

HALF-TITANOCENE CHLORIDES 2-(BENZIMIDAZOL-2-YL)QUINOLIN-8-OLATES: SYNTHESIS, CHARACTERIZATION AND ETHYLENE (CO-)POLYMERIZATION BEHAVIOR*

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Abstract A series of half-titanocene chloride 2-(benzimidazol-2-yl)quinolin-8-olates **C1–C6** were synthesized by treating the lithium salts of the ligand with CpTiCl_3 . All the complexes were characterized by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and elemental analyses, and the crystal structure of **C3** and **C6** was measured by X-ray. These half-titanocene complexes showed moderate catalytic activities toward ethylene polymerization (up to $1840 \text{ kg}\cdot\text{mol}^{-1}(\text{Ti})\cdot\text{h}^{-1}$) when activated with MMAO, affording the high molecular weight polymers. And they also exhibited good activity for copolymerization of ethylene and α -olefin with low content of co-monomer.

Keywords: Half-titanocene; 2-(Benzimidazol-2-yl)quinolin-8-ol; Ethylene polymerization; Co-polymerization.

INTRODUCTION

Metallocene catalytic systems produce advanced polyolefins with controlled molecular weights and dispersity, and show better stereospecificity and copolymerization behavior with α -olefins^[1, 2]. In the practicing commercialization, the bridged half-metallocene pre-catalysts have been explored and used as the CGC type catalysts^[3–5]. The non-bridged half-metallocene pre-catalysts of the type CpMLX_n ($\text{M} = \text{Ti, Zr, Hf}$; $\text{L} =$ anionic ligand; $\text{X} =$ halogen or alkyl) have been extensively and intensively investigated through employing different anionic ligands^[6] including aryloxy^[7, 8], ketimide^[9], acetamidinato^[10–12], iminophenoxy^[13, 14], pyridinylalkyloxy^[15] and *N*-substituted (iminomethyl)pyrrolides^[16] and so on^[17, 18]. The non-bridged half-metallocene pre-catalysts maintained the advantages of the metallocene^[2] and CGC pre-catalysts^[4], and showed unique catalytic properties with various co-monomers^[6]. The half-titanocene complexes with multi-dentate anionic ligands (**A–E**, Scheme 1) have been synthesized and showed high activities in ethylene (co-)polymerization. The pre-catalysts bearing imino-indolate (**A**) showed good activity ($8.32 \times 10^6 \text{ g/mol(Ti)}$) for ethylene co-polymerization with 1-hexene as well as methyl-10-undecenoate^[19], while half-titanocene having pyridylbenzimidazole (**B**) exhibited higher activity for ethylene polymerization ($10^7 \text{ g/mol(Ti)}\cdot\text{h}$) at high temperature of 100°C ^[20]; so did their analogues (**C–E**)^[21–24]. Recently the 2-benzimidazol-8-ethoxyquinolines were used for nickel complex pre-catalysts in ethylene oligomerization and showed better thermal stability^[25], 2-(benzimidazol-2-yl)quinolin-8-ols are extensively prepared and used in preparing the half-titanocene complexes (this work, Scheme 1), which show

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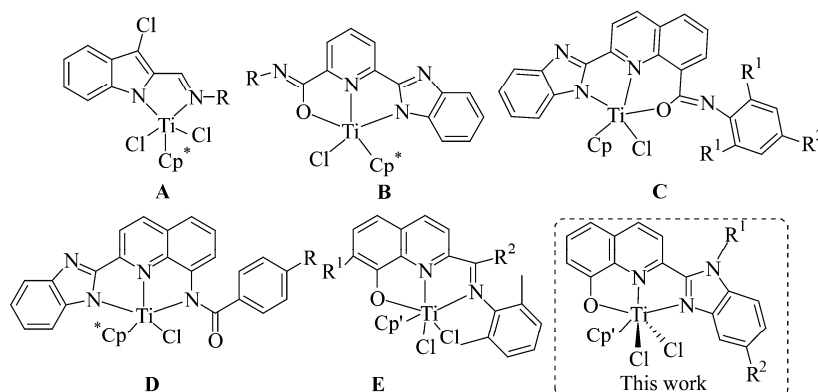
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high activities in ethylene polymerization and co-polymerization, more importantly giving polyethylenes with ultrahigh molecular weights. Herein the synthesis and characterization of the title complexes are reported along with their catalytic performances in detail.



