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Synthesis, characterization and ethylene oligomerization and polymerization of 2-(*1H*-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridylchromium chlorides

Liwei Xiao [a,*], Min Zhang [b], Wen-Hua Sun [b]

[a] *Department of Chemistry, Langfang Teacher's College, Langfang 065000, China*
[b] *Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

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ABSTRACT

A series of N^N^N tridentate chromium complexes (**C1**–**C6**) bearing 2-(*1H*-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridine derivatives was synthesized and characterized by elemental and spectroscopic analysis along with single-crystal X-ray crystallography. X-ray crystallographic analyses reveal chromium complex **C1** as a distorted six-coordinated octahedral geometry. On treatment with modified methylaluminoxane (MMAO), the chromium complexes exhibited high activities for ethylene oligomerization (up to 1.50×10^6 g mol^{-1} (Cr) h^{-1}) and polymerization (up to 2.06×10^6 g mol^{-1} (Cr) h^{-1}) at 10 atm ethylene pressure. Various reaction parameters were investigated in detail, and less steric hindrance and electron-withdrawing substituents of ligands enhance the catalytic activities of their chromium complexes.

1. Introduction

Chromium is the key element in the silica-supported Phillips [1] and Union Carbide [2–4] catalytic systems commercially used for the polymerization of olefins. The importance of these catalysts has drawn much attention in developing Cr(III) complexes ligated by a variety of ligands, including both cyclopentadienyl-based [5–16] and non-cyclopentadienyl-based systems [17–31]. Cp-free complexes are quite prone to steric and electronic modifications, chromium complexes are capable of producing oligomers and/or polymers with different properties [32–34]. Various chromium complexes coordinated by anionic ligands have been explored such as monodentate Cr–pyrrolyl complexes [35] and different multi-chelate models such as N^O [23–25], N^N [19–22,36–38], N^N^N [26]. Moreover, chromium complexes containing various P^P or P^N^P [39–46], P^P^P [47], S^N^S [41,42,47], C^N^C [48], N^N^O [31,49], N^S^N [50] and N^N^N^N [51] ligands have also been investigated. Recently, chromium complexes ligated with neutral N^N^N ligands, such as triazacyclohexane [26,27], bis(imino)pyridines [30,31,52], (2-pyridylmethyl)amines [53], bis(oxazolinyl)pyridine [54], bis(benzimidazolyl)pyridines [55,56], tridentate pyrazolyl ligand [57] and 2,6-bis(azolylmethyl)pyridine [58] have attracted great attentions due to their highly catalytic activities in ethylene oligomerization and polymerization. In our course of developing new chromium complexes as catalysts for ethylene reactivity, chromium complexes containing N^N^N ligands (Scheme 1) such as 2,6-bis(2-benzimidazolyl)pyridine (A) [55], 2-imino-1,10-phenanthrolines (B) [59], 2-quinoxalinyl-6-iminopyridine (C) [60] and 2-(1-isopropyl-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines (D) [61] showed good catalytic activities towards ethylene oligomerization or/and polymerization. Regarding to catalytic behaviors showed by other metal complexes, the metal complexes bearing 2-(1-methyl-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridine (E) [62,63] showed better activities than their analogues with 1-isopropyl group (D) [64]. Recently, the iron(II) and cobalt(II) complexes bearing 2-(*1H*-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridyl derivatives [65] showed better activities than their alkylated analogues (D and E) [62,64]. These results indicated that the alkyl groups on benzimidazole of ligands greatly affect the catalytic performance of metal complexes. Comparing with chromium complexes containing 1-isopropyl group on benzimidazole of ligands [61], a series of chromium (III) complexes bearing (2-(*1H*-2-benzimidazolyl)-6-(1-(arylimino)-ethyl)pyridines is synthesized and characterized. The investigation of their catalytic activities towards ethylene reactivity shows better results than the performance by their analogues [61]. Herein we report the synthesis and characterization of the chromium complexes bearing 2-(*1H*-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines. Furthermore, their catalytic behaviors towards ethylene oligomerization and polymerization are investigated in detail under different reaction conditions.

2. Experimental

2.1. General considerations

All manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed and distilled over

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[*] Corresponding author. Tel.: +86 316 2188617; fax: +86 10 62618239.
E-mail address: xiaoliwei2000@sina.com (L. Xiao).

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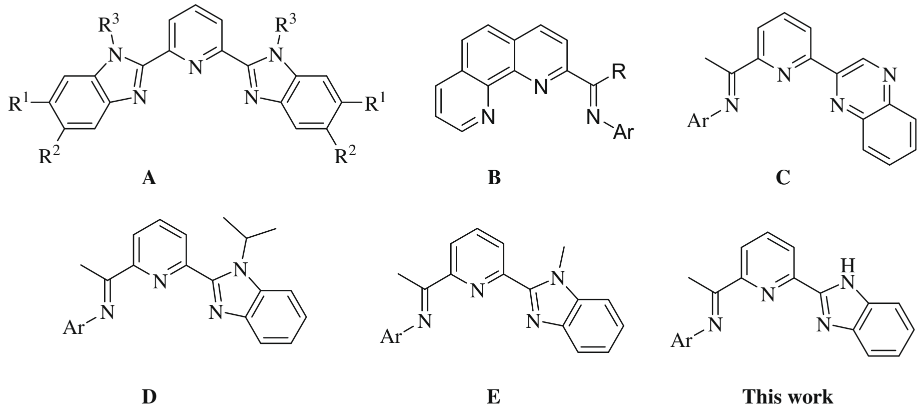


