

# Chromium complexes ligated by 2-carbethoxy-6-iminopyridines: Synthesis, characterization and their catalytic behavior toward ethylene polymerization

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## Abstract

The titled chromium complexes (**C1–C6**) were prepared by the reaction of  $\text{CrCl}_3(\text{THF})_3$  with the corresponding 2-carbethoxy-6-iminopyridines (**L1–L6**) in dichloromethane. All the complexes were characterized by IR spectroscopy and elemental analysis. The unambiguous solid-state structures of **C1**, **C3** and **C5** were determined by X-ray crystallography. The chromium core was found to be coordinated by a molecule of 2-carbethoxy-6-iminopyridine and three atoms of chlorine to form a distorted octahedral coordination geometry. Activated with ethylaluminum dichloride ( $\text{EtAlCl}_2$ ), these complexes showed notable catalytic activities for ethylene polymerization. The nature of the ligands and reaction parameters affected the properties of the resultant polyethylenes.

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## 1. Introduction

Catalysts consisted of  $\text{CrO}_x/\text{SiO}_2$  are well-known practical catalysts in polyolefin industry, and those catalysts produce one-third of the worldwide commercial high-density polyethylenes (HDPE) [1]. The resultant polyethylenes are known to display unique properties due to the ultra-broad molecular weight distribution, short and long chain branches and are suitable for the blow-molding process [2]. In spite of their practical impact for the past 50 years, the states of the active species and the polymerization mechanism of these catalysts are still unclear [3]. In addition, the heterogeneous nature of these systems is responsible for certain heterogeneities in the produced polymers, which might not be desirable for some applications [4].

The discovery of metallocene not only provided highly active catalysts [5] but also opened the way to trace the processes of industrial engineering back to the concepts of their academic science about the active sites and catalytic mechanism [6]. Along with the development of measuring equipments, organometallic chemists have speeded up their research works in order to investigate the catalytic sites and design single site catalysts. Their extension in polyolefins has fast driven the application of transition metal complexes as catalysts in olefin polymerization [7]. There are many reports published concerning various transition metal complexes as catalysts [8] and the design of functional catalysts based on new ligands [9]. Chromium complexes bearing various ligands of  $\text{N}^{\wedge}\text{N}$ ,  $\text{N}^{\wedge}\text{N}^{\wedge}\text{N}$ ,  $\text{N}^{\wedge}\text{O}$  and  $\text{N}^{\wedge}\text{S}^{\wedge}\text{N}$  as homogeneous catalysts have attracted considerable attention [10,11]; however, there are only few reports on the mechanism and active sites [12]. In our earlier works, we studied the 2,6-bis(2-benzimidazolyl)pyridyl chromium chlorides as catalysts for ethylene reactivity, and also reported that nickel, iron and cobalt complexes bearing 2-carbethoxy-6-iminopyridines exhibited promising results exhibited for ethylene reactivity [13]. There-

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fore, we prepared chromium complexes ligated by 2-carbethoxy-6-iminopyridines (N<sup>N</sup>O ligands) and carefully explored their reactivity toward ethylene in the presence of various cocatalysts. During the course of our study, Small et al. reported an analogous chromium complex containing 2-acetyl-6-iminopyridines, which afforded low molecular weight polyethylene waxes and polyethylene upon activation with MAO [12d].

We herein present the syntheses and identification of a series of chromium complexes containing 2-carbethoxy-6-iminopyridines. We, recently, found that the reaction with ethylene in the presence of MAO afforded oligomers, whereas polyethylene could be obtained when the reaction is performed in the presence of Et<sub>2</sub>AlCl [13a]. We, thus, explored factors affecting the catalysts toward their performance in ethylene polymerization and/or oligomerization in the presence of Al cocatalysts under various conditions.

## 2. Experimental

### 2.1. General procedures

All manipulations of the moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques. The IR spectra were obtained on a Perkin-Elmer FT-IR 2000 spectrophotometer using the KBr discs in the range of 4000–400 cm<sup>-1</sup>. Elemental analyses were performed on a Flash EA 1112 micro analyzer. The distribution of oligomers obtained was measured on a Varian VISTA 6000 GC spectrometer and a HP 5971A GC-MS detector. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the PE samples were recorded on a Bruker DMX-300 MHz instrument at 135 °C in 1,2-dichlorobenzene-*d*<sub>4</sub> using TMS as an internal standard. Molecular weights and polydispersity indices (PDI) of PE were determined by a PL-GPC220 at 150 °C with 1,2,4-trichlorobenzene as eluent. Melting points of the polymers were obtained on a Perkin-Elmer DSC-7 in the standard DSC run mode. The instrument was initially calibrated for melting point of an indium standard at a heating rate of 10 °C/min. The polymer sample was first equilibrated at 10 °C and then heated to 160 °C at a rate of 10 °C/min to remove thermal history. The sample was then cooled to 10 °C at a rate of 10 °C/min. A second heating cycle was used for collecting DSC thermogram data at a ramping rate of 10 °C/min.