Scheme 1 Half-titanocene pre-catalysts bearing multidentate ligands

EXPERIMENTAL

General Consideration

All manipulations of air and/or moisture-sensitive compounds were performed under nitrogen atmosphere in a glovebox or using standard Schlenk techniques. Methylaluminoxane (MAO, 1.46 mol/L in toluene) was purchased from Albemarle and other reagents were purchased from Aldrich or Acros Chemicals. Modified methylaluminoxane (MMAO, 1.93 mol/L in heptane) was purchased from Akzo Nobel Corp. Potassium hydride (KH), purchased from Beijing Regent Chemicals, was washed with hexane before use to remove contained mineral oil. Toluene, *n*-hexane, *n*-heptane and isoprene were refluxed over sodium and benzophenone, distilled, and then stored over activated molecular sieves (4 Å) for 24 h under nitrogen atmosphere. Dichloromethane (CH₂Cl₂), 1-hexene, and 1-octene were refluxed over calcium hydride, distilled, and then stored over activated molecular sieves (4 Å) for 24 h in a glovebox prior to use. CDCl₃ was dried over activated 4 Å molecular sieves. IR spectra were recorded on a Perkin Elmer FT-IR 2000 spectrometer using KBr disc in the range of 4000–400 cm⁻¹. Elemental analysis was performed on a Flash EA 1112 microanalyzer. ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard. DSC trace and melting points of polyethylene were obtained from the second scanning run on a Perkin-Elmer DSC-7 at a heating rate of 10 K/min. ¹³C-NMR spectra of the polymers were recorded on a Bruker DMX-300 MHz instrument at 112 °C in deuterated 1,2-dichlorobenzene with TMS as an internal standard.

Synthesis of Complexes

Dichloro(η⁵-cyclopentadienyl)titanium 2-(1-methylbenzimidazol-2-yl)quinolin-8-olate (**C1**)

To a stirred solution of 2-(1-methyl-benzimidazol-2-yl)quinolin-8-ol (0.551 g, 2 mmol) in dry dichloromethane (30 mL) at -78 °C, 4 mL of a *n*-BuLi solution in hexane (0.5 mol/L) was dropwisely added over a 5 min period by a syringe. The resultant mixture was allowed to warm to room temperature and stirred for additional 4 h, and a yellow suspension was obtained. After the reaction was finished, the reaction mixture was filtered through a Celite pad using a glass filter. The yellow lithium salt was dried under vacuum. In a solution of lithium salt in 30 mL cool dichloromethane, 0.438 g (2.00 mmol) CpTiCl₃ was added at -78 °C, the resultant mixture was slowly warmed up to room temperature and stirred for additional 24 h. After the solvent evaporation, the residue was extracted with CH₂Cl₂ (5 × 20 mL), and the filtrate was combined and concentrated into about 20 mL. The concentrated solution was covered with *n*-heptane and kept for three days to obtain brown crystals of dichloro(η⁵-cyclopentadienyl)titanium 2-(1-methylbenzimidazol-2-yl)quinolin-8-olate (**C1**) in 75% yield

(0.23 g). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , TMS): δ 8.28 (s, 1H), 7.83 (d, 2H, $J = 8.19$ Hz), 7.64 (d, $J = 8.7$ Hz, 1H), 7.53 (t, $J = 8.01$ Hz, 1H), 7.40 (d, $J = 8.1$ Hz, 1H), 7.26 (m, 2H), 7.13 (Cp, 5H), 3.88 (m, 2H, Ar-CH₂). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , TMS): δ 152.33, 149.96, 148.37, 142.73, 137.44, 137.34, 137.20, 128.78, 128.20, 124.07, 123.10, 122.94, 120.51, 118.31, 111.03, 110.13, 33.25. Anal. Calcd. For $\text{C}_{22}\text{H}_{17}\text{N}_3\text{Cl}_2\text{OTi}$: C, 57.67; H, 3.74; N, 9.17. Found: C, 57.77; H, 3.76; N, 9.15.