Scheme 1. Model ligands for effective chromium catalysts.

sodium and benzophenone, while dichloromethane was dried and distilled over CaH_2. Methylaluminoxane (MAO) was purchased from Lanzhou Research Center of PetroChina, while modified methylaluminoxane (MMAO) and diethylaluminumchloride (Et_2AlCl) were purchased from Akzo Nobel Corp. and Acros Chemicals, respectively. 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 analysis was performed with a VARIAN CP-3800 gas chromatograph equipped with a flame ionization detector and a 30 m (0.2 mm i.d., 0.25 μm film thickness). The selectivity for the linear α-olefin was defined as (amount of linear α-olefin of all fractions)/(total amount of oligomer products) in percentage. The resultant solution of ethylene reactivity was quenched with 5% HCl–acidic ethanol. The precipitated polyethylene (PE) was collected by filtration, washed with ethanol, dried under vacuum at 60 °C to constant weight, weighed and characterized. Melting points of PEs were measured on a Perkin–Elmer DSC-7 differential scanning calorimetry (DSC) analyzer. Under a nitrogen atmosphere, a sample of about 4 mg was heated from 20 to 160 °C at a rate of 10 °C/min and kept for 5 min at 160 °C in order to remove the thermal history, then cooled at a rate of 10 °C/min to 20 °C. The DSC trace and the melting points of the samples were obtained from the second scanning run.

2.2. Preparation of chromium(III) complexes C1–C6

The ligands **L1**–**L6** were prepared according to our previous work [65]. Complexes **C1**–**C6** were synthesized by the reaction of $CrCl_3(THF)_3$ with the corresponding ligands in dichloromethane. A typical synthetic procedure for **C1** is as follows: ligand **L1** (0.15 g, 0.44 mmol) prior dissolved in a minimum volume of CH_2Cl_2 was added to a solution of $CrCl_3(THF)_3$ (0.16 g, 0.44 mmol) in CH_2Cl_2 (10 ml), and the mixture was stirred at room temperature for 9 h. The solvent was then removed *in vacuo* to afford a green solid, which was washed with hexane and dried *in vacuo.* The complex **C1** was obtained as green powder (0.20 g, 0.40 mmol) in 91%. IR (KBr; cm^{-1}): 3386(br m), 3056(s), 2952(w), 2911(w), 1591(s), 1480(s), 1416(s), 1373(m), 1322(m), 1300(w), 1276(w), 1216(w), 1096(m), 1038(m), 857(w), 793(m), 754(vs). Anal. Calc. for $C_{22}H_{20}Cl_3CrN_4$ (498.78): C, 52.98; H, 4.04; N, 11.23. Found: C, 53.03; H, 4.06; N, 11.18%.

C2: Green powder, 87% yield. IR (KBr; cm^{-1}): 3386(br m), 3062(s), 2966(s), 2909(w), 1590(s), 1480(s), 1456(s), 1417(vs), 1371(s), 1322(m), 1301(w), 1277(w), 1236(w), 1037(w), 985(w), 858(w), 815(m), 791(m), 753(vs). Anal. Calc. for $C_{24}H_{24}Cl_3CrN_4$ (526.83): C, 54.72; H, 4.59; N, 10.63. Found: C, 54.67; H, 4.53; N, 11.68%.

C3: Green powder, 91% yield. IR (KBr; cm^{-1}): 3392(br m), 3067(m), 2967(s), 2926(w), 1591(s), 1494(m), 1417(s), 1367(s), 1322(m), 1300(w), 1275(w), 1234(w), 1132(w), 1056(w), 855(w), 815(m), 806(m), 754(vs). Anal. Calc. for $C_{26}H_{28}Cl_3CrN_4$ (554.88): C, 56.28; H, 5.09; N, 10.10. Found: C, 56.34; H, 5.14; N, 10.04%.

C4: Green powder, 83% yield. IR (KBr; cm^{-1}): 3406(br m), 3065(m), 2953(w), 2915(w), 1586(s), 1481(vs), 1419(vs), 1371(m), 1321(m), 1277(w), 1216(m), 1154(m), 1038(w), 853(m), 816(w), 752(vs). Anal. Calc. for $C_{23}H_{22}Cl_3CrN_4$ (512.8): C, 53.87; H, 4.32; N, 10.93. Found: C, 53.82; H, 4.29; N, 10.99%.

C5: Green powder, 82% yield. IR (KBr; cm^{-1}): 3388(br m), 3067(m), 2973(m), 1589(s), 1482(s), 1435(vs), 1369(m), 1322(m), 1278(w), 1230(m), 1097(w), 860(w), 817(m), 786(m), 750(vs). Anal. Calc. for $C_{20}H_{14}Cl_5CrN_4$ (539.61): C, 44.52; H, 2.62; N, 10.38. Found: C, 44.57; H, 2.58; N, 10.32%.

C6: Green powder, 85% yield. IR (KBr; cm^{-1}): 3570(br w), 3062(m), 2972(w), 1601(m), 1482(m), 1427(s), 1369(s), 1320(w), 1225(m), 1113(w), 858(w), 820(w), 763(m), 747(vs). Anal. Calc. for $C_{20}H_{14}Br_2Cl_3CrN_4$ (628.52): C, 38.22; H, 2.25; N, 8.91. Found: C, 38.16; H, 2.20; N, 8.95%.

