



Chromium(III) complexes bearing 2-benzoxazolyl-6-arylimino-pyridines: Synthesis and their ethylene reactivity

Rong Gao^a, Tongling Liang^a, Fosong Wang^a, Wen-Hua Sun^{a,b,*}

^a Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^b State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

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ABSTRACT

A series of chromium(III) complexes bearing 2-benzoxazolyl-6-aryliminopyridines was synthesized and characterized by IR spectroscopic and CHN analysis. The X-ray crystallographic analysis of complex **Cr3** revealed a distorted octahedral geometry. When activated by Et₂AlCl, MAO or MMAO, these chromium complexes exhibited activities towards ethylene reactivity. High activities of ethylene oligomerization (up to $9.19 \times 10^6 \text{ g mol}^{-1} (\text{Cr}) \text{ h}^{-1}$) were observed in the catalytic system using MMAO as a cocatalyst, meanwhile good activities of ethylene polymerization were achieved (up to $5.20 \times 10^5 \text{ g mol}^{-1} (\text{Cr}) \text{ h}^{-1}$) by using MAO as a cocatalyst. Various reaction parameters were investigated in detail, and the steric and electronic effects of ligands were discussed.

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1. Introduction

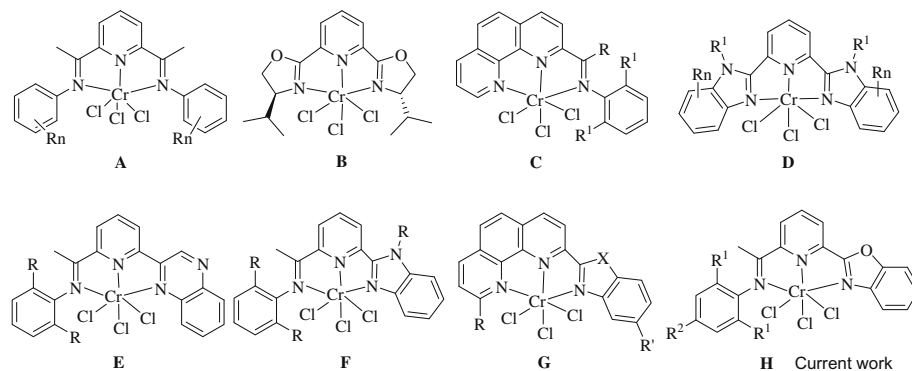
Philips catalyst, based on heterogeneous chromium trioxide, has provided polyethylenes (PE) with unique properties such as suitable for blow-molding process due to the ultra-broad molecular weight distribution of PE [1]. In spite of their practical applications for the last 50 years, the active species and the polymerization mechanism of these catalysts are still unclear [2–4]. It is well known that heterogeneous catalysts result in multi-site active species in olefin polymerization [5–7], however, homogeneous catalysts provide the opportunity in understanding the active species and polymerization/oligomerization mechanism which might be helpful in designing advanced catalysts [8–10]. On the other hand, chromium catalysts are still being the only practicing catalysts for the on-purpose process for ethylene trimerization or tetramerization [11–19]. Therefore it has attracted for designing homogeneous catalysts of chromium complexes through developing multidentate ligands, such as N^N (iminopyrrolide [20,21], β-diketiminato [21–25], bis(phosphoranimine)methanide [26] and bis(imidazole) [27,28]), N^O [29–31], P^P or P^NP [32–39], P^PP [40], N^PN [41], S^NS [34,35,42], N^SN [43], C^NC [44], N^NO [45,46] and N^NN [47], as well as N^NN ligands such as (2-pyridylmethyl)amines [48], bis(imino)pyridines

(**A**, Scheme 1) [45,49–51], bis(oxazolynyl)pyridine (**B**, Scheme 1) [52], 2-imino-1,10-phenanthrolines (**C**, Scheme 1) [53] and 2,6-bis(benzimidazolyl)pyridines (**D**, Scheme 1) [54,55], etc.

In the past few years, we have studied the chromium complexes bearing tridentate ligands such as 2,6-bis(benzimidazolyl)pyridines (**D**, Scheme 1) [55], 2-quinoxalynyl-6-iminopyridine (**E**, Scheme 1) [56], 2-(1R-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines (**F**, Scheme 1) [57,58], and 2-benzazole-1,10-phenanthrolines (X = N, O or S) (**G**, Scheme 1) [59]. All these chromium catalysts showed high productivity in ethylene oligomerization and polymerization. In general, the catalytic activities were fairly affected by varying substituents of ligands within typical complex catalysts. Moreover different hetero-atoms in the frameworks of ligands also significantly affected the catalytic activities. Typically showing in chromium complex catalysts bearing 2-benzazole-1,10-phenanthrolines (X = N, O or S) (**G**, Scheme 1) [59], the catalytic activities strictly followed the trend O > N > S. Enlightened by such tendency as well as the effect of R substituents of ligands of chromium complexes bearing 2-(1R-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines (**F**, Scheme 1) [57,58] on catalytic activity for ethylene oligomerization and polymerization, herein activity of chromium complexes ligated by 2-(2-benzoxazolyl)-6-(1-(arylimino)ethyl)pyridines was necessarily considered. The 2-(2-benzoxazolyl)-6-(1-(arylimino)ethyl)pyridines were previously prepared and used for preparing nickel complexes, which performed high activity in ethylene oligomerization [60]. In current work, the chromium complexes (**H**, Scheme 1) were synthesized by reacting 2-benzoxazolyl-6-iminopyridines with chromium trichloride in dichloromethane. Employing cocatalyst, either