### 2.2. Synthesis of complexes (Scheme 1)

#### 2.2.1. 2-Carbethoxy-6-[1-((2,6-dimethylphenyl)imino)ethyl]pyridine chromium(III) complex (C1)

Freshly distilled dichloromethane was added to ligand **L1** (0.296 g, 1 mmol) and CrCl<sub>3</sub>(THF)<sub>3</sub> (0.372 g, 1 mmol) at the room temperature and the mixture was stirred for 12 h. The green precipitate was filtered and washed with diethyl ether. The desired complex **C1** (0.390 g, 0.86 mmol) was obtained as green powder in yield 86.0%. IR (KBr): 1642; 1587; 1467; 1407; 1381; 1341; 1291; 1217; 1097; 992; 851; 768 cm<sup>-1</sup>. Anal. Calcd. for C<sub>18</sub>H<sub>20</sub>Cl<sub>3</sub>CrN<sub>2</sub>O<sub>2</sub>: C, 47.54; H, 4.43; N, 6.16. Found: C, 47.44; H, 4.60; N, 6.33%.

#### 2.2.2. 2-Carbethoxy-6-[1-((2,6-diethylphenyl)imino)ethyl]pyridine chromium(III) complex (C2)

Using the procedure described for **C1**, complex **C2** (0.429 g, 0.89 mmol) was obtained as green powder in yield 89.1%. IR (KBr): 3428; 2965; 1645; 1587; 1458; 1406; 1380; 1341; 1284; 1094; 850; 802; 767; 397 cm<sup>-1</sup>. Anal. Calcd. for C<sub>20</sub>H<sub>24</sub>Cl<sub>3</sub>CrN<sub>2</sub>O<sub>2</sub>: C, 49.76; H, 5.01; N, 5.80. Found: C, 49.54; H, 4.81; N, 6.03%.

#### 2.2.3. 2-Carbethoxy-6-[1-((2,6-diisopropylphenyl)imino)ethyl]pyridine chromium(III) complex (C3)

Using the procedure described for **C1**, complex **C3** (0.433 g, 0.85 mmol) was obtained as green powder in yield 85.0%. IR (KBr): 3430; 2974; 1649; 1587; 1463; 1343; 1284; 849; 763; 398 cm<sup>-1</sup>. Anal. Calcd. for C<sub>20</sub>H<sub>24</sub>Cl<sub>3</sub>CrN<sub>2</sub>O<sub>2</sub>: C, 51.73; H, 5.52; N, 5.48. Found: C, 51.58; H, 5.53; N, 5.21%.

#### 2.2.4. 2-Carbethoxy-6-[1-((2,6-difluorophenyl)imino)ethyl]pyridine chromium(III) complex (C4)

Using the procedure described for **C1**, complex **C4** (0.428 g, 0.93 mmol) was obtained as green powder in yield 92.6%. IR (KBr): 1641; 1589; 1475; 1383 cm<sup>-1</sup>. Anal. Calcd. for C<sub>16</sub>H<sub>14</sub>Cl<sub>3</sub>CrF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 41.54; H, 3.05; N, 6.06. Found: C, 41.17; H, 3.29; N, 5.98%.

#### 2.2.5. 2-Carbethoxy-6-[1-((2,6-dichloridephenyl)imino)ethyl]pyridine chromium(III) complex (C5)

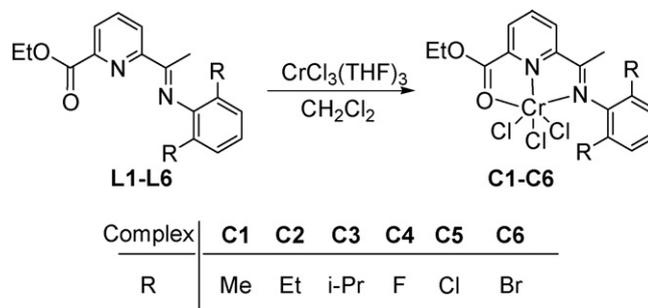
Using the procedure described for **C1**, complex **C5** (0.461 g, 0.93 mmol) was obtained as green powder in yield 92.8%. IR (KBr): 1644; 1586; 1436; 1411. Anal. Calcd. for C<sub>16</sub>H<sub>14</sub>Cl<sub>5</sub>CrN<sub>2</sub>O<sub>2</sub>: C, 38.78; H, 2.85; N, 5.65. Found: C, 38.50; H, 3.01; N, 5.33%.

#### 2.2.6. 2-Carbethoxy-6-[1-((2,6-dibromophenyl)imino)ethyl]pyridine chromium(III) complex (C6)

Using the procedure described for **C1**, complex **C6** (0.575 g, 0.99 mmol) was obtained as green powder in yield 98.5%. IR (KBr): 1645; 1584; 1412; 1379. Anal. Calcd. for C<sub>16</sub>H<sub>14</sub>Br<sub>2</sub>Cl<sub>3</sub>CrN<sub>2</sub>O<sub>2</sub>: C, 32.88; H, 2.41; N, 4.79. Found: C, 32.68; H, 2.56; N, 4.45%.