Dichloro(η^5 -cyclopentadienyl)titanium 2-(1-ethylbenzimidazol-2-yl)quinolin-8-olate (C2)

Using the same procedure as for the synthesis of **C1**, **C2** was obtained as dark blue solid in 67% yield (0.17 g). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , TMS): δ 8.44 (d, $J = 8.3$ Hz, 1H, quino-H), 8.35 (d, $J = 8.1$ Hz, 1H, quino-H), 8.02 (d, $J = 8.6$ Hz, 1H, quino-H), 7.72 (t, $J = 8.0$ Hz, 1H, quino-H), 7.63–7.53 (m, 3H), 7.41 (Cp, 5H), 7.00 (d, $J = 7.8$ Hz, 1H), 4.72–4.69 (m, 2H, Ar-CH₂CH₃), 1.69 (t, $J = 6.8$ Hz, 3H, Ar-CH₂CH₃). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , TMS): δ 164.4, 161.6, 147.1, 138.4, 137.5, 134.7, 132.4, 131.7, 129.4, 125.7, 124.5, 123.5, 122.4, 120.6, 119.3, 110.9, 105.2, 29.8, 14.3. Anal. Calcd. For $\text{C}_{23}\text{H}_{19}\text{N}_3\text{Cl}_2\text{OTi}$: C, 58.50; H, 4.06; N, 8.90. Found: C, 58.57; H, 4.11; N, 8.95.

Dichloro(η^5 -cyclopentadienyl)titanium 2-(1-isopropylbenzimidazol-2-yl)quinolin-8-olate (C3)

Using the same procedure as for the synthesis of **C1**, **C3** was obtained as dark blue solid in 84% yield (0.35 g). $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 8.46 (d, $J = 8.5$ Hz, 1H, quino-H), 8.32 (d, $J = 8.5$ Hz, 1H, quino-H), 7.98 (d, $J = 8.6$ Hz, 1H, quino-H), 7.79 (d, $J = 8.3$ Hz, 1H, quino-H), 7.72 (t, $J = 8.0$ Hz, 1H, quino-H), 7.55 (t, $J = 7.7$ Hz, Ar-H), 7.48–7.42 (m, 2H, Ar-H), 7.39 (s, 5H, Cp), 6.99 (d, $J = 7.8$ Hz, 1H, Ar-H), 5.62–5.56 (m, 1H, CH(CH₃)₂), 1.88 (d, $J = 6.8$ Hz, 6H, CH(CH₃)₂). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , TMS): δ 152.18, 150.13, 148.59, 143.66, 137.29, 134.67, 130.96, 128.83, 128.15, 123.67, 123.39, 122.63, 120.95, 118.29, 113.11, 111.03, 47.31, 21.57. Anal. Calcd. For $\text{C}_{24}\text{H}_{21}\text{N}_3\text{Cl}_2\text{OTi}$: C, 59.29; H, 4.35; N, 8.64. Found: C, 59.23; H, 4.39; N, 8.60.

Dichloro(η^5 -cyclopentadienyl)titanium 2-(5-chloro-1-methylbenzimidazol-2-yl)quinolin-8-olate (C4)

Using the same procedure as for the synthesis of **C1**, **C4** was obtained as dark blue solid in 42% yield (0.15 g). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , TMS): δ 9.72 (s, 1H); 8.44 (d, $J = 8.60$ Hz, 1H); 8.33 (d, $J = 8.60$ Hz, 1H); 7.14 (s, 5H, Cp); 7.79 (d, $J = 8.70$ Hz, 1H); 7.48 (t, $J = 7.60$ Hz, 1H); 7.45 (d, $J = 7.70$ Hz, 1H); 7.40 (d, $J = 8.6$ Hz, 1H); 7.21 (d, $J = 7.2$ Hz, 1H); 4.48 (s, 3H, CH₃). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , TMS): δ 154.16, 151.66, 148.18, 143.39, 138.26, 137.62, 136.69, 129.20, 129.10, 127.39, 124.04, 122.35, 119.44, 118.54, 113.24, 112.97, 33.67. Anal. Calcd. For $\text{C}_{22}\text{H}_{16}\text{N}_3\text{Cl}_3\text{OTi}$: C, 53.64; H, 3.27; N, 8.53. Found: C, 53.66; H, 3.26; N, 8.55.