* Corresponding author. Address: Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. Tel.: +86 10 62557955; fax: +86 10 62618239.

E-mail address: whsun@iccas.ac.cn (W.-H. Sun).



Scheme 1. Representative catalysts of chromium complexes.

methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), these chromium complexes indeed showed high productivity in ethylene oligomerization and polymerization. Herein, the synthesis and characterization of these titled chromium complexes are reported, and their catalytic behaviors towards ethylene reactivity are discussed along with various reaction conditions.

2. Results and discussion

2.1. Synthesis and characterization of chromium complexes

A series of 2-(2-benzoxazolyl)-6-(1-(arylimino)-ethyl)pyridine (**L1–L6**) derivatives was prepared following previously reported procedures [60]. The chromium complexes **Cr1–Cr6** were prepared by the stoichiometric reactions of $\text{CrCl}_3 \cdot 3\text{THF}$ and corresponding ligands in dichloromethane (Scheme 2). After mixing both solutions, its color changed immediately into green, and some precipitates were observed. The reaction mixture was stirred at room temperature for 6 h to insure the reaction completion. Diethyl ether was added to further precipitate dissolved chromium complex in dichloromethane solution. The green solids were collected by filtration, washed with diethyl ether and dried under vacuum. All the complexes are air-stable powders and characterized by FT-IR spectroscopy. Elemental analysis confirmed that the complexes are in LCrCl_3 composition. From FT-IR analysis, $\text{C}=\text{N}$ stretching frequencies of **Cr1–Cr6** are shifted into lower values ($1618\text{--}1619\text{ cm}^{-1}$) comparing to those of the free ligands ($1644\text{--}1651\text{ cm}^{-1}$).

In addition, the structure of complex **Cr3** was confirmed by single-crystal X-ray diffraction. Single-crystals of **Cr3** were grown from their dichloromethane solutions layered with diethyl ether. The molecular structures were determined by X-ray diffraction. Selected bond lengths and angles are collected in Table 1. In the molecular structure of **Cr3** (Fig. 1), three coordinated nitrogen atoms and three chlorides are situated around the chromium center in a meridional manner. The N(2), N(3), Cl(2) and Cl(3) atoms

Table 1

Selected bond lengths (Å) and angles ($^\circ$) for complex **Cr3**.

Cr(1)–N(1)	2.012(3)	Cr(1)–N(2)	2.080(3)
Cr(1)–N(3)	2.122(3)	Cr(1)–Cl(1)	2.261(1)
Cr(1)–Cl(3)	2.318(1)	Cr(1)–Cl(2)	2.349(1)
O(1)–C(6)	1.351(4)	O(1)–C(5)	1.397(5)
C(12)–N(3)	1.283(4)	N(2)–C(6)	1.299(4)
N(1)–Cr(1)–N(2)	77.77(1)	N(1)–Cr(1)–N(3)	77.35(1)
N(2)–Cr(1)–N(3)	155.02(1)	N(1)–Cr(1)–Cl(1)	177.84(1)
N(2)–Cr(1)–Cl(1)	102.10(9)	N(3)–Cr(1)–Cl(1)	102.85(8)
N(1)–Cr(1)–Cl(3)	87.68(1)	N(2)–Cr(1)–Cl(3)	85.99(9)
N(3)–Cr(1)–Cl(3)	90.75(9)	Cl(1)–Cr(1)–Cl(3)	94.46(4)
N(1)–Cr(1)–Cl(2)	84.67(9)	N(2)–Cr(1)–Cl(2)	83.77(9)
N(3)–Cr(1)–Cl(2)	96.16(9)	Cl(1)–Cr(1)–Cl(2)	93.18(5)
Cl(3)–Cr(1)–Cl(2)	168.31(4)		