2.3. Procedure for oligomerization and polymerization at 1 atm ethylene

The catalyst precursor was dissolved in 30 ml toluene in a Schlenk tube stirred under nitrogen atmosphere with a magnetic stirrer, and the reaction temperature was controlled by a water bath. The reaction was initiated by adding the desired amount of cocatalyst under ethylene atmosphere. After the desired time, a small amount of the reaction solution was collected with a syringe and was quenched by the addition of 5% aqueous HCl. Analysis by gas chromatography (GC) was carried out to determine the distribution of oligomers formed. The remaining solution was quenched with 5% HCl–acidic ethanol, and the precipitated polyethylene was collected by filtration, washed with ethanol, dried under vacuum at 60 °C to constant weight, weighed, and finally characterized.

2.4. Procedure for oligomerization and polymerization at 10 atm ethylene

These reactions were carried out in a 250 ml stainless steel autoclave reactor equipped with a mechanical stirrer and a temperature controller. The desired amount of cocatalyst, a toluene solution of the chromium complex (30 ml), and toluene (70 ml) were added to the reactor in this order under an ethylene atmosphere. When the reaction temperature was achieved, ethylene at the desired pressure (10 atm) was introduced to start the

Table 1
Crystal data and structure refinement for **C1**.

	C1
Formula	$C_{22}H_{20}Cl_3CrN_4{\cdot}DMF$
Formula weight	571.87
Temperature (K)	133(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	*P2(1)/c*
a (Å)	9.3944(2)
b (Å)	13.999(2)
c (Å)	19.920(3)
α (°)	90
β (°)	97.825(3)
γ (°)	90
Volume (Å^3)	2595.4(8)
Z	4
D_{calcd} (g m^{-3})	1.464
μ (mm^{-1})	0.778
F (0 0 0)	1180
Crystal size (mm)	0.17 × 0.13 × 0.05
θ range (°)	3.09–25.50
Limiting indicates	$-11 \leqslant h \leqslant 11$
	$-16 \leqslant k \leqslant 16$
	$-23 \leqslant l \leqslant 24$
Number of reflections collected	18 237
number of unique reflections	4825
R_{int}	0.0433
Completeness to θ (%)	99.7% (θ = 25.50°)
Absorption correction	empirical
Number of parameters	325
Goodness-of-fit (GOF) on F^2	1.064
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0511
	wR_2 = 0.1306
R indices (all data)	R_1 = 0.0579
	wR_2 = 0.1351
Largest difference in peak and hole (e Å^{-3})	0.324, –0.334

reaction. After 30 min, a small amount of the reaction solution was collected. The reaction was terminated by the addition of 5% aqueous HCl and the mixture was analyzed by the gas chromatography (GC) to determine the distribution of oligomers obtained. The remaining solution was quenched with HCl–acidified ethanol (5%) The precipitated polymer was collected by filtration, washed with ethanol, dried under vacuum at 60 °C to constant weight, weighed, and finally characterized.

2.5. X-ray crystallographic studies

Single-crystal X-ray diffraction measurement for **C1** was carried out Rigaku AFC10 Saturn 724+ diffractometer with graphite-monochromated Mo Kα radiation (λ = 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 hydrogen atoms except of H_{4N} (bond to N4) were placed in calculated positions; the H_{4N} was located from difference map and freely refined. Structure solution and refinement were performed by using the SHELXL-97 package [66]. Crystal data and processing parameters for complexes **C1** are summarized in Table 1.

3. Results and discussion

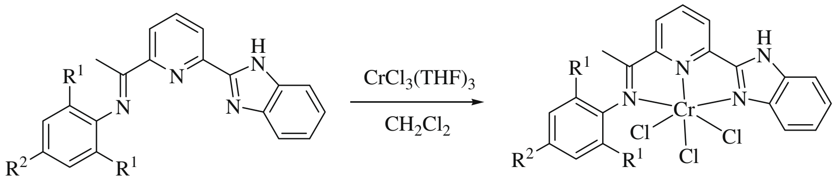
3.1. Synthesis and characterization of the chromium complexes *C1–C6*

2-(*1H*-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridylchromium(III) trichlorides **C1–C6** were prepared through the treatment of 2-(*1H*-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridyl derivatives with 1 equiv. of $CrCl_3(THF)_3$ in CH_2Cl_2 at room temperature (Scheme 2). The resultant products were isolated as air-stable green powders in good yields and characterized by IR spectra and elemental analysis.

The identity of the complexes **C1–C6** was established based on IR spectroscopic and element analysis. Compared to the IR spectra of the free ligands **L1–L6** [65], the C═N stretching vibrations in complexes **C1–C6** were shifted to lower frequencies in the range of 1586–1601 cm^{-1}, indicating an effective coordination interaction between the imino nitrogen atom and the chromium center. In addition, crystals of **C1** have been subject to single-crystal X-ray diffraction studies.