Dichloro(η^5 -cyclopentadienyl)titanium 2-(5-chloro-1-ethylbenzimidazol-2-yl)quinolin-8-olate (C5)

Using the same procedure as for the synthesis of **C1**, **C5** was obtained as dark blue solid in 49% yield (0.17 g). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , TMS): δ 8.54 (d, $J = 8.6$ Hz, 1H); 8.33 (d, $J = 8.4$ Hz, 1H); 7.86 (s, 1H); 7.80 (s, 1H); 7.54 (t, $J = 8.0$ Hz, 1H); 7.42 (d, $J = 8.8$ Hz, 2H); 7.35 (d, $J = 8.6$ Hz, 1H); 7.27 (d, $J = 7.5$ Hz, 1H); 4.87 (q, $J = 7.1$ Hz, 2H); 1.68 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , TMS): δ 152.29, 150.33, 147.98, 143.61, 137.44, 137.36, 135.08, 129.00, 128.65, 128.36, 124.54, 123.04, 120.28, 118.42, 117.07, 110.89, 41.11, 15.54. Anal. Calcd. For $\text{C}_{23}\text{H}_{18}\text{N}_3\text{Cl}_3\text{OTi}$: C, 54.53; H, 3.58; N, 8.29. Found: C, 54.58; H, 3.56; N, 8.25.

Dichloro(η^5 -cyclopentadienyl)titanium 2-(5-chloro-1-isopropylbenzimidazol-2-yl)quinolin-8-olate (C6)

Using the same procedure as for the synthesis of **C1**, **C6** was obtained as dark blue solid in 52% yield (0.21 g). $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 8.44 (d, $J = 6.8$ Hz, 1H, quino-H), 8.28 (s, 1H, quino-H), 7.97 (d, $J = 6.9$ Hz, 1H, quino-H), 7.73 (t, $J = 8.2$ Hz, 1H, quino-H), 7.43 (t, $J = 8.8$ Hz, 1H, quino-H), 7.36 (s, 5H, Cp), 6.99 (d, $J = 7.8$ Hz, 1H, Ar-H), 5.61–5.54 (m, 1H, CH(CH₃)₂), 1.84 (d, $J = 5.8$ Hz, 6H, CH(CH₃)₂). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 165.5, 151.4, 142.6, 139.7, 138.2, 137.3, 132.6, 131.9, 131.2, 129.4, 124.6, 123.5, 122.3, 118.8, 116.7, 116.4, 115.0, 111.8, 51.4, 29.8, 21.9. Anal. Calcd. For $\text{C}_{24}\text{H}_{20}\text{N}_3\text{Cl}_3\text{OTi}$: C, 55.36; H, 3.87; N, 8.07. Found: C, 55.37; H, 3.86; N, 8.03.

X-ray Structure Determination

Crystals of **C3** and **C6** suitable for single-crystal X-ray analysis were obtained by laying *n*-heptane on the

dichloromethane solutions. Single-crystal X-ray diffraction for **C3** and **C6** was performed on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 173(2) K. Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 . All non-hydrogen atoms were refined anisotropically. Structure solution and refinement were performed by using the SHELXL-97 package^[26]. Crystal data collection and refinement details are given in Table 1.

Table 1. Crystallographic data and refinement details for complexes **C3** and **C6**

	C3	C6
Empirical formula	C ₂₄ H ₂₁ Cl ₂ N ₃ OTi	C ₂₄ H ₂₀ Cl ₃ N ₃ OTi
Formula weight	486.24	520.68
Crystal color	Red	Red
Temperature (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/n	P-1
<i>a</i> (Å)	14.295(3)	9.989(2)
<i>b</i> (Å)	9.4525(19)	10.936(2)
<i>c</i> (Å)	18.107(4)	12.409(3)
α (°)	90	87.62(3)
β (°)	91.95(3)	69.25(3)
γ (°)	90	79.83(3)
Volume (Å ³)	2445.2(9)	1247.3(4)
<i>Z</i>	4	2
D _{calc} (mg m ⁻³)	1.321	1.386
μ (mm ⁻¹)	0.588	0.685
<i>F</i> (000)	1000	532
Crystal size (mm)	0.23 × 0.12 × 0.07	0.25 × 0.22 × 0.20
θ range (°)	1.79–25.00	1.76–27.48
Limiting indices	–16 ≤ <i>h</i> ≤ 15, –11 ≤ <i>k</i> ≤ 11, –16 ≤ <i>l</i> ≤ 21	–12 ≤ <i>h</i> ≤ 12, –14 ≤ <i>k</i> ≤ 14, –16 ≤ <i>l</i> ≤ 16
No. of rflns collected	10365	10651
No. of unique rflns	4291	5548
R _{int}	0.0664	0.0336
Completeness to θ (%)	99.9 ($\theta = 25.00$)	97.4 ($\theta = 27.48$)
Goodness-of-fit on F^2	1.044	1.081
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	R1 = 0.0744, wR2 = 0.1766	R1 = 0.0534, wR2 = 0.1548
<i>R</i> indices (all data)	R1 = 0.0989, wR2 = 0.1900	R1 = 0.0602, wR2 = 0.1598
Largest diff peak, hole (e Å ⁻³)	0.376, –0.387	0.595, –0.521