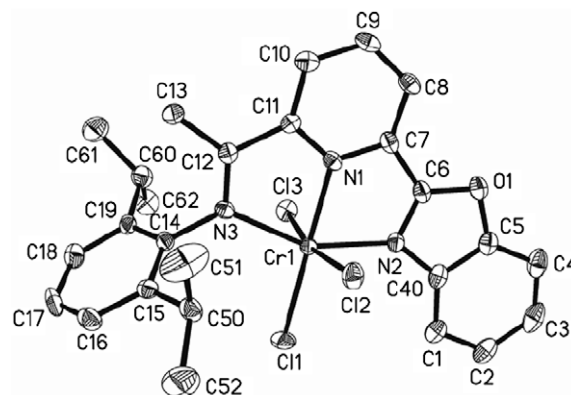
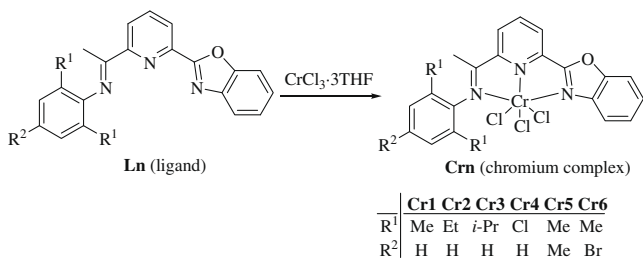


Fig. 1. Molecular structure of **Cr3**. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms and solvent have been omitted for clarity.

locate in an equatorial plane, and the two axial bonds nearly form a straight angle ($\text{N}(1)\text{--Cr}(1)\text{--Cl}(1)$, $177.84(1)^\circ$). Most of bond angles in the equatorial plane are close to right angle ($\text{N}(2)\text{--Cr}(1)\text{--Cl}(2)$, $83.77(9)^\circ$; $\text{Cl}(2)\text{--Cr}(1)\text{--N}(3)$, $96.16(9)^\circ$; $\text{N}(3)\text{--Cr}(1)\text{--Cl}(3)$, $90.75(9)^\circ$; $\text{N}(2)\text{--Cr}(1)\text{--Cl}(3)$, $85.99(9)^\circ$). The axial bond $\text{Cr}(1)\text{--N}(1)$ (pyridine) length ($2.012(3)\text{ \AA}$) is 0.07 \AA shorter than the $\text{Cr}(1)\text{--N}(2)$ (benzoxadazole) bond length ($2.080(3)\text{ \AA}$) and about 0.11 \AA shorter than the $\text{Cr}(1)\text{--N}(3)$ (arylimino) bond length ($2.122(3)\text{ \AA}$).

The values of three $\text{Cr}\text{--Cl}$ bond lengths are close to each other, where the $\text{Cr}(1)\text{--Cl}(1)$ bond ($2.261(1)\text{ \AA}$) located at *trans* position to N(1) being shorter than $\text{Cr}(1)\text{--Cl}(2)$ ($2.349(1)\text{ \AA}$) and $\text{Cr}(1)\text{--Cl}(3)$ ($2.318(1)\text{ \AA}$) bond at *cis* position. The imino $\text{N}(3)\text{--C}(12)$ bond length is $1.283(4)\text{ \AA}$, proving typical $\text{C}=\text{N}$ bond character. The phenyl ring linking to the imino group orients nearly perpendicularly to the coordination plane with dihedral angle of 77.8° . Similar



Scheme 2. Synthesis of chromium complexes.

phenomena have been observed in reported chromium complexes ligated by bis(imino)pyridine [45,49,56], 2-carboxy-6-imino-pyridines [46], 2-benzimidazolyl-6-aryliminopyridine [57,58], 2-quinoxaliny-6-iminopyridine [56] and 2-imino-1,10-phenanthrolines [53].

Interestingly, each of the pyridine ring overlaps with another benzoxazole ring of the contiguous chromium complex in a “face-to-face” fashion, with the relevant plane-to-plane distance of 3.43 Å, and center-to-center distance of 4.52 Å (Fig. 2). The well-stacked structure in the solid state is formed by self-assembly of molecules driven by intermolecular π - π stacking. Similar observations were found in their nickel analogues [60].

2.2. Ethylene oligomerization and polymerization

2.2.1. Cocatalyst selection

The effects of different cocatalysts on ethylene reactivity were initially investigated to choose the most suitable cocatalyst. In general, title complexes showed low activity at ambient pressure, therefore, we tested their performance in ethylene activation at 10 atm of ethylene pressure. The chromium(III) complex **Cr1** was evaluated with various organoaluminium compounds such as methylaluminoxane (MAO), modified methylaluminoxane (MMAO) and Et_2AlCl (Table 2). The catalytic system with Et_2AlCl showed low activity in ethylene oligomerization, but good activity in ethylene polymerization. However, high productivity could be achieved by the catalytic system of complex **Cr1** combined with MAO or MMAO. It might be attributed to different steric effect and alkylating capability of employed cocatalysts, which resulted in various chain-transfer rates to aluminum. Therefore, further investigations were carried out with cocatalyst as either MMAO or MAO.