3.2. Molecular structure

Crystals of complex **C1** suitable for X-ray structure determination were grown from its *N*,*N*-dimethylformamide (DMF) solutions layered with diethyl ether. The molecular structure of complex **C1** is depicted in Fig. 1. In the molecular structure of complex **C1** (Fig. 1), the crystal structure of **C1** confirms its geometry as a distorted octahedron and the three coordinated nitrogen atoms and the three chlorides are situated around the chromium center in a meridional manner. The N1, N3, Cl1, and Cl3 atoms could be located in the equatorial plane with a mean deviation of 0.1835 Å, and the two axial bonds nearly form a straight line through the metal center (N(2)–Cr(1)–Cl(2), 178.38(8)°). All the bond angles in the equatorial plane are very close to a right angle (N(3)–Cr(1)–Cl(1), 93.35(7)°; N(3)–Cr(1)–Cl(3), 90.35(7)°; N(1)–Cr(1)–Cl(1), 86.62(8)°; N(1)–Cr(1)–Cl(3), 87.67(8)°). The axial Cr(1)–N(2) bond length (2.016(3) Å) is shorter by 0.036 Å than the Cr(1)–N(1) bond length (2.052(3) Å) and by 0.1379 Å than the Cr(1)–N(3) bond length (2.154(2) Å), which is in accordance with some other chromium complexes [57,58]. The Cr–Cl bond lengths span a relatively narrow range with the Cr(1)–Cl(2) bond (2.2787(9) Å) located at a *trans* position to N(2) being slightly shorter than the Cr(1)–Cl(1) (2.3321(9) Å) and Cr(1)–Cl(3) (2.3157(9) Å) bonds in the *cis*-position. A similar phenomenon was observed with the reported bis(imino)pyridine chromium complexes [30,31,52]. The imino N(3)–C(13) bond length is 1.291(4) Å with the typical character of a C═N double bond. The



L1–L6

	C1	C2	C3	C4	C5	C6
R^1	Me	Et	*i*-Pr	Me	Cl	Br
R^2	H	H	H	Me	H	H

Scheme 2. Preparation of chromium complexes **C1–C6**.

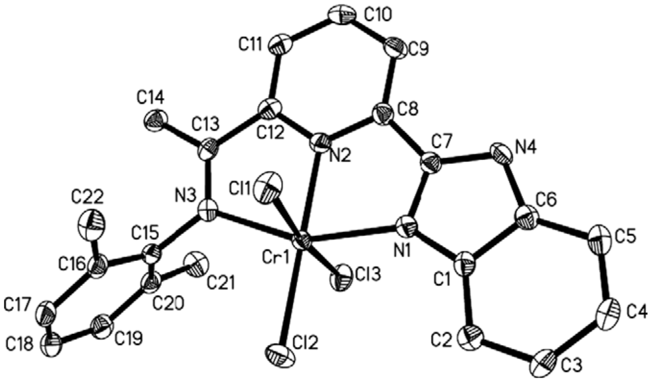


Fig. 1. ORTEP drawing complex **C1** with thermal ellipsoids at the 50% probability. Hydrogen atoms and solvent (DMF) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Cr(1)–N(1) = 2.052(3), Cr(1)–N(2) = 2.016(3), Cr(1)–N(3) = 2.154(2), Cr(1)–Cl(1) = 2.3321(9), Cr(1)–Cl(2) = 2.2787(9), Cr(1)–Cl(3) = 2.3157(9), N(1)–C(1) = 1.385(4), N(1)–C(7) = 1.329(4), N(2)–C(8) = 1.343(4), N(2)–C(12) = 1.346(4), N(3)–C(13) = 1.291(4), N(3)–C(15) = 1.462(4); N(1)–Cr(1)–N(2) = 78.28(1), N(1)–Cr(1)–N(3) = 154.61(1), N(2)–Cr(1)–N(3) = 76.39(1), N(1)–Cr(1)–Cl(1) = 86.62(8), N(2)–Cr(1)–Cl(1) = 86.52(7), N(3)–Cr(1)–Cl(1) = 93.35(7), Cl(1)–Cr(1)–Cl(2) = 92.07(3), N(1)–Cr(1)–Cl(2) = 100.85(8), N(2)–Cr(1)–Cl(2) = 178.38(8), N(3)–Cr(1)–Cl(2) = 104.52(7), N(2)–Cr(1)–Cl(3) = 88.98(7), N(1)–Cr(1)–Cl(3) = 87.67(8), N(3)–Cr(1)–Cl(3) = 90.35(7), Cl(2)–Cr(1)–Cl(3) = 92.35(3), and Cl(3)–Cr(1)–Cl(1) = 173.34(4).

atoms of the pyridine ring and C(13), N(3) of the imino group as well as the chromium atom form a plane. The mean deviation is 0.028 Å with the largest deviation from the plane being 0.0628 Å at Cr(1). The phenyl ring linking to the imino group is oriented nearly perpendicularly to the coordination plane with a dihedral angle of 98.4°.

3.3. Ethylene oligomerization and polymerization

3.3.1. The selection of cocatalysts

Complex **C1** was used as model catalyst to select suitable reaction parameters. When the catalyst was combined with various organoaluminium compounds such as methylaluminoxane (MAO), modified methylaluminoxane (MMAO) or diethylaluminium chloride (Et_2AlCl), it showed different catalytic performance and the results were collected in Table 2. At ambient pressure, the catalytic system activated with Et_2AlCl only produced butenes in low activity (Entry 1, Table 2). Treatment of complex **C1** with MAO catalyzed ethylene to obtain both oligomers and polymers (Entry 2, Table 2). The activities for both oligomerization and polymerization were further increased when MMAO was employed (Entry 3, Table 2).

Table 2
Effect of cocatalysts on ethylene reactivity[a].

