Polymerization studies

3.3.1. Ethylene homopolymerizations

The zirconium complexes **3a–c** are effective for the polymerization of ethylene but not for propylene under different reaction conditions upon activation with MAO. All polymerization runs of ethylene were carried out in toluene and each with 2.5 μ mol amount of metal catalyst. The polymerizations by $Cp[2-Bu^t-6-(C_6H_{11}NCH)C_6H_3O]ZrCl_2$ (**3d**) under identical conditions were applied for comparison. The polymerization results are listed in Table 3.

It was shown that the Al/Zr ratio from 200 to 2000 was effective for the ethylene polymerization and a constant loading of 1000 equivalents MAO was employed for most of the polymerization runs.

In order to investigate the influence of polymerization time on catalytic activity, ethylene was polymerized for 5, 15 and 30 min by using **3a** as catalyst. Although the catalytic activities of bis[N-(3-t-butylsalicylidene)-anilinato] zirconium(IV) dichloride [8] slightly decreased from 15 to 30 min, the activities of complex **3a** slightly increase with the increase of polymerization time from 15 (Run 2) to 30 min (Run 3), and a 0.5 times increase of the viscosity average molecular weights (M_{η}) can also be observed clearly. These facts indicate that the active species of complex **3a** can steady exist for relative long time at this temperature.

The effect of polymerization temperature on catalytic activity is summarized in Fig. 2. It is clear that the catalytic activities increase in the order of 3b < 3c < 3d < 3a within the temperature range of 70–90 °C. Only the complex 3a exhibits higher catalytic activity than the unsubstituted Cp complex 3d. On the contrary, the complexes 3b and 3c show lower activities. Generally electron-donating ligands weaken the bonds between the metal center and other ligands, which induce a better catalytic reactivity of the complex. Besides electronic factors, steric factors also play an impor-

Table 3	
The polymerization of ethylene with 3a-d /MAO systems. ^a	

Run	Cat.	Al/Zr	Time (min)	Yield (g)	Act. (Kg PE/mol Zr h)	$M_{\eta}^{b}(\times 10^{3})$	$M_{\rm w}^{\rm c}$ (×10 ³)	$M_{\rm w}/M_{\rm n}^{\rm c}$
1	3a	1000	5	0.163	782	246		
2	3a	1000	15	0.379	606	436	287/3.7 ^d	2.34/1.97
3	3a	1000	30	0.784	627	684		
4	3b	1000	15	0.410	656	690	327	3.68
5	3c	200	15	0.223	357	612		
6	3c	1000	15	0.608	973	503	334	3.10
7	3c	2000	15	0.504	806	447		
8	3d	1000	15	0.399	638	458	195	5.93

^a All polymerization runs were performed in toluene with total volume of 25 mL over 15 min at 50 °C, 10 bar ethylene pressure and 2.5 µmol catalyst.

^b Intrinsic viscosity was determined in decahydronaphthalene at 135 °C and viscosity average molecular weight was calculated using the relation: $[\eta] = 6.77 \times 10^{-4} M_{\eta}^{0.67}$.

^d The GPC trace has double distributions.



Fig. 2. Influence of polymerization temperature on activity. (Polymerization conditions: $[Zr] = 1.0 \times 10^{-4} \text{ mol/L}$, Al/Zr = 1000, 15 min, ethylene (10 bar), 25 mL of toluene.)

tant role in final catalytic behavior. Therefore for complexes 3a-c, the introduction of bulkier substituents decreases the reactivity, obviously the bulky groups on Cp is not favor for the coordination of C=C bond of the monomer to metal center.

At 70 °C, the complex **3a** displays the highest catalytic activity $(1.15 \times 10^6 \text{ g PE/mol Zr h})$ among the investigated complexes. Comparably, complexes **3b** and **3c** show the maximal activities at 50 °C. These results indicate that suitable donor substituent such as small steric bulky alkyl is benefit to increase the catalytic activity and stability of active species at higher temperature. These results are similar to other mixed salicylaldiminato cyclopentadienyl complexes of group 4 metals [24], as Lancaster reported that zirconium complex $(C_5H_5)[3-Bu^t-2-(0)C_6H_3CH=N(C_6F_5)]ZrCl_2$ was stable at 60 °C. Furthermore, when compared with Liu's report [39] that bis(salicylaldiminato) zirconium complex, [3-Bu^t-2- $(O)C_6H_3CH=N(C_6H_{11})]_2ZrCl_2$, showed the highest activities at the temperature of 30 °C, these mixed salicylaldiminato cyclopentadienyl complexes exhibit more thermal stability.