2.2.2. Ethylene oligomerization and polymerization with cocatalyst of MMAO

2.2.2.1. Effects of the molar ratio of Al/Cr and reaction temperature. The influences of Al/Cr molar ratio and reaction temperature on ethylene reactivity were studied with **Cr1**/MMAO system. Increasing the Al/Cr molar ratio from 500 to 1000, its productivity of ethylene oligomerization and polymerization greatly enhanced (entries 1–3, Table 3). However, further increasing the Al/Cr molar ratio to 1200 resulted in lower activities of both oligomerization and polymerization of ethylene (entry 4, Table 3). The distribution of oligomers and α -olefin selectivity were less affected by the Al/Cr

Table 2

Selection of suitable cocatalyst based on **Cr1**.^a

Entry	Cocat.	Al/Cr	Oligomer activity ^b	Polymer activity ^c
1	MAO	1000	1.56	5.20
2	MMAO	1000	6.44	0.17
3	Et_2AlCl	200	trace	1.70

^a Conditions: 5 μmol of **Cr1**; 10 atm ethylene; 30 min, 60 °C; 100 mL toluene.

^b In units of $10^6 \text{ g mol}^{-1} (\text{Cr}) \text{ h}^{-1}$.

^c Polymerization activity: $10^5 \text{ g mol}^{-1} (\text{Cr}) \text{ h}^{-1}$

molar ratio. In view of these observations, further experiments were performed at molar ratio of Al/Cr at 1000.

Due to the high selectivity of α -olefins in resultant oligomers, the obtained polyethylenes are generally considered of high linearity. DSC analysis reveals that there are several compositions in obtained polymers, including a main peak around 122–128 °C and broad shoulders range from 90 to 110 °C. Changing the Al/Cr molar ratios from 500 to 1200, the profile of DSC curves is similar except for the main peak position. The phenomena demonstrate that polyethylenes have different components, which also have been observed in our previous research [53,57,58] and literatures [51,61–64]. The broad molecular weight distribution of polymers is in agreement with the wide distribution of oligomers, therefore, it is meaningless to measure their molecular weights and distributions by gel permeation chromatography (GPC).

Elevating the reaction temperature from 20 to 60 °C, production of oligomers markedly increased (entries 3 and 5–8, Table 3). However, ethylene polymerization activity first increased then decreased with best activity observed at 40 °C. This phenomenon is similar with chromium complexes ligated by 2,6-bisbenzimidazolylpyridine [55], but it is different from chromium(III) complexes bearing 2-benzimidazolyl-6-aryliminopyridine [57,58] which perform best activity at 20 °C. Further increasing the reaction temperature to 70 °C, both oligomerization and polymerization of the ethylene decreased. It is due to the decomposition of some active species and lower ethylene solubility [10,65] at higher temperature. Meanwhile formation of polyethylene was further decreased due to faster β -hydrogen elimination than chain propagation at higher temperature. Moreover, the selectivity for α -olefin decreased along with reaction temperatures elevated from 20 to 70 °C, and this could be attributed to the faster chain transfer or isomerization at higher temperature.

Elevating the reaction temperature from 20 to 40 °C shows a little change on the melting point of the polyethylenes (entries 5–7, Table 3). Further increasing the reaction temperature up to 70 °C, melting points of the polyethylenes decrease from 128.4 to 124.0 °C (entries 3 and 8–9, Table 3). This can be attributed to faster chain transfer or termination rate at higher temperature making the polymers with low melting points. In general, optimum condition with best productivity was observed at 60 °C regarding to its activity and selectivity of α -olefins. Therefore, more investigations of other complexes were carried out at 60 °C.

2.2.2.2. Lifetime of active species. It is one of the most important factors of any catalyst remaining active in reasonable period for its feasibility of industrial applications. Therefore the effect of reaction time on catalytic activity was studied using the **Cr1**/MMAO system with an Al/Cr molar ratio of 1000 at 60 °C. Within 60 min, the catalytic productivity decreased along with extending reaction time from 20 min to 60 min (entries 3, and 10–13, Table 3). Increasing the reaction time from 20 to 60 min, the main peaks of the DSC curves for the resultant polyethylenes first increased then decreased with broad shoulders at lower temperature. Similar phenomena were also observed in polyethylenes obtained by