### 2.3. X-ray crystallography measurement

The single-crystal X-ray diffraction for complexes **C1** and **C5** was carried out on a Bruker Smart 1000 CCD diffractometer with



Scheme 1. Synthesis of complexes **C1**–**C6**.

Table 1  
Crystallographic data and refinement for **C1**, **C3** and **C5**

	<b>C1</b>	<b>C3</b>	<b>C5</b>
Formula	C <sub>19</sub> H <sub>22</sub> Cl <sub>5</sub> CrN <sub>2</sub> O <sub>2</sub>	C <sub>23</sub> H <sub>30</sub> Cl <sub>5</sub> CrN <sub>2</sub> O <sub>2</sub>	C <sub>16</sub> H <sub>14</sub> Cl <sub>5</sub> CrN <sub>2</sub> O <sub>2</sub>
fw	539.64	595.74	495.54
Crystallographic system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2(1)/c</i>	<i>P2(1)/c</i>	<i>P2(1)/c</i>
<i>a</i> (Å)	8.320(3)	17.872(4)	8.3797(2)
<i>b</i> (Å)	14.360(4)	10.724(2)	27.6092(8)
<i>c</i> (Å)	19.810(7)	15.887(3)	9.6062(2)
$\alpha$ (°)	90	90	90
$\beta$ (°)	101.360(2)	111.25(3)	115.141(1)
$\gamma$ (°)	90	90	90
<i>V</i> (Å <sup>3</sup> )	2320.4(13)	2838.0(10)	2011.91(9)
<i>Z</i>	4	4	4
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.545	1.394	1.636
Absolute coefficient, $\mu$ (mm <sup>-1</sup> )	1.087	0.896	1.246
<i>F</i> (000)	1100	1228	996
$\theta$ range (°)	2.10–27.48	1.22–25.01	1.48–25.06
No. of data collected	17698	4386	6138
No. of unique data	5293	4386	3527
<i>R</i> (%)	0.0629	0.0600	0.0672
<i>R</i> <sub>w</sub> (%)	0.1673	0.1399	0.1272
Goodness of fit	0.945	0.895	1.194

graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293(2) K, respectively. Intensity data of complexes **C3** were collected on a Rigaku RAXIS Rapid IP diffractometer at 293(2) K with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected. The structures were solved by direct methods and refined by full-matrix least-squares on F<sub>2</sub>. Each H atom was placed in a calculated position. Structure solution and refinement were performed using the SHELXL-97 Package. Crystal data and processing parameters are summarized in Table 1. Crystallographic data of complexes **C1**, **C3** and **C5** have been deposited within the Cambridge Crystallographic Data Center, CCDC 617982, 617983 and 617984, respectively.

#### 2.4. General procedure for ethylene polymerization at 1 atm ethylene pressure

A flame dried three-neck round flask was loaded with the complex **C1–C6** and vacuum-filled three times by nitrogen. Then ethylene was charged together with freshly distilled toluene and stirred for 10 min. MAO was added by a syringe. The reaction mixture was stirred under 1 atm ethylene pressure for a required time interval, and the catalytic reaction was terminated with acidified water. An aliquot of the reaction mixture was analyzed by GC and GC–MS.

#### 2.5. General procedure for ethylene polymerization at 10 atm ethylene pressure

Ethylene polymerization was carried out in a 250 ml autoclave stainless steel reactor equipped with a mechanical stirrer and a temperature controller. The desired amount of EtAlCl<sub>2</sub>, 30 ml toluene solution of chromium complex and 70 ml of

toluene were added to the reactor in this order under ethylene atmosphere. Ethylene (10 atm pressures) was introduced at the reaction temperature to commence the reaction and was stopped after the desired time range. A small amount of the reaction solution was collected, terminated by the addition of 5% aqueous hydrogen chloride and then analyzed by gas chromatography (GC) for the distribution of obtained oligomers. The residual solution was quenched with HCl-acidified ethanol (5%). The precipitated polymer was collected by filtration, washed with ethanol, dried in vacuum at 60 °C until constant weight, weighed and finally characterized.

### 3. Results and discussion

#### 3.1. Synthesis of pyridylimine chromium(III) complexes

The ester-substituted pyridylimine ligands **L1–L6** [2-CO<sub>2</sub>Et-6-(2,6-R<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=CCH<sub>3</sub>) C<sub>5</sub>H<sub>3</sub>N (**1**: R = CH<sub>3</sub>; **2**: R = Et; **3**: R = *i*-Pr; **4**: R = F; **5**: R = Cl; **6**: R = Br)] were prepared according to the reported procedures [13b]. The chromium complexes (**C1–C6**) were obtained by treating the dichloromethane solution of CrCl<sub>3</sub>(THF)<sub>3</sub> with the corresponding ligand (**L1–L6**) at room temperature. These complexes showed high stability in both solution and solid and could be identified by FT-IR and elemental analysis; however, the NMR spectrum could not be obtained due to their paramagnetic nature. The IR spectra of the ligands showed that the C=N stretching frequencies appeared in the range of 1640–1655 cm<sup>-1</sup> [13b], while the C=N stretching vibrations shifted toward lower frequency bands between 1619 and 1625 cm<sup>-1</sup> with weak intensities for complexes **C1–C6**. The results indicate the coordination interaction between the imino nitrogen atom and the chromium center. Moreover, the C=O stretching vibrations in IR spectra showed a slight red shift by ca. 10–20 cm<sup>-1</sup> for the chromium complexes.