Entry	Cocatalyst	Al/Cr	Oligomer		Polymer
			Distribution[b]	Activity[c]	Activity[c]
1	Et_2AlCl	200	C_4–C_6	5.0	no
2	MAO	1000	C_4–C_{32}	3.5	12.5
3	MMAO	1000	C_4–C_{32}	8.4	17.5

[a] Reaction conditions: 5 μmol **C1**; 1 atm ethylene; 30 min; and 30 mL toluene.
[b] Oligomers distribution determined by GC.
[c] In units of 10^4 g mol^{-1} (Cr) h^{-1}.

3.3.2. Effect of reaction parameters

The influences of the Al/Cr molar ratio and reaction temperature on ethylene reactivity were studied with the **C1**/MMAO system and the results are listed in Table 3. As shown in Table 3, increasing the Al/Cr molar ratio from 500 to 1500 led to great enhancement of both ethylene oligomerization and polymerization activities (Entries 1–3, Table 3). A further increase in the Al/Cr molar ratio to 2000 resulted in decreased oligomerization and polymerization activity (Entry 4, Table 3). However, the distribution of oligomers and the selectivity for α-olefins were not significantly affected by the Al/Cr ratio. At the ratio of Al/Cr 1500, both the productivity and the selectivity for α-olefins reached satisfied results. Therefore, the further experiments were performed with the Al/Cr molar ratio of 1500. It was noteworthy that the oligomer distribution showed an unprecedented small amount of C_6, which makes the distribution of oligomers doesn't follow the Schulz-Flory or Poisson rules. This is similar to the reported observation [61], in which the chromium system showed much lower activity towards ethylene trimerization.

The catalytic system of **C1** with 1500 equiv. of MMAO under 1 atm ethylene was further investigated under different reaction temperatures. As shown in Table 3, it can be found that the activities of both oligomerization and polymerization decreased sharply with the increase of the temperature from 20 to 60 °C, which can be explained by the decomposition of some active species and lower ethylene solubility at higher temperature. In addition, elevation of the temperature from 20 to 60 °C led to a slightly decreased selectivity for α-olefins from 97.5% to 88.7%. This may be attributed to the faster isomerization of α-olefins into internal olefins at elevated temperature, and internal olefins are generally more stable than α-olefins. A similar influence of temperature on the oligomers produced with chromium-based systems has been reported [55,60,61].

3.3.3. Effect of the ligand environment

The alkyl or halogen substituents (R^1) on the imino-N aryl ring had great influence on catalytic performance. For complexes **C1**–**C3**, somewhat reduced catalytic activity was observed for the sterically bulkier catalysts. This was clearly revealed by comparing the 2,6-diisopropyl substituted **C3** with 2,6-dimethyl substituted

Table 3
Selection the optimum condition with **C1**/MMAO at 1 atm ethylene[a].

Entry	Al/Cr	T (°C)	Oligomers distribution[b]						Polyethylene	
			$C_4/\Sigma C$	$C_6/\Sigma C$	$C_8/\Sigma C$	$\geqslant C_{10}/\Sigma C$	α-Olefin%	A_o[c]	A_p[c]	T_m (°C)[d]
1	500	20	17.8	4.8	11.5	65.7	92.8	4.5	8.1	122.3
2	1000	20	16.9	4.9	6.2	72.0	91.4	7.2	16.7	122.4
3	1500	20	19.0	6.8	10.9	63.3	97.5	10.6	20.0	125.0
4	2000	20	22.8	8.4	5.4	62.3	91.6	8.2	12.7	119.7
5	1500	40	19.7	6.5	4.5	69.3	92.3	7.1	8.3	122.4
6	1500	60	35.3	6.4	5.2	43.1	88.7	5.0	5.1	124.3

[a] Reaction conditions: 5 μmol **C1**; MMAO as cocatalyst, 1 atm ethylene; and 30 mL of toluene, 30 min.
[b] Oligomers distribution determined by GC.
[c] In units of 10^4 g mol^{-1} (Cr) h^{-1}.
[d] Determined by DSC.

Table 4
Polymerization and oligomerization with **C1**–**C6**/MMAO at 1 atm ethylene[a].

Entry	Catalyst	Oligomer distribution[b]						Polyethylene	
		$C_4/\Sigma C$	$C_6/\Sigma C$	$C_8/\Sigma C$	$\geqslant C_{10}/\Sigma C$	α-Olefin%	A_o[c]	A_p[c]	T_m (°C)[d]
1	**C1**	19.0	6.8	10.9	63.3	97.5	10.8	20.0	125.0
2	**C2**	17.3	7.3	7.9	67.5	95.4	6.5	14.7	124.6
3	**C3**	22.6	7.0	9.8	60.6	95.5	5.8	11.4	127.6
4	**C4**	13.8	7.8	12.7	65.7	95.4	10.6	26.2	119.3
5	**C5**	23.9	8.9	10.7	56.5	96.1	18.6	23.7	116.8
6	**C6**	21.8	6.6	9.3	60.3	94.5	13.9	20.6	122.3

[a] Reaction conditions: 5 μmol Cr complex; 1 atm ethylene, the ratio of MMAO to chromium complex is 1500, 30 mL toluene, 30 min, 20 °C.
[b] Oligomers distribution determined by GC.
[c] In units of 10^4 g mol^{-1} (Cr) h^{-1}.
[d] Determined by DSC.