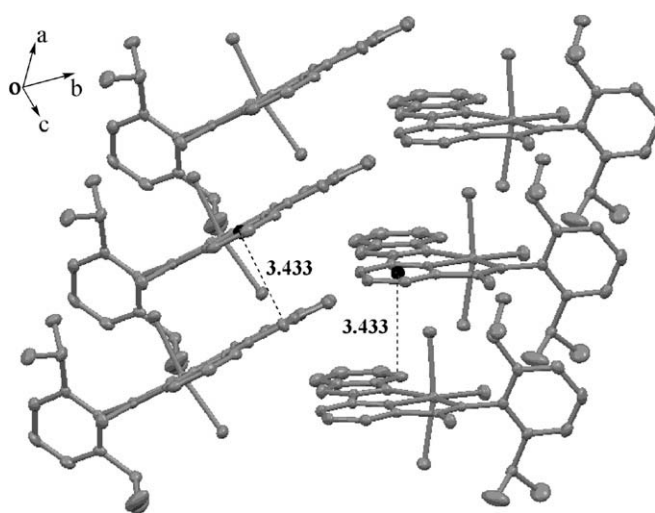


Fig. 2. A view of the stacking interactions in complex **Cr1**.

Table 3
Polymerization and oligomerization of ethylene with **Cr1**/MMAO.^a

Entry	Al/Cr	t (min)	T (°C)	Oligomer distribution (%) ^b				Polyethylene		
				C ₄ /ΣC	C ₆ /ΣC	C _{≥8} /ΣC	α-C ₄ (%)	A ₀ ^c	A _p ^d	T _m (°C) ^e
1	500	30	60	64.7	26.4	8.9	97.9	4.55	0.40	122.4
2	800	30	60	69.0	23.8	7.2	98.2	5.37	0.54	123.8
3	1000	30	60	66.9	25.0	8.1	98.0	6.44	1.71	125.3
4	1200	30	60	64.9	26.7	8.4	98.2	5.09	0.79	123.6
5	1000	30	20	–	–	–	–	Trace	0.62	128.5
6	1000	30	30	73.4	26.6	0	99.2	0.86	1.07	128.5
7	1000	30	40	68.6	24.9	6.5	98.6	3.62	11.4	128.4
8	1000	30	50	65.6	26.2	8.2	97.5	4.46	6.36	125.4
9	1000	30	70	62.9	27.1	10.0	97.9	4.08	0.32	124.0
10	1000	20	60	80.1	19.9	0	99.6	9.19	1.86	122.4
11	1000	40	60	63.8	27.0	9.2	98.2	5.31	1.65	123.5
12	1000	50	60	65.2	26.8	8.0	97.9	4.52	1.64	124.0
13	1000	60	60	64.6	26.4	9.0	97.2	3.82	1.60	124.0

^a Conditions: 5 μmol of **Cr1**; 10 atm ethylene; 100 mL toluene.^b Determined by GC; ΣC denotes the total amounts of oligomers.^c Oligomerization activity: 10⁶ g mol⁻¹ (Cr) h⁻¹.^d Polymerization activity: 10⁴ g mol⁻¹ (Cr) h⁻¹.^e Determined by DSC.

chromium(III) catalysts bearing 2-benzimidazolyl-6-arylimino-pyridine [57] and 2-benzazole-1,10-phenanthrolines [59].

2.2.2.3. Effect of the ligand environment. Upon activation with modified methylaluminoxane (MMAO), all the chromium complexes exhibited good activities towards ethylene oligomerization and moderate activity towards ethylene polymerization. As shown in Table 4 (entries 1–6), the ligand environment, regarding to their substituents on aryl ring linked to imino-N atom, has great influences on the catalytic behaviors of chromium complexes on ethylene reactivity. The chromium complexes (**Cr1–Cr3**) containing bulky alkyl-substituents at the *ortho*-positions of the aryl rings showed lower activity. It might be explained that bulkier substituents slow down ethylene coordination and hinder chain propagation. These results were consistent with the results obtained with their analogues [50,57,58]. Meanwhile complexes bearing halogen groups on the imino-N aryl ring showed lower activity in ethylene activation as well as lower α-olefin selectivity and higher portion of C₄ fraction in the oligomers. These results agreed with our previous computational conclusion on the relationship of catalytic activity with the net charge of early-transition metal complexes. The electron-withdrawing substituents will increase the positive charge of the center metal, enhance the M–R bond strength and make the insertion of ethylene harder, which results in lower catalytic activity for olefin activation [66]. In addition, complexes **Cr5** and **Cr6** possessing a substituent at the *para*-position of the imino-N aryl ring exhibited much lower activity and produced fewer

Table 4
Polymerization and oligomerization of ethylene with **Cr1–Cr4**/MMAO.^a

Entry	Cat.	Oligomer distribution (%) ^b				Polyethylene		
		C ₄ /ΣC	C ₆ /ΣC	C _{≥8} /ΣC	α-C ₄ (%)	A ₀ ^c	A _p ^d	T _m (°C) ^e
1	Cr1	66.9	25.0	8.1	98.0	6.44	1.71	125.3
2	Cr2	64.4	26.0	9.6	98.5	4.64	1.14	121.4
3	Cr3	73.0	21.6	5.4	98.6	4.33	1.00	129.8
4	Cr4	87.5	11.2	1.3	94.2	4.02	1.90	119.9
5	Cr5	68.6	24.3	7.1	97.6	4.88	0.73	128.8
6	Cr6	70.6	21.4	8.0	97.7	3.07	0.62	125.7