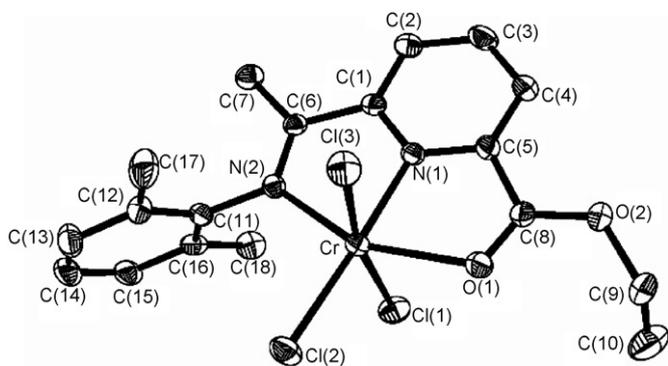


Fig. 1. The molecular structure of complex **C1**. The hydrogen atoms and the solvated  $\text{CH}_2\text{Cl}_2$  are omitted for clarity.

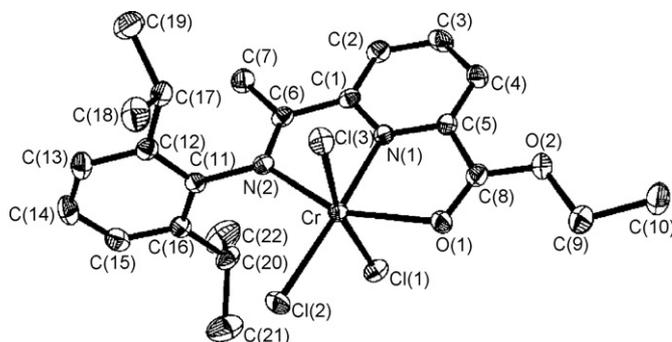


Fig. 2. The molecular structure of complex **C3**. The hydrogen atoms and the solvated  $\text{CH}_2\text{Cl}_2$  are omitted for clarity.

### 3.2. Structure determinations

Single crystals of the complexes **C1**, **C3** and **C5** for X-ray diffraction were obtained and their molecular structures are depicted in Figs. 1–3, respectively. Their selected bond lengths and bond angles are listed in Table 2. There is a solvated  $\text{CH}_2\text{Cl}_2$  in the crystal lattice of **C1** and **C3** without bond interaction between the solvent molecule and the chromium atom. Because the coordination geometry of the complexes **C1**, **C3** and **C5** are highly similar, only the structure of **C1** is described in detail.

Crystals of **C1** were grown from a dichloromethane solution layering with hexane. Fig. 1 shows that the carbonyl oxygen atom O(1) also coordinates with the chromium center and, therefore, the ligand chelates the metal core in  $\text{N}^2\text{N}^1\text{O}$  tridentate

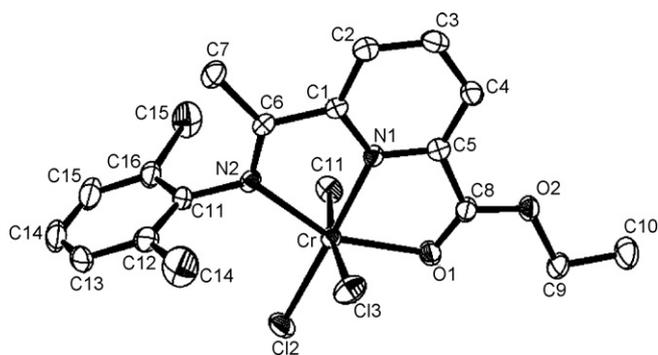


Fig. 3. The molecular structure of complex **C5**. The hydrogen atoms are omitted for clarity.

Table 2  
Selected bond lengths and bond angles for complexes **C1**, **C3** and **C5**