The GPC data are obtained for different complexes (Table 3) and the traces have broad distributions. It is found that the complexes with alkyl substituent on Cp ring give higher molecular weight polyethylenes with narrower distributions than the complex **3d** with unsubstituted Cp ($M_w = 1.95 \times 10^5$ and $M_w/M_n = 5.93$, Run 8). The results are similar to other mono(salicylaldiminato) catalysts, for example, complex [3-Bu^t-2-(O)C₆H₃CH=N(C₆F₅)]ZrCl₃ (THF) [35] afforded polyethylenes with molecular distributions M_w/M_n from 2.8 to 4.6 at -20 to 60 °C. Scott reported that bis(salicylaldiminato) titanium catalysts may form different catalytically active species through inter- or intra-molecular alkylization reaction of the ligand imine moiety [40]. Similar by-reactions are conceivable for these mixed-ligand complexes, and in comparison with the complexes **3a**–**c** the unsubstituted Cp complex **3d** is obviously easier to get multiple catalytic active species though such byreactions due to its less steric hindrance.

Considering that the signal of unsaturated carbon is not found in the ¹³C NMR spectra, it seems reasonable that the polymer chains are terminated by chain migration to MAO, which is further supported by the results that increasing Al/Zr molar ratio leads to the fall of molecular weight (Table 3, Runs 5–7). According to ¹³C NMR analyses, the polyethylene produced with complexes **3a–d** can be divided into two types. One is highly linear polyethylene produced with unsubstituted Cp complex **3d** and *tert*-butyl substituted Cp complex **3b**, and the other type is also linear polyethylene but with isopropyl end group produced with *n*-butyl substituted Cp complex **3a** and tetramethyl substituted Cp complex **3c**.

Fig. 3 shows the ¹³C NMR spectrum of polyethylene obtained with complex **3c**, similar spectrum is obtained for complex **3a**. In Fig. 3, the chemical shifts at 14.06, 22.86, 32.16 ppm are assigned as the terminated propyl group of linear polyethylene as suggested by Wilhelm [41]. However, none of open-literatures gave explanation on the chemical shifts at 23.03 and 36.97 ppm [42–45]. Thereby, we use the program of CALMOD reported by Cheng and Bennett [46] to calculate the chemical shifts at 23.03, 29.30 and 36.97 ppm, which prove to more likely belong to the terminal iso-butyl group (Table 4). Therefore, the ¹³C NMR spectroscopic analyses indicate that these polymers are linear polyethylenes partially end-capped with isopropyl group. The work on the possible mechanism of forming isopropyl end is still in progress.

3.3.2. Ethylene/1-hexene copolymerizations

All of the complexes **3a–c** can catalyze the copolymerization of ethylene/1-hexene and the results are illustrated in Fig. 4. The catalytic activities are closely dependant on the employed catalyst and the 1-hexene feeds. The tetramethyl substituted Cp complex **3c** showed the highest catalytic activity.

The introduction of the 1-hexene affects the catalytic activities of complexes **3a–c** in different ways. Although the 1-hexene possesses stronger electron-donating ability than ethylene which conduces to the coordination of 1-hexene to the active species and stabilizes the cationic active species, the insertion rate of 1-hexene is always slower than that of ethylene as the steric hindrance increases [47]. The final results of the copolymerization are also related to the structure of the catalysts. Complexes **3a** and **3c** show increased activities with the increase of 1-hexene feeds. On the other hand, complex **3b** displays decreased activity with the increase of 1-hexene feeds, probably the steric factors play a more important role when compared to the electronic factors caused by 1-hexene insertion into the propagation chain. In comparison with complexes **3a–c**, complex **3d** reaches the highest activity at 1-hexene feed of 1 mL and then a declined tendency is displayed,



Fig. 3. ¹³C NMR spectrum of the polyethylene obtained with 3c as catalyst (Run 6).

Table 4

¹³C NMR chemical shift assignments for the polyethylene end group.

Terminal of linear PE		C ₁	C ₂	C ₃	C ₄	C ₅	C ₆
$C_1 - C_2 (C) - C_3 - C_4 - C_5 - C_6 - PE$	calculated value observed value	22.90 23.03	28.36 29.30	39.62 36.97	27.03	30.34 30.32	30.04 30.00
$C_1 - C_2 - C_3 - C_4 - C_5 - C_6 - PE$	calculated value observed value	14.05 14.06	22.55 22.86	32.05 32.16	29.59 29.56	29.94	29.99 30.00

which however is a general phenomenon in the copolymerization of ethylene and 1-hexene [47].