^a Conditions: 5 μmol of catalyst; 1000 equiv. of MMAO; 10 atm ethylene; 60 °C; 30 min; 100 mL toluene.^b Determined by GC.^c Oligomerization activity: 10⁶ g mol⁻¹ (Cr) h⁻¹.^d Polymerization activity: 10⁴ g mol⁻¹ (Cr) h⁻¹.^e Determined by DSC.

polymers in the products than that of the corresponding complexes **Cr1**. The current observations are different to the results observed from the chromium(III) complexes bearing bis(imino)pyridines [50], 2-benzimidazolyl-6-aryliminopyridine [57,58] and 2-benzazole-1,10-phenanthrolines [59]. This may be due to the introduction of a substituent in the *para*-position of the imino-N aryl ring affected the solubility of complexes in toluene solvent, which influenced their behavior in ethylene activation.

Compared with chromium(III) complexes bearing 2-benzimidazole-6-(1-aryliminoethyl)pyridines (best activity at 20 °C) [57,58], the title complexes present higher catalytic activities for ethylene oligomerization, as well as better thermal stability at 60 °C, however, chromium(III) complexes bearing 2-benzimidazole-6-(1-aryliminoethyl)pyridines showed best activity at 20 °C. Similar trends also had been observed in chromium complexes ligated by 2-benzazolyl-1,10-phenanthrolines [59]. The introduction of benzoxazole substituent on the ligand backbone is helpful in increasing the stability of the active center. And similar phenomenon also have been observed in the nickel analogues ligated by 2-benzimidazole-6-(1-aryliminoethyl)pyridines [60].

2.2.3. Ethylene oligomerization and polymerization with MAO as cocatalyst

According to data listed in Table 2, MAO was proved to be the best activator for ethylene polymerization, but showed lower productivity (oligomers and polymers) compare to **Cr1**/MMAO system. So we investigated the influences of reaction temperature on ethylene reactivity with **Cr1**/MMAO system. Varying molar ratio of MAO/**Cr1**, the best performance happened at 1000 of the Al/Cr molar ratio. Elevating the reaction temperature from 20 to 70 °C, the activities for both oligomerization and polymerization were first increased and then decreased with optimum condition at 60 °C (Table 5). In general, the activities of ethylene polymerization with MAO are more than ten times higher than the catalytic system with MMAO under same reaction conditions. It might be attributed to the trace amount of more bulky isobutyl group in MMAO that generated species which hindered the insertion reaction of ethylene [67,68]. In addition, different alkylating and chain-transfer rate between MMAO and MAO also lead to different ethylene activities showed by **Cr1**/MMAO and **Cr1**/MAO. It is common to see that the selectivity for α-olefin decreased with elevating reaction temperature from 20 to 70 °C.

The melting points of polyethylenes obtained by **Cr1**/MAO systems (entries 1–5, Table 5) are around 133.1–133.4 °C which are

Table 5
Polymerization and oligomerization of ethylene with **Cr1**/MAO.^a

Entry	T (°C)	Oligomer distribution (%) ^b				Polyethylene		
		C ₄ / ΣC	C ₆ / ΣC	C ₈ / ΣC	α-C ₄ (%)	A _o ^c	A _p ^d	T _m (°C) ^e
1	20	63.7	32.7	3.6	100	0.02	0.80	133.4
2	40	63.1	26.4	10.5	99.6	0.15	1.20	133.2
3	50	63.8	26.6	9.6	99.4	0.89	3.44	133.1
4	60	64.2	26.6	9.2	99.4	1.56	5.20	133.4
5	70	60.5	27.9	11.6	98.7	0.63	3.00	133.2

^a Conditions: 5 μmol of **Cr1**; 10 atm ethylene; 1000 equiv. of MAO; 30 min; 100 mL toluene.

^b Determined by GC.

^c Oligomerization activity: 10⁶ g mol⁻¹ (Cr) h⁻¹.

^d Polymerization activity: 10⁵ g mol⁻¹ (Cr) h⁻¹.

^e Determined by DSC.

Table 6
Crystal data and structure refinement details for **Cr3**.