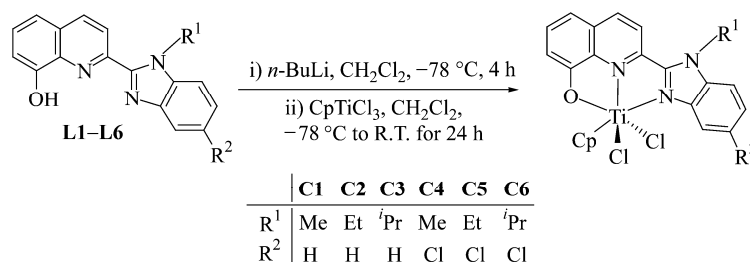
Procedures for Ethylene Polymerization and Copolymerization

A stainless steel autoclave (0.5 L) equipped with a mechanical stirrer and a temperature controller was heated in vacuum at 80 °C and recharged with ethylene three times, then cooled to room temperature under ethylene atmosphere. A toluene solution of the titanium pre-catalyst (with co-monomer) was transferred into the reactor. After the desired reaction temperature was reached and the required amount of co-catalyst (with 100 mL volume in total) was added, the autoclave was immediately pressurized to 1.0 MPa. The ethylene pressure was kept constant during the reaction through feeding ethylene. After a due time, the feeding ethylene was stopped, and the autoclave was placed in a water-ice bath for one hour. The resultant mixture was poured into 10% HCl-ethanol solution, and the solid polymer was collected and washed with water and ethanol several times and dried under vacuum to constant weight.

RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes C1–C6

By metal-chloride exchange employed in our previously synthesizing titanium complexes, all the complexes **C1–C6** were prepared from moderate to good yields (42%–84%) in the stoichiometric reaction of CpTiCl_3 with corresponding potassium 2-(1H-benzimidazol-2-yl)quinolin-8-olates in CH_2Cl_2 (Scheme 2). All these complexes were characterized by ^1H -/ ^{13}C -NMR spectra and elemental analysis.



Scheme 2 Synthesis of titanium complexes **C1–C6**

Two representative complexes **C3** and **C6** were measured by the single crystal X-ray diffraction. The molecular structures are illustrated in Fig. 1 and Fig. 2, respectively, and the selected bonds and angles are tabulated in Table 2.

As shown in Fig. 1, complex **C3** contains one ligand, together with a Cp ring and two chlorides, which form a pseudo octahedral geometry at the titanium center. The dihedral angle between the quinoline ($\text{C1–C2–C3–C4–C5–C7–C8–C9–N1–C6}$) and benzimidazole ($\text{C10–N2–C14–C15–C16–C17–C18–C19–N3}$) plane is 14.80° , which is identical to their nickel analogs^[25]. The bond distances of Ti–N (2.140(4) Å, 2.272(4) Å) are in the range commonly observed for titanium complexes, but the Ti1–N2 is much longer than Ti1–N1 in bond length. The Ti–Cl bond lengths ($\text{Ti1–Cl1} = 2.4512(18)$ Å, $\text{Ti1–Cl2} = 2.4371(16)$ Å) are different. The bond angle of $\angle(\text{N1–Ti1–Cl1})$ and $\angle(\text{N1–Ti1–Cl2})$ are 76.76° and 76.52° , respectively. The distance between the centroid of Cp ring and titanium atom is 2.073 Å, whilst the Ti1–C bond lengths are slightly different with the range of 2.362 Å to 2.420 Å ($\Delta(\text{Ti–C}) = 0.058$ Å). The dihedral angle defined by the quinoline ring and Cp ring is 89.33° , which is near to a right angle.