	<b>C1</b>	<b>C3</b>	<b>C5</b>
Bond lengths (Å)			
Cr–N(1)	2.012(3)	2.024(3)	2.024(4)
Cr–N(2)	2.102(3)	2.152(4)	2.133(4)
Cr–O(1)	2.160(3)	2.168(3)	2.122(4)
Cr–Cl(1)	2.3120(11)	2.3191(15)	2.3126(17)
Cr–Cl(2)	2.2814(11)	2.2949(15)	2.2861(16)
Cr–Cl(3)	2.3124(12)	2.2982(15)	2.2935(18)
Bond angles (°)			
N(1)–Cr–N(2)	76.87(12)	76.31(16)	75.89(16)
N(2)–Cr–O(1)	153.09(11)	153.62(13)	152.74(16)
N(1)–Cr–O(1)	76.50(11)	77.32(14)	76.85(15)
N(1)–Cr–Cl(1)	88.93(9)	86.21(11)	88.45(12)
N(2)–Cr–Cl(1)	93.52(9)	95.22(11)	92.70(12)
O(1)–Cr–Cl(1)	82.36(8)	83.76(10)	86.48(13)
N(1)–Cr–Cl(2)	177.62(9)	176.89(13)	178.18(13)
N(2)–Cr–Cl(2)	100.81(9)	100.61(10)	102.29(12)
O(1)–Cr–Cl(2)	105.85(8)	105.76(9)	104.96(11)
N(1)–Cr–Cl(3)	86.22(9)	87.42(10)	88.00(13)
N(2)–Cr–Cl(3)	95.84(9)	93.72(11)	93.74(12)
O(1)–Cr–Cl(3)	86.05(8)	84.34(10)	85.39(13)
Cl(1)–Cr–Cl(2)	91.78(5)	93.68(6)	91.80(6)
Cl(1)–Cr–Cl(3)	168.20(5)	167.49(5)	171.68(7)
Cl(2)–Cr–Cl(3)	93.50(5)	93.26(6)	91.98(7)

tate fashion. The geometry around the chromium atom could be described as a distorted octahedron. The Cr–N (pyridine) bond distance (2.012(3) Å) is about 0.09 Å shorter than the Cr–N(imino) bond distance (Cr–N2, 2.102(3) Å). The plane of the phenyl ring is oriented approximately orthogonal to the coordination plane with the angle of 77.7°. It is worthwhile to mention, that the bond angle of Cl(1)–Cr–Cl(2) and Cl(1)–Cr–Cl(3) are 91.77(5)° and 168.21°, respectively, and the distances between the chromium and the *trans*-disposed chlorides are significantly different from the distance found for the chloride in the *mer* position. The bond length of Cr–Cl(2) (2.2814(11) Å) is shorter than the bond length of Cr–Cl(1) (2.3120(11) Å) and Cr–Cl(3) (2.3124(12) Å).

Crystals of **C3** were grown from a dichloromethane solution layering with hexane. Its molecular structure is depicted in Fig. 2. The coordination geometry around the chromium center of **C3** is similar to that of **C1** in spite of the presence of isopropyl group in place of the methyl groups in the *ortho*-positions of the phenyl ring. The plane of the phenyl ring is also oriented approximately orthogonal to the coordination plane making an angle of 95.4°, which is much larger than that of complex **C1** (77.7°). Like the structure of complex **C1**, two chlorides are *trans*-disposed and the other chloride is in the *mer* position.

Crystals of **C5** were obtained by diffusing hexane layer into its dichloromethane solution. X-ray structure (as shown in Fig. 3) determination indicates that its structure is quite similar to those of **C1** and **C3**. The coordination geometry around the chromium is found to be a distorted octahedron and the bond lengths (Cr–N) are close to those of complexes **C1** and **C3**. The dihedral angle between the plane of the benzene ring and the coordination plane is 83.0°. However, the Cr–O bonding length of **C5** (2.122(4) Å) is much shorter than that of **C1** (2.160(3) Å) or **C3** (2.168(3) Å),

which may be due to electron-withdrawing effect of the *ortho*-group in the benzene ring.

### 3.3. Ethylene oligomerization and polymerization

All of the complexes were tested for ethylene reactivity with various cocatalysts in toluene under both ambient pressure and 10 atm.

#### 3.3.1. The effect of different cocatalysts on ethylene reactivity

The chromium complex **C1** was used to select suitable reaction parameters. It was found to be inactive for ethylene polymerization without cocatalyst. When combined with various organo-aluminum compounds such as modified methylaluminoxane (MMAO), diethylaluminum chloride (DEAC), ethylaluminum dichloride (EADC) and triethylaluminum (TEA) in toluene, **C1** showed different behavior for ethylene polymerization. The **C1**/MMAO, **C1**/EADC, **C1**/MAO systems showed considerable activity for ethylene polymerization at 1 atm ethylene, while the **C1**/DEAC and **C1**/TEA system were not effective for ethylene polymerization under the same conditions (Table 3). Moreover, among the active systems, the **C1**/EtAlCl<sub>2</sub> system showed the highest activity for ethylene polymerization, and the other two catalytic systems produced polymers along with some oligomers. The difference of the catalytic activity when different cocatalysts are employed may imply that the initial formation of active Cr species is involved with alkylation by alkylaluminum cocatalyst, which was discussed previously [14].

Therefore, EtAlCl<sub>2</sub> is selected as the cocatalyst for the further study and discussion.

#### 3.3.2. The effect of Al/Cr on ethylene reactivity and properties of resulting polymers

To probe the effects of reaction parameters on the ethylene reactivity, polymerization behavior was typically investigated via changing the amounts of EtAlCl<sub>2</sub>, reaction temperature, reaction solvent, reaction time and ethylene pressure.