Cr3 ·CH ₂ Cl ₂	
Empirical formula	C ₂₇ H ₂₉ Cl ₅ CrN ₃ O
Formula weight	640.78
T (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2 ₁ /n
a (Å)	8.0537(16)
b (Å)	33.997(7)
c (Å)	10.516(2)
α (°)	90
β (°)	97.14(3)
γ (°)	90
V (Å ³)	2857.0(10)
Z	4
D _{calc} (Mg m ⁻³)	1.490
μ (mm ⁻¹)	0.895
F(0 0 0)	1316
Crystal size (mm)	0.35 × 0.31 × 0.04
θ range (°)	2.04–25.00
Limiting indices	−9 ≤ h ≤ 9; −40 ≤ k ≤ 38; −12 ≤ l ≤ 12
Number of reflections collected	9576
Number of unique reflections	5013
Completeness to θ (%)	99.5 (θ = 25.00°)
Absorption correction	Multi-scan
Number of parameters	334
Goodness of fit (GOF) on F ²	1.137
Final R indices (I > 2σ(I))	R ₁ = 0.0544, wR ₂ = 0.1010
R indices (all data)	R ₁ = 0.0919, wR ₂ = 0.1099
Largest difference peak and hole (e Å ⁻³)	0.549, −0.427

higher than 124–128.5 °C observed for polyethylenes by **Cr1**/MAO systems. The melting curves show a narrower peak for each sample, indicating the crystalline properties of resultant polyethylenes, which were quite similar and little affected by varying reaction temperatures from 20 to 70 °C. The molecular weights of polyethylenes were not measured by GPC because it is not commercially considerable for the catalytic system produced polyethylenes in good activity with oligomers as a trouble.

3. Conclusion

The newly synthesized chromium complexes bearing 2-benzoxazolyl-6-aryliminopyridines displayed high activities up to 9.19 × 10⁶ g mol⁻¹ (Cr) h⁻¹ for ethylene oligomerization upon treatment with MMAO. The substituents on either *ortho*- or *para*-position of aryl ring linked on imino-N atoms affected the catalytic activities of chromium complexes, in which the activity is favored

with less bulky substituent on *ortho*-position of imino-N aryl rings. Meanwhile lower catalytic activity for ethylene activation was observed by introducing chlorine atom at the *ortho*- or bromine atom at the *para*-position of imino-N aryl rings. Using MAO as a cocatalyst, the **Cr1** displayed good activities up to 5.20 × 10⁵ g mol⁻¹ (Cr) h⁻¹ for ethylene polymerization.

4. Experimental

4.1. General considerations

All manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium-benzophenone and distilled under argon prior to use. Methylaluminoxane (MAO, a 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane, 3A) were purchased from Akzo Nobel Corp. Diethylaluminum chloride (Et₂AlCl, 1.7 M in toluene) was purchased from Acros Chemicals. Other reagents were purchased from Beijing Chemicals. FT-IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using an HPMOD 1106 microanalyzer. GC analyses were performed with a Varian CP-3800 gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) CP-Sil 5 CB column. The yield of oligomers was calculated by referencing with the mass of the solvent on the basis of the prerequisite that the mass of each fraction was approximately proportional to its integrated areas in the GC trace. Selectivity for the linear α-olefin was defined as (amount of linear α-olefin of all fractions)/(total amount of oligomer products) in percent. Melting points of the polymers were obtained on a Perkin-Elmer DSC-7 instrument in the standard DSC run mode. The instrument was initially calibrated for the melting point of an indium standard at a heating rate of 50 °C/min. The polymer sample was first equilibrated at 50 °C and then heated to 160 °C at a rate of 30 °C/min to remove thermal history. The sample was then cooled to 50 °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.

4.2. Synthesis of chromium complexes

4.2.1. General procedure

A solution of CrCl₃·3THF in dichloromethane was added dropwise to a solution of the ligand in dichloromethane. The reaction mixture was stirred at room temperature for 6 h then some precipitate formed. The resulting precipitate was collected, washed with diethyl ether and dried in vacuum. All of the complexes were prepared in high yield using the same procedure.

4.2.2. (E)-2,6-dimethyl-N-(1-(6-(benzoxazol-2-yl)pyridin-2-yl)-ethylidene)benzenamine CrCl₃ (**Cr1**)

Obtained as green powder in 98.0% yield. FT-IR (KBr; cm⁻¹): 1618(ν_{C=N}) (m), 1565 (w), 1536 (m), 1446 (m), 1382 (s), 1283 (m), 1213 (w), 1037 (w), 858 (w), 791 (m), 770 (s). Anal. Calc. for C₂₂H₁₉Cl₃CrN₃O (499.76): C, 52.87; H, 3.83; N, 8.41. Found: C, 52.54; H, 4.04; N, 8.22%.