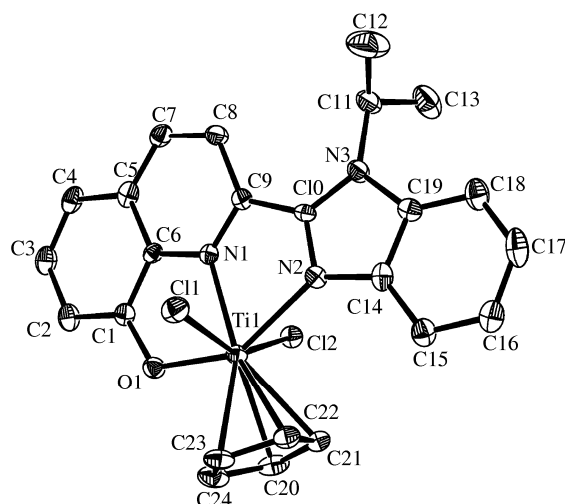


Fig. 1 ORTEP drawing of the molecular structure of **C3** (ellipsoids enclose 30% electronic density; H atoms are omitted for clarity.)

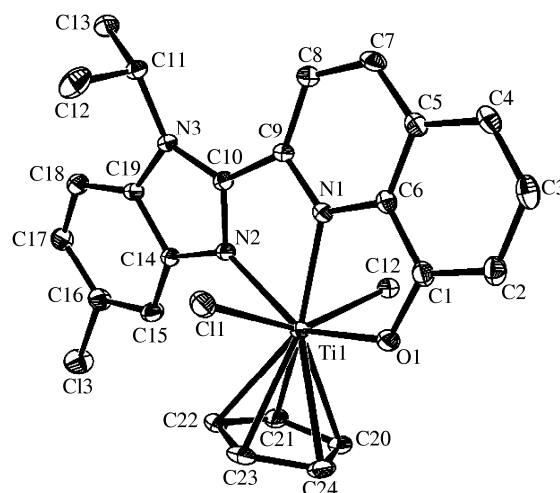


Fig. 2 ORTEP drawing of the molecular structure of **C6** (ellipsoids enclose 30% electronic density; H atoms are omitted for clarity).

Table 2. Selected bond lengths (Å) and angles (°) for **C3** and **C6**

	C3	C6
Bond lengths (Å)		
Ti1—O1	1.965(4)	1.961(2)
Ti1—N1	2.140(4)	2.155(2)
Ti1—N2	2.272(4)	2.289(2)
Ti1—Cl1	2.4512(18)	2.4496(13)
Ti1—Cl2	2.4371(16)	2.4475(11)
Ti1—Cp _{cent}	2.073	2.085
Bond angles (°)		
O1—Ti1—N1	76.54(15)	76.31(9)
O1—Ti1—N2	146.91(15)	146.44(8)
N1—Ti1—N2	70.37(15)	70.31(9)
O1—Ti1—Cl1	90.39(12)	92.13(7)
N1—Ti1—Cl1	76.76(12)	75.52(7)
N2—Ti1—Cl1	82.06(12)	83.05(7)
O1—Ti1—Cl2	91.95(11)	88.09(7)
N1—Ti1—Cl2	76.52(11)	76.94(7)
N2—Ti1—Cl2	80.74(11)	81.23(7)
Cl1—Ti1—Cl2	151.84(6)	151.58(3)

Figure 2 shows the complex **C6** possesses a similar geometry around the titanium center and titanium is coordinated by tridentate ligand, Cp ring and two chlorine atoms. Comparison with those of complex **C3** indicates that there are no distinct differences in bond lengths and angles except for the longer distance of Ti—N2. This is probably due to the electron withdrawing group of Cl on benzimidazole ring in complex **C6**, and it will affect the catalytic performance for olefin polymerization.

Catalytic Behavior for Ethylene Polymerization by Complexes C1–C6

First, the reaction conditions for ethylene polymerization were optimized by employing pre-catalyst **C2**. Due to the better catalytic performances observed in the presence of MMAO than MAO, therefore detailed investigations have been carried out by employing MMAO and results were collected in Table 3.