C1 or 2,6-diethyl substituted **C2** (Entry 3 versus Entry 1 or 2, Table 4). This can perhaps be attributed to the fact that more bulky isopropyl groups at *ortho*-positions of the imino-N aryl ring on imino-C may prevent the insertion of ethylene to catalytic sites, therefore leading to lower catalytic activity. Complexes **C5** and **C6**, containing 2,6-dihalogen substituted ligands, exhibited relatively higher oligomerization activities than complexes **C1**–**C4** bearing alkyl groups (compare Entry 5 and 6 with Entries 1–4, Table 4). The improved catalytic activity can be ascribed to the more electrophilic nature of the chromium center after the introduction of the electron-withdrawing substituents on the *ortho*-positions of phenyl group. The result is similar to our previous work [61].

As shown in Table 4, the T_m peaks of the resultant polymers obtained at ambient pressure ranged from 116.8 to 127.6 °C, which were lower than those catalyzed by 2-quinoxalinyl-6-iminopyridine chromium complexes [60], which can be mainly ascribed to the lower molecular weights resulted from 2-benzimidazole-6-iminopyridine chromium complexes. Furthermore, the high contents of α-olefins of oligomers obtained partly indicate that the PEs produced may terminate with C=C end group. Due to both oligomers and PEs formed in catalytic system, the GPC measurements for molecular weights and molecular weight distributions of PEs might be not meaningful. It would be next challenge to find suitable reaction conditions for either oligomers or PE in the catalytic system. Regarding to molecular weights of resultant PEs, it is common to accept higher molecular weights corresponded to higher melting points. The PEs obtained by the complexes (**C1**–**C3**) containing 2,6-dialkyl-substituted possessed higher T_m than those by the complexes (**C5** and **C6**) containin 2,6-dihalogen-substituted.

3.3.4. Ethylene oligomerization and polymerization at 10 atm ethylene

The results of catalytic behavior employing **C1**–**C6** under 10 atm ethylene pressure are summarized in Table 5. The data indicated that the ethylene pressure significantly affected the catalytic behavior of all complexes including catalytic activities, oligomer distributions and PE properties. Comparing with the catalytic behavior at ambient pressure (Table 4), the higher catalytic activities along with longer chain oligomers up to the range of C_4–C_{36} could be obtained with increased ethylene pressure. The catalytic activities for both oligomerization and polymerization increased by nearly one order of magnitude at 10 atm ethylene.

The ligand environment has exerted similar influences on catalytic behaviors as those found at ambient pressure. For example, for complexes **C1**–**C3** bearing alkyl-substituted (Entries 1–3, Table 5), more bulky substituents at the *ortho*-positions of the imino-N aryl ring led to decrease of activity. Similar with that of result found at ambient pressure, 2,6-dihalogensubstituted complex **C5** and **C6** showed higher productivity than the 2,6-dialkylsubstituted analogues **C1, C2** and **C3 (**Entries 5 and 6 vs Entries 1–3, Table 5) at 10 atm ethylene pressure.

At 10 atm ethylene, the T_m peak of the resultant polymers obtained at 10 atm ranged from 118.4 to 126.2 °C and the effects of the ligand environments on the T_m values were in accorded with the results at ambient pressure, which indicates the increased ethylene pressure didn't show obvious influence on the thermal properties of PEs obtained (compare Table 4 with Table 5).

It is notable that this series of chromium complexes containing N–H bond on benzimidazole group showed higher activities than those of N–*i*Pr analogues [61]. For instance, under 1 atm ethylene, complexes **C1** containing N–H bond showed combined catalytic productivity up to 3.06×10^5 g mol^{-1} (Cr) h^{-1} (Entry 1: 1.06×10^5 g mol^{-1} (Cr) h^{-1} and 2.00×10^5 g mol^{-1} (Cr) h^{-1} for oligomerization activity and polymerization activity, respectively, Table 4), which is higher than that of its analogue containing isopropyl substituted [61] (5.1×10^4 g mol^{-1} (Cr) h^{-1}, Entry 3, Table 3 in Ref. [61]). Tentatively, these results suggest that N–H functionality is essential for high activity and selectivity with this ligand system, which could be caused by their deprotonation to give anionic amide ligands when activated by MMAO. The anionic amide ligands could be free or form N–Al species (anion–cation pair) to increase their catalytic activity. These results are in agreement with previous literatures [42,55].

Table 5
Polymerization and oligomerization with **C1–C6**/MMAO at 10 atm ethylene[a].

Entry	Catalyst	Oligomer distribution[b]						Polyethylene	
		$C_4/\Sigma C$	$C_6/\Sigma C$	$C_8/\Sigma C$	$\geqslant C_{10}/\Sigma C$	α-Olefin%	A_o[c]	A_p[c]	T_m (°C)[d]
1	**C1**	18.7	7.9	10.6	62.8	95.3	9.2	16.1	120.2
2	**C2**	17.8	6.9	9.5	65.8	97.7	7.1	12.1	121.1
3	**C3**	21.1	13.2	11.1	54.6	95.7	6.8	8.6	126.2
4	**C4**	12.7	6.7	10.2	73.9	96.5	7.8	20.6	122.7
5	**C5**	17.1	9.4	7.5	66.0	96.9	15.0	20.1	118.4
6	**C6**	22.4	8.2	12.5	56.9	96.1	12.5	14.5	123.8

[a] Reaction conditions: 5 μmol cat., 10 atm ethylene, Al/Cr = 1500, 100 mL toluene, 30 min, 20 °C.
[b] Oligomers distribution determined by GC.
[c] In units of 10^5 g mol^{-1} (Cr) h^{-1}.
[d] Determined by DSC.