4.2.3. (E)-2,6-diethyl-N-(1-(6-(benzoxazol-2-yl)pyridin-2-yl)-ethylidene)benzenamine CrCl₃ (**Cr2**)

Obtained as green powder in 95.4% yield. FT-IR (KBr; cm⁻¹): 1619(ν_{C=N}) (m), 1563 (w), 1537 (m), 1446 (m), 1386 (vs), 1283 (s), 1212 (w), 1037 (w), 858 (w), 790 (m), 763 (s). Anal. Calc. for C₂₄H₂₃Cl₃CrN₃O (527.81): C, 54.61; H, 4.39; N, 7.96. Found: C, 54.77; H, 4.51; N, 8.04%.

4.2.4. (E)-2,6-diisopropyl-N-(1-(6-(benzoxazol-2-yl)pyridin-2-yl)-ethylidene)benzenamine CrCl₃ (**Cr3**)

Obtained as green powder in 96.6% yield. FT-IR (KBr; cm⁻¹): 1618($\nu_{C=N}$) (m), 1560 (w), 1535 (m), 1446 (m), 1384 (vs), 1281 (m), 1180 (w), 1040 (w), 850 (w), 787 (s), 758 (s). Anal. Calc. for C₂₆H₂₇Cl₃CrN₃O (555.87): C, 56.18; H, 4.90; N, 7.56. Found: C, 56.42; H, 5.11; N, 7.48%.

4.2.5. (E)-2,6-dichoro-N-(1-(6-(benzoxazol-2-yl)pyridin-2-yl)-ethylidene)benzenamine CrCl₃ (**Cr4**)

Obtained as green powder in 90.8% yield. FT-IR (KBr; cm⁻¹): 1619($\nu_{C=N}$) (m), 1564 (w), 1536 (m), 1434 (s), 1386 (s), 1284 (m), 1088 (w), 1036 (w), 861 (w), 788 (s). Anal. Calc. for C₂₀H₁₃Cl₄CrN₃O (540.6): C, 44.43; H, 2.42; N, 7.77. Found: C, 44.57; H, 2.64; N, 7.62%.

4.2.6. (E)-2,4,6-trimethyl-N-(1-(6-(benzoxazol-2-yl)pyridin-2-yl)-ethylidene)benzenamine CrCl₃ (**Cr5**)

Obtained as green powder in 91.2% yield. FT-IR (KBr; cm⁻¹): 1619($\nu_{C=N}$) (m), 1566 (w), 1536 (m), 1444 (m), 1386 (vs), 1282 (m), 1219 (m), 1036 (m), 856 (w), 759 (s). Anal. Calc. for C₂₃H₂₁Cl₃CrN₃O (513.79): C, 53.77; H, 4.12; N, 8.18. Found: C, 53.46; H, 4.41; N, 8.22%.

4.2.7. (E)-4-bromo-2,6-dimethyl-N-(1-(6-(benzoxazol-2-yl)pyridin-2-yl)ethylidene)benzenamine CrCl₃ (**Cr6**)

Obtained as green powder in 88.0% yield. FT-IR (KBr; cm⁻¹): 1619($\nu_{C=N}$) (m), 1563 (w), 1535 (m), 1445 (s), 1386 (s), 1282 (m), 1180 (w), 1036 (w), 851 (w), 788 (s). Anal. Calc. for C₂₂H₁₈BrCl₃CrN₃O (578.66): C, 45.66; H, 3.14; N, 7.26. Found: C, 45.78; H, 3.22; N, 7.37%.

4.3. Crystal structure determination

Single-crystal of **Cr3** suitable for X-ray diffraction studies were obtained by slow evaporation of diethyl ether to its methanol solution. Single-crystal X-ray diffraction studies for **Cr3** were carried out on a Rigaku RAXIS Rapid IP diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). 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. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package [69]. Crystal data and processing parameters for **Cr3** are summarized in Table 6.

4.4. General procedure for ethylene activation

Ethylene oligomerization at 10 atm ethylene pressure was carried out in a 500 ml autoclave stainless steel reactor equipped with a mechanical stirrer and a temperature controller. Briefly, toluene, the desired amount of cocatalyst, and a toluene solution of the catalytic precursor (the total volume was 100 mL) were added to the reactor in this order under an ethylene atmosphere. When the desired reaction temperature was reached, ethylene at 10 atm pressure was introduced to start the reaction, and the ethylene pressure was maintained by constant feeding of ethylene. After 30 min, the reaction was stopped. A small amount of the reaction solution was collected, the reaction was terminated by the addition of 5% aqueous hydrogen chloride, and then this mixture was analyzed by gas chromatography (GC) to determine the distribution of oligomers obtained. The remaining solution was quenched with HCl-acidified ethanol (5%), and the precipitated polyethylene was

filtered, washed with ethanol, and dried under vacuum at 60 °C to constant weight.

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Appendix A. Supplementary material

CCDC 733233 contains the supplementary crystallographic data for **Cr3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.07.039.

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