The effect of the Al/Cr ratio on the polymerization activity was investigated with **C1** and the results are shown in Table 3. With Al/Cr molar ratios in the range of 50–300, the system demonstrated fairly high catalytic activity. The increase in the Al/Cr ratio to 1000 led to noticeable increase in polymerization activity; however, further increase led to a slight decrease in the activity. This correlation between the polymer productivity and the Al/Cr molar ratio suggests that the chain transfer to aluminum might occur with a consequence effect of ceased polymer chain pregnancy [15]. In addition, The  $M_w$  value decreased rapidly and the narrower molecular distribution was observed upon increase in the Al/Cr molar ratio for complex **C1** (entries 9, 11, 12 in Table 3), also corroborating to some extent the occurrence of chain transfer to Al. The Al/Cr ratio had little effect on the  $T_m$  of resultant polyethylene.

#### 3.3.3. The effect of reaction temperature on ethylene reactivity and properties of resultant polymers

The effect of temperature on polymerization activity was investigated with **C3** and the results are shown in Table 4.

Table 3  
The result of **C1** with different cocatalysts for ethylene polymerization<sup>a</sup>

Entry	Cocatalyst	Al/Cr	Oligomer activity <sup>b,c</sup>	Polymer			
				Activity <sup>b</sup>	$M_w^d (\times 10^4)$	$M_w/M_n^d (\times 10^4)$	$T_m$ (°C) <sup>e</sup>
1	Et <sub>2</sub> AlCl	50	– <sup>f</sup>	–			
2	Et <sub>2</sub> AlCl	150	–	Trace			
3	Et <sub>2</sub> AlCl	500	–	Trace			
4	MMAO	500	41.3	1.26	n.d. <sup>g</sup>	n.d.	130.1
5	MMAO	1000	24.8	2.16	n.d.	n.d.	129.0
6	MMAO	1500	42.2	2.14	n.d.	n.d.	128.7
7	EtAlCl <sub>2</sub>	50	–	Trace			
8	EtAlCl <sub>2</sub>	150	–	Trace			
9	EtAlCl <sub>2</sub>	300	–	1.18	7.06	5.46	132.9
10	EtAlCl <sub>2</sub>	500	–	2.90	n.d.	n.d.	132.0
11	EtAlCl <sub>2</sub>	1000	–	3.61	5.07	5.21	132.4
12	EtAlCl <sub>2</sub>	1500	–	2.64	2.38	3.84	131.5
13	Et <sub>3</sub> Al	100	–	Trace			
14	Et <sub>3</sub> Al	300	3.29	Trace			
15	Et <sub>3</sub> Al	500	25.3	Trace			
16	Et <sub>3</sub> Al	1000	–	Trace			
17	MAO	1000	4.37	1.28	n.d.	n.d.	134.2

<sup>a</sup> General condition: 5 μmol complex; ethylene pressure 1 atm; temperature 25 °C; 0.5 h; toluene 30 ml.

<sup>b</sup> 10<sup>4</sup> g mol<sup>-1</sup>(Cr)h<sup>-1</sup>.

<sup>c</sup> Determined by GC and GC–MS.

<sup>d</sup> Determined by GPC.

<sup>e</sup> Determined by DSC.

<sup>f</sup> No activity.

<sup>g</sup> Not determined.

Table 4  
The result of complexes with EtAlCl<sub>2</sub> for polymerization of ethylene at 1 atm<sup>a</sup>

Entry	Complex	°C	t (min)	Polymerization			
				Activity <sup>b</sup>	M <sub>w</sub> <sup>c</sup> (×10 <sup>4</sup> )	M <sub>w</sub> /M <sub>n</sub>	T <sub>m</sub> <sup>d</sup> (°C)
1	<b>C1</b>	25	30	3.69	5.07	5.21	132.4
2	<b>C2</b>	25	30	4.88	3.12	5.46	131.0
3	<b>C3</b>	25	30	5.46	3.01	4.19	132.4
4	<b>C4</b>	25	30	5.11	2.87	5.21	131.4
5	<b>C5</b>	25	30	5.60	4.08	5.00	131.6
6	<b>C6</b>	25	30	7.4	6.82	15.92	131.5
7	<b>C3</b>	0	30	2.40	10.6	3.12	134.1
8	<b>C3</b>	40	30	5.22	0.54	4.67	107.2, 125.9 <sup>e</sup>
9	<b>C3</b>	60	30	1.78	0.10	1.91	77.3, 105.4 <sup>e</sup>
10	<b>C3</b>	25	60	6.60	n.d.	n.d.	n.d. <sup>f</sup>
11	<b>C3</b>	25	120	6.00	n.d.	n.d.	132.7
12 <sup>g</sup>	<b>C3</b>	25	30	Trace	n.d.	n.d.	n.d.
13 <sup>h</sup>	<b>C3</b>	25	30	3.0	n.d.	n.d.	134.9
14 <sup>i</sup>	<b>C3</b>	25	30	Trace	n.d.	n.d.	n.d.

<sup>a</sup> General conditions: 5 μmol complex; 1 atm ethylene pressure; 30 ml toluene.