4. Conclusion

A series of tridentate chromium(III) complexes ligated by 2-(*1H*-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines was prepared and characterized. Upon activation with modified methylalumoxane (MMAO), the chromium complexes afforded good activity for ethylene oligomerization and polymerization. In most cases, polyethylene was major product, meanwhile higher carbon number olefins usually accounted for the majority of the oligomers produced. It was notable that the oligomer distribution does not follow the Schulz-Flory or Poisson rules due to relatively lower amount of C_6. Employing higher ethylene pressure and lower reaction temperature, the catalytic systems generally resulted in higher activities along with better α-olefin selectivities of oligomers. For the complexes (**C1**–**C3**) bearing alkyl-substituted, more bulky substituents at the *ortho*-positions of the imino-N aryl ring led to decrease of their activities. In addition, the complex **C5** and **C6** containing 2,6-dihalogensubstituted showed higher productivity than the analogues **C1, C2** and **C3** having 2,6-dialkylsubstituted. However, reaction parameters and ligand environment exhibited little influences on the α-olefin selectivity and the product (oligomers and PE) compositions.

Supplementary data

CCDC 729547 contains the supplementary crystallographic data for **C1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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References

[1] J.P. Hogan, R.L. Banks, US Patent 2,825,721, Phillips Petroleum Co., 1958.
[2] G.L. Karapinka, Ger. Offen. D.E. 1,808,388, Union Carbide Corp., 1970.
[3] F.J. Karol, G.L. Karapinka, C. Wu, A.W. Dow, R.N. Johnson, W.L. Carrick, J. Polym. Sci., Polym. Chem. Ed. 10 (1972) 2621.
[4] G.L. Karapinka, US Patent 3,709,853, Union Carbide Corp., 1973.
[5] B.J. Thomas, S.K. Noh, G.K. Schulte, S.C. Sendlinger, K.H. Theopold, J. Am. Chem. Soc. 113 (1991) 893.
[6] G. Bhandari, Y. Kim, J.M. McFarland, A.L. Rheingold, K.H. Theopold, Organometallics 14 (1995) 738.
[7] Y. Liang, G.P.A. Yap, A.L. Rheingold, K.H. Theopold, Organometallics 15 (1996) 5284.
[8] P.A. White, J. Calabrese, K.H. Theopold, Organometallics 15 (1996) 5473.
[9] K.H. Theopold, Chemtech 27 (1997) 26.
[10] R. Emrich, O. Heinemann, P.W. Jolly, C. Krüger, G.P.J. Verhownik, Organometallics 16 (1997) 1511.
[11] K.H. Theopold, Eur. J. Inorg. Chem. (1998) 15.
[12] A. Döhring, J. Göhre, P.W. Jolly, B. Kryger, J. Rust, G.P.J. Verhownik, Organometallics 19 (2000) 388.
[13] V.R. Jensen, K. Angermund, P.W. Jolly, K.J. Børve, Organometallics 19 (2000) 403.
[14] A. Döhring, V.R. Jensen, P.W. Jolly, W. Thiel, J.C. Weber, Organometallics 20 (2001) 2234.
[15] M. Enders, P. Fernández, G. Ludwig, H. Pritzkow, Organometallics 20 (2001) 5005.
[16] A. Döhring, V.R. Jensen, P.W. Jolly, W. Thiel, J.C. Weber, in: R. Blom, A. Follestad, E. Rytter, M. Tilset, M. Ystenes (Eds.), Organometallic Catalysts and Olefin Polymerization, Springer-Verlag, Berlin, 2001, p. 127.
[17] M.P. Coles, V.C. Gibson, Polym. Bull. 33 (1994) 529.
[18] M.P. Coles, C.I. Dalby, V.C. Gibson, I.R. Little, E.L. Marshall, M.H. Ribeiro da Costa, S. Mastroianni, J. Organomet. Chem. 591 (1999) 78.
[19] V.C. Gibson, P.J. Maddox, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 1651.
[20] W.-K. Kim, M.J. Fevola, L.M. Liable-Sands, A.L. Rheingold, K.H. Theopold, Organometallics 17 (1998) 4541.
[21] V.C. Gibson, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, Eur. J. Inorg. Chem. (2001) 1895.
[22] L.A. McAdams, W.-K. Kim, L.M. Liable-Sands, A.I. Guzei, A.L. Rheingold, K.H. Theopold, Organometallics 21 (2002) 952.
[23] V.C. Gibson, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans. (1999) 827.
[24] V.C. Gibson, S. Mastroianni, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, Dalton Trans. (2000) 1969.