Table 3. Ethylene polymerization by **C1–C6** with MMAO ^a

Run	Pre-cat.	<i>t</i> (min)	Al/Ti	<i>T</i> (°C)	Polym (g)	Act ^b	<i>T</i> _m ^c (°C)
1	C2	30	4000	20	0.186	3.72	133.9
2	C2	30	5000	20	0.534	10.7	134.1
3	C2	30	6000	20	0.60	12.0	132.4
4	C2	30	7000	20	0.394	7.88	134.5
5	C2	30	8000	20	0.576	11.5	134.3
6	C2	30	6000	40	0.855	17.1	134.4
7	C2	30	6000	60	0.38	7.60	135.6
8	C2	30	6000	80	0.188	3.76	134.0
9	C2	20	6000	40	0.545	16.4	133.6
10	C2	10	6000	40	0.297	17.8	134.7
11	C1	30	6000	40	0.501	10.2	133.2
12	C3	30	6000	40	0.615	12.3	134.2
13	C4	30	6000	40	0.518	10.4	133.2
14	C5	30	6000	40	0.919	18.4	134.8
15	C6	30	6000	40	0.668	13.4	135.4

^a Condition: 1 μmol complex, toluene (total volume 100 mL), 1.0 MPa; ^b 10⁵ g·mol⁻¹(Ti)·h⁻¹; ^c Determined by DSC

Increasing the Al/Ti ratios from 4000 to 8000 (Runs 1–5, Table 3), the highest activity is achieved at an Al/Ti molar ratio of 6000 (Run 3, Table 3), such phenomenon can be well clarified by the influence of the Al concentration on the termination of polymer chains^[27, 28]. Regarding the thermal stability of complex **C2**, increasing temperature led to a decrease in catalytic activity from $1.71 \times 10^6 \text{ g} \cdot \text{mol}^{-1}(\text{Ti}) \cdot \text{h}^{-1}$ at 40 °C to $3.75 \times 10^5 \text{ g} \cdot \text{mol}^{-1}(\text{Ti}) \cdot \text{h}^{-1}$ at 80 °C (Runs 3, 6–8, Table 3), probably caused by the part deactivation of the active species at higher temperatures. The lower activity at elevated temperatures was also observed within the system of Cp₂TiCl₂, its cause was imaged as bimolecular disproportionate termination^[29–31]. Within the **C2**/MMAO system (runs 3, 9–10, Table 3), interestingly, the activities were observed likely constant along extending the reaction time, indicating the stable active species formed.

Employing the optimized condition with Al/Ti ratio 6000 at 40°C within 30 min, the catalytic behaviors of complexes **C1–C6** were investigated and their results were tabulated in Table 2. All the pre-catalysts generally showed high activities in the range of 1020–1840 kg·mol⁻¹(Ti)·h⁻¹ (Runs 11 – 15, Table 3). Both substituents on the imidazolyl (R¹) and phenyl (R²) groups affected catalytic performances with the order as **C2** (R¹ = Et, R² = H) > **C3** (R¹ = *i*Pr, R² = H) > **C1** (R¹ = Me, R² = H), **C5** (R¹ = Et, R² = Cl) > **C6** (R¹ = *i*Pr, R² = Cl) > **C4** (R¹ = Me, R² = Cl). The chloro-involvement induced better activity for their complexes, such as **C4** > **C1**, **C5** > **C2**, and **C6** > **C3**, illustrating the positive effect of the electron-withdrawing substituents due to electron donation from the η⁵-cyclopentadienyl group.

All the obtained polyethylene samples have high *T*_m around 134 °C, suggesting the high linear characteristics. The GPC measurements were not succeeded because these polyethylenes showed very poor solubility in 1,2-dichlorobenzene, indicating their high molecular weights.