<sup>b</sup> 10<sup>4</sup> g mol<sup>-1</sup>(Cr) h<sup>-1</sup>.

<sup>c</sup> Determined by GPC.

<sup>d</sup> Determined by DSC.

<sup>e</sup> Broad melting peak.

<sup>f</sup> Not determined.

<sup>g</sup> Solvent dichloromethane.

<sup>h</sup> Solvent chlorobenzene.

<sup>i</sup> Solvent hexane.

Comparing the data (entries 3, 7–9 in Table 4), we observed that the catalytic activities increased gradually to maximum value and then decreased rapidly with increasing reaction temperature, which is very different from our previous result [13c]. This phenomenon can be explained as follows: at lower temperature, the pre-catalyst might not be fully activated, while the catalytic species are possibly unstable and solubility of ethylene in toluene is lower at higher temperature.

However, the reaction temperature had a remarkable effect on the T<sub>m</sub>, molecular weight and molecular weight distribution of the resultant polyethylenes. Increasing the temperature from 0 to 60 °C, the T<sub>m</sub> of the resultant polyethylene decreased rapidly and the DSC curves gave broader melting peaks. Meanwhile, the molecular weight of the polymers also decreased sharply from (10.6 to 0.10) × 10<sup>4</sup>. The GPC traces (as shown in Fig. 4) clearly displayed the decreasing trends of molecular weights, which can be explained by frequent β-hydride elimination at elevated temperature. At 40 °C, the molecular weight trace of produced PE displayed bimodal behavior with broad molecular weight distribution, which might be attributed to the formation of different active species after activation by EtAlCl<sub>2</sub> [16]. Some literature also reported that chain transfer to aluminum might result in broad multimodal distribution of PE [17].

### 3.3.4. The effect of reaction time and solvent on ethylene reactivity and properties of resulting polymers

Higher catalytic activity is observed at reaction time of 60 min compared with 30 min (Table 4, entries 3 and 10), which indicates the existence of the induction period. The effect of solvent on the catalytic activity was studied with **C3** and the results (Table 4) showed that **C3** exhibited higher activity of ethylene

polymerization in toluene (entry 3) than in other solvents such as dichloromethane and chlorobenzene (entries 12–14).

### 3.3.5. The effect of ethylene pressure on ethylene reactivity and properties of resulting polymers

The results of polymerizations performed under 10 atm pressure employing complexes **C1**–**C6** are summarized in Table 5. The data indicated that the ethylene pressure considerably influenced the yields, molecular weights and molecular weight distributions of the resultant polymers. First, significant increment in the productivities of the catalysts were observed (**C5**: 5.60 × 10<sup>4</sup> g mol<sup>-1</sup>(Cr) h<sup>-1</sup>

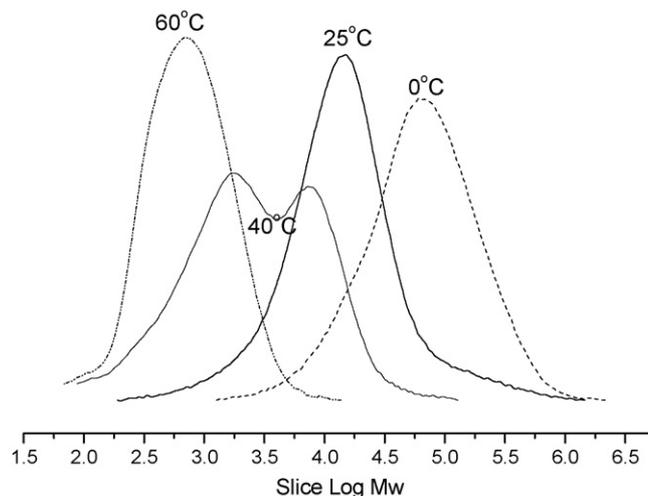


Fig. 4. GPC curves of the polyethylene obtained by **C3** at different temperatures (entries 3, 7–9 in Table 4).

Table 5

The result of complexes with EtAlCl<sub>2</sub> for polymerization of ethylene at 10 atm<sup>a</sup>

Entry	Complex	Ethylene pressure	Polymerization			
			Activity <sup>b</sup>	$M_w^c$ ( $\times 10^4$ )	$M_w/M_n$	$T_m^d$ ( $^\circ\text{C}$ )
1	<b>C1</b>	10	1.47	12.1	3.57	133.9
2	<b>C2</b>	10	1.52	n.d.	n.d.	134.5
3	<b>C3</b>	10	2.08	10.7	3.24	134.6
4	<b>C4</b>	10	1.73	n.d.	n.d.	134.1
5	<b>C5</b>	10	2.33	8.10	2.87	134.4
6	<b>C5</b>	5	1.76	4.54	3.36	133.9
7	<b>C6</b>	10	1.70	n.d.	n.d.	134.4

n.d., not determined.