In Table 5, the copolymerization activities increase in the order of **3b** < **3d** < **3c**. The catalytic activities of *n*-butyl Cp complex **3a** and tetramethyl Cp complex **3c** are 27–38% higher than that of the unsubstituent complex **3d** with the 1-hexene feeds of 2 mL, which are all higher than the corresponding activities of ethylene homopolymerization. The viscosity average molecular weights (M_{η}) of copolymers are all lower than those of polymers of ethylene homopolymerization. It is noticeable that the M_{η} of copolymers obtained with complexes **3a–c** lie on the similar level with those of corresponding polyethylenes, but the molecular weight of the copolymer obtained with complex **3d** is seven times lower than that of the corresponding homopolymer. The results indicate that the introduction of alkyl on Cp can increase the catalytic activity and inhibit to a certain degree the decrease of molecular weight of copolymer.



Fig. 4. Influence of 1-hexene feed on the copolymerization of ethylene/1-hexene. (Copolymerization conditions: $[Zr] = 1.0 \times 10^{-4} \text{ mol/L}$, Al/Zr = 1000, 50 °C, 15 min, ethylene (10 bar), 25 mL of toluene.)

Table 5

The copolymerization of ethylene/1-hexene with 3a-d/MAO systems.^a

Run	Cat. ^b	Yield (g)	Act. ^c	$M_{\eta}^{\rm d}$ (×10 ³)	1-Hexene incorporation ^e (%)
9	3a	0.708	1130	322	1.39
10	3b	0.393	629	334	0.89
11	3c	0.768	1230	264	1.14
12	3d	0.603	890	68	1.44

^a All polymerization runs were performed in toluene with total volume of 25 mL over 15 min at 50 $^{\circ}$ C, 10 bar ethylene pressure and 2.0 mL 1-hexene.

 b 1.0 \times 10 $^{-4}$ mol/L (2.5 $\mu mol)$ catalyst and 0.10 mol/L (2.5 mmol) MAO as co-catalyst.

^c Kg copolymer/mol Zr h.

^d Intrinsic viscosity was determined in decahydronaphthalene at 135 °C and the viscosity average molecular weight was calculated using the relation: [η] = 6.77 × 10⁻⁴ $M_{\rm n}^{0.67}$.

^e Estimated from ¹³C NMR spectra of obtained copolymer [48].

General speaking, the *ansa*-metallocene complexes [49] or bis(salicylaldiminato) complexes [50] usually exhibit excellent efficiencies for ethylene/ α -olefin copolymerizations, but the mixed salicylaldiminato complexes show low 1-hexene incorporation level [24] in ethylene/1-hexene copolymerization. Lancaster reported 1-hexene incorporation of 1.3–2.1% with monocyclopentadienyl phenoxyimine zirconium complexes. The ethylene/1-hexene copolymers obtained with the complexes **3a–c** characterized by ¹³C NMR spectroscopic method in high temperature have 1hexene incorporation contents of 0.89–1.39%, which are slightly lower than that with complex **3d** (1.44%). The low levels of 1-hexene incorporation are probably due to the inherent steric bulkiness of these complexes.

4. Conclusion

Three new alkyl-substituted cyclopentadienyl salicylaldiminato zirconium complexes were prepared and showed high activities for ethylene homopolymerization. Within the temperature range of 70–90 °C, complex **3a** with *n*-butyl substituted Cp exhibited higher catalytic activities and the more bulky complexes **3b** and **3c** exhibited lower catalytic activities than the unsubstituted Cp complex **3d**, indicating that suitable alkyl substituent on Cp ring is benefit to catalytic activity.

The GPC and ¹³C NMR spectroscopic analyses indicate that complexes 3a-c can catalyze ethylene polymerization to produce linear polyethylene with broad distributions which is however narrower than that obtained with unsubstituted complex **3d**.

The complexes **3a–c** can also catalyze the copolymerization of ethylene/1-hexene but with low level of 1-hexene incorporation in copolymer. The complexes **3a** and **3c** showed higher catalytic activities in copolymerization than ethylene homopolymerization and the *tert*-butyl cyclopentadienyl salicylaldiminato zirconium complex **3b** afforded ethylene/1-hexene copolymer of higher molecular weight.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.06.010.

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