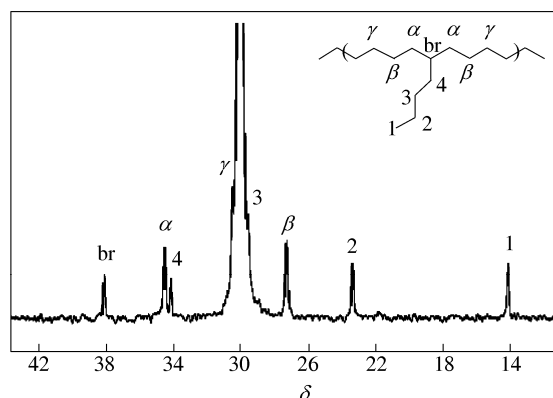
Catalytic Behavior for Ethylene Co-polymerization with α-Olefin

In exploring the co-polymerization behavior, trials of complex **C6**/MMAO in ethylene with 1-hexene or 1-octene were conducted, and the results were collected in Table 4. In comparison with the ethylene homopolymerization (Table 3), the activities were decreased in the copolymerization. The worse results were obtained along with increasing the monomer concentration (Runs 1–3, 4–6 in Table 4), indicating a negative effect of co-monomer. The incorporation of co-monomer within the obtained polyethylenes was approved by their ¹³C-NMR spectra.

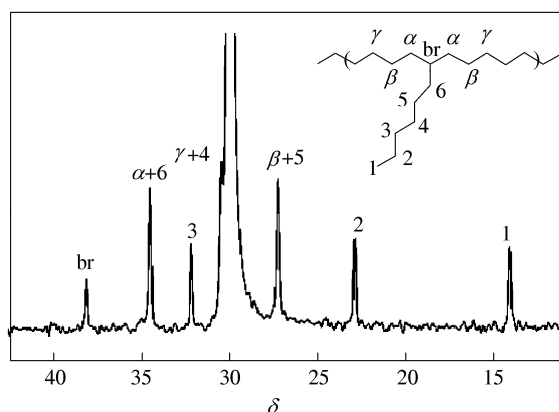
Table 4. Ethylene copolymerization by **C6** with MMAO^a

Run	Monomer	Concentration (mol/L)	Polymer (g)	Activity ^b	T_m^c (°C)
1	1-Hexene	0.4	0.59	11.8	126.7
2	1-Hexene	0.7	0.39	7.80	119.2
3	1-Hexene	1	0.25	5.00	116.8
4	1-Octene	0.4	0.228	4.56	120.1
5	1-Octene	0.7	0.213	4.26	118.3
6	1-Octene	1	0.165	3.30	126.5

^a Condition: 1 μ mol complex **C6**, toluene (total volume 100 mL), Al/Ti = 6000, 30 min, 40 °C, 1.0 MPa; ^b 10^5 g·mol⁻¹(Ti)·h⁻¹; ^c Determined by DSC

**Fig. 3** ¹³C-NMR spectrum of ethylene/1-hexene co-polymer by the **C6**/MAO system (Run 2, Table 4)

The ¹³C-NMR spectrum of the ethylene/1-hexene co-polymer revealed typical characteristics of linear low density polyethylene^[32, 33], and indicated the incorporation of 2.46 mol% of 1-hexene (Fig. 3). The monomer sequence distributions determined from the ¹³C-NMR spectrum showed that the obtained poly(ethylene-1-hexene) contained ethylene (EEE), EHE, EHH, HEH, etc^[34]. By the same way, the ethylene/1-octene co-polymer was also measured by high temperature ¹³C-NMR spectroscopy, and the results indicated the incorporation of 1-octene was 3.05 mol% (Fig. 4) which is higher than the incorporation of 1-hexene.

**Fig. 4** ¹³C-NMR spectrum of ethylene/1-octene co-polymer by the **C6**/MAO system (Run 4, Table 4)

SUMMARY

The half-titanocene chloride 2-(benzimidazol-2-yl)quinolin-8-olates were synthesized and fully characterized along with the molecular structures of **C3** and **C6** by single-crystal X-ray analysis. Employing MMAO as co-catalysts, all title complex pre-catalysts performed good activities toward ethylene polymerization (up to

1840 kg·mol⁻¹(Ti)·h⁻¹), affording polyethylenes with the ultra high molecular weights and high T_m . Though the negative influence of co-monomer was observed, the copolymerization of ethylene with α -olefin was indeed conducted and approved by the ¹³C-NMR spectra of the obtained polyethylenes. Therefore half-titanocene complex pre-catalysts should be important for further research interest in both co-polymerization for low-density polyethylenes and solely ethylene polymerization for polyethylenes with ultrahigh molecular weights.

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