<sup>a</sup> General conditions: 5  $\mu\text{mol}$  complex; temperature 25  $^\circ\text{C}$ ; reaction time 0.5 h; 100 ml toluene.<sup>b</sup>  $10^5 \text{ g mol}^{-1}(\text{Cr})\text{h}^{-1}$ .<sup>c</sup> Determined by GPC.<sup>d</sup> Determined by DSC.

at 1 atm;  $1.76 \times 10^5 \text{ g mol}^{-1}(\text{Cr})\text{h}^{-1}$  at 5 atm;  $2.33 \times 10^5 \text{ g mol}^{-1}(\text{Cr})\text{h}^{-1}$  at 10 atm). When the corresponding data in Tables 4 and 5 are compared, higher  $M_w$  and narrower distribution were observed for most complexes at higher pressure. The GPC traces shown in Fig. 5 clearly illustrated that higher pressure led to higher molecular weight, which is attributed to the faster rates of ethylene insertion and alkyl chain propagation at a higher ethylene concentration (pressure) [16]. In addition, the  $T_m$  of the resultant polymers at 10 atm ranged from (133.9 to 134.6)  $^\circ\text{C}$ ; these  $T_m$ s are higher than those of polyethylenes at 1 atm (range from 131.5 to 132.4  $^\circ\text{C}$ ).

### 3.3.6. The effect of ligands environment on ethylene reactivity and properties of resulting polymers

The data listed in Table 4 (at 1 atm) and 5 (at 10 atm) showed that the structure of the ligands considerably affected their polymerization activities and the properties of the resulting polyethylenes. These complexes provided an insight into the steric and electronic effects on the catalyst behavior. Catalytic activity for the N<sup>^</sup>N<sup>^</sup>O coordinated chromium systems is largely

dependent on the size of the *ortho*-substituents of the imino-aryl ring. Contrary to the results reported by Small et al. [12d], the polymerization activities varied in the orders of **C1** < **C2** < **C3** and **C4** < **C5** < **C6** (either at 1 atm or at 10 atm), which may contribute to the more readily deactivation of the active species due to the smaller size of the substituents on the *ortho*-position of the benzene ring. Gibson reported that the catalytic precursors containing the pyridylimine ligands lacking sufficient steric bulk in the *ortho*-aryl positions are more easily deactivated through an interaction with alkylaluminum reagents [18]. In general, the complexes containing the halides showed slightly higher activity than complexes with alkyl-substituents, which may be due to a more electrophilic chromium center induced by the electron-withdrawing substituents. This caused an enhancement of the interaction between the chromium atom and the  $\pi$ -electrons of the ethylene monomer, which resulted in accelerated ethylene insertion in the growing step [19].

The ligand environment also affected the  $M_w$  and  $M_w/M_n$  of the obtained polymer. The methyl-substituted catalyst produced higher molecular weight ( $M_w$ ) than the isopropyl-substituted system (both in 1 and 10 atm). This is surprising in comparison with previous reports that demonstrated a higher molecular weight for polyethylenes produced with bulkier ligands. However, in our study, repeated ethylene polymerizations demonstrated consistent results for both the catalyst activity and the molecular weight of the obtained polyethylenes, which is in agreement with the results obtained with its iron analogue [13b]. Especially for **C6** (entry 6 in Table 3), the  $M_w$  and  $M_w/M_n$  are much higher than those of the other complexes. The real reason is unclear. In addition, under the same condition, the ligand environment showed only little effect on the  $T_m$  of the resulting polymer.

## 4. Conclusions

The octahedral chromium(III) complexes ligated by 2-carboxy-6-iminopyridines were synthesized and characterized. The polymerization behavior of these chromium complexes was highly dependent on the cocatalysts employed and reaction conditions. Notable catalytic activity was observed in

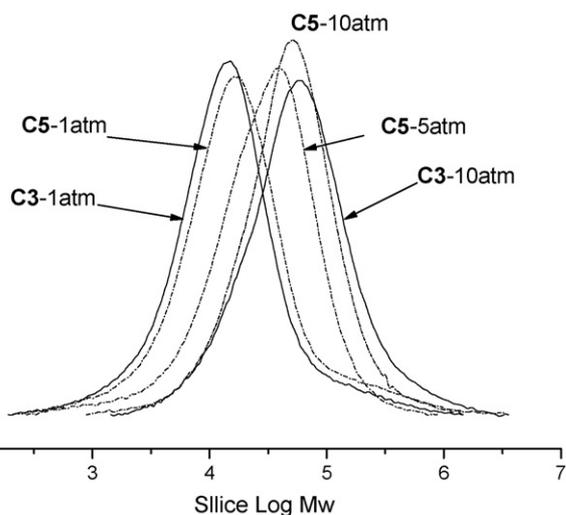


Fig. 5. GPC curves of the polyethylene obtained by both **C3** and **C5** at different pressures.

the presence of  $\text{EtAlCl}_2$  and the resultant polyethylenes were obtained with different molecular weights ( $(0.9\text{--}12) \times 10^4$ ) and broad distributions (1.91–15.92). The polymerization conditions and catalysts greatly affected the catalytic activity and the properties for the resultant polyethylenes. The molecular weight can be thus controlled by choosing the suitable reaction conditions and catalyst.

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