[25] D.J. Jones, V.C. Gibson, S.M. Green, P.J. Maddox, Chem. Commun. (2002) 1038.
[26] R.D. Köhn, M. Haufe, S. Mihan, D. Lilge, Chem. Commun. (2000) 1927.
[27] R.D. Köhn, M. Haufe, G. Kociok-Köhn, S. Grimm, P. Wasserscheid, W. Keim, Angew. Chem., Int. Ed. 39 (2000) 4337.
[28] R.D. Köhn, G. Seifert, G. Kociok-Köhn, S. Mihan, D. Lilge, H. Mass, in: R. Blom, A. Follestad, E. Rytter, M. Tilset, M. Ystenes (Eds.), Organometallic Catalysts and Olefin Polymerization, Springer-Verlag, Berlin, 2001, p. 147.
[29] H. Ikeda, T. Manoi, Y. Nakayama, H. Yasuda, J. Organomet. Chem. 648 (2002) 226.
[30] M.A. Esteruelas, A.M. López, L. Méndez, M. Oliván, E. Onate, Organometallics 22 (2003) 395.
[31] B.L. Small, M.J. Carney, D.M. Holman, C.E. O'Rourke, J.A. Halfen, Macromolecules 37 (2004) 4375.
[32] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem., Int. Ed. 38 (1999) 428.
[33] V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283.
[34] J.T. Dixon, M.J. Green, F.M. Hess, D.H. Morgan, J. Organomet. Chem. 689 (2004) 3641.
[35] M.E. Lashier, EP Patent 0780353, Phillips Petroleum Company, 1995.;
W.K. Reagan, T.M. Pettijohn, J.W. Freeman, E.A. Benham, US Patent 5786431, Phillips Petroleum Co., 1998.;
M. E. Lashier, EP 0780353A1, Phillips Petroleum Co., 1997.
[36] V.C. Gibson, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, Dalton Trans. (2002) 4017.
[37] L.A. MacAdams, G.P. Buffone, C.D. Incarvito, A.L. Rheingold, K.H. Theopold, J. Am. Chem. Soc. 127 (2005) 1082.
[38] P. Wei, D.W. Stephan, Organometallics 21 (2002) 1308.
[39] A. Carter, S.A. Cohen, N.A. Cooley, A. Murphy, J. Scutt, D.F. Wass, Chem. Commun. (2002) 858.
[40] D.S. McGuinness, P. Wasserscheid, W. Keim, C. Hu, U. Englert, J.T. Dixon, C. Grove, Chem. Commun. (2003) 334.
[41] M.E. Bluhm, O. Walter, M. Döring, J. Organomet. Chem. 690 (2005) 713.
[42] D.S. McGuinness, P. Wasserscheid, D.H. Morgan, J.T. Dixon, Organometallics 24 (2005) 552.
[43] K. Blann, A. Bollmann, J.T. Dixon, F.M. Hess, E. Killian, H. Maumela, D.H. Morgan, A. Neveling, S. Otto, M.J. Overett, Chem. Commun. (2005) 620.
[44] M.J. Overett, K. Blann, A. Bollmann, J.T. Dixon, F. Hess, E. Killian, H. Maumela, D.H. Morgan, A. Neveling, S. Otto, Chem. Commun. (2005) 622.
[45] T. Agapie, S.J. Schofer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 126 (2004) 1304.
[46] A. Bollmann, K. Blann, J.T. Dixon, F.M. Hess, E. Killian, H. Maumela, D.S. McGuinness, D.H. Morgan, A. Neveling, S. Otto, M. Overett, A.M.Z. Slawin, P. Wasserscheid, S. Kuhlmann, J. Am. Chem. Soc. 126 (2004) 14712.
[47] R.J. Baker, P.G. Edwards, Dalton Trans. (2002) 2960.
[48] D.S. McGuinness, V.C. Gibson, D.F. Wass, J.W. Steed, J. Am. Chem. Soc. 125 (2003) 12716.
[49] W. Zhang, W.-H. Sun, X. Tang, T. Gao, S. Zhang, P. Hao, J. Chen, J. Mol. Catal. A: Chem. 265 (2007) 159.
[50] J. Liu, Y. Li, J. Liu, Z. Li, J. Mol. Catal. A: Chem. 244 (2006) 99.
[51] N.J. Robertson, M.J. Carney, J.A. Halfen, Inorg. Chem. 42 (2003) 6876.
[52] Y. Nakayama, K. Sogo, H. Yasuda, T. Shiono, J. Polym. Sci. Part A: Polym. Chem. 43 (2005) 3368.
[53] M.J. Carney, N.J. Robertson, J.A. Halfen, L.N. Zakharov, A.L. Rheingold, Organometallics 23 (2004) 6184.
[54] M.A. Esteruelas, A.M. López, L. Méndez, M. Oliván, E. Oñate, New J. Chem. 26 (2002) 1542.
[55] W. Zhang, W.-H. Sun, S. Zhang, J. Hou, K. Wedeking, S. Schultz, R. Frohlich, H. Song, Organometallics 25 (2006) 1961.
[56] A.K. Tomov, J.J. Chirinos, D.J. Jones, R.J. Long, V.C. Gibson, J. Am. Chem. Soc. 127 (2005) 10166.
[57] J. Zhang, A. Li, T.S. Andy Hor, Organometallics 28 (2009) 2935.
[58] J. Hurtado, D. Mac-Leod, A. Muñoz-Castro, R. Arratia-Pérez, R. Quijada, G. Wu, R. Rojas, M. Valderrama, J. Organomet. Chem. 694 (2009) 2636.
[59] S. Zhang, S. Jie, Q. Shi, W.-H. Sun, J. Mol. Catal. A: Chem. 276 (2007) 174.
[60] S.A. Amolegbe, M. Asma, M. Zhang, G. Li, W.-H. Sun, Aust. J. Chem. 61 (2008) 397.
[61] Y. Chen, W. Zuo, P. Hao, S. Zhang, K. Gao, W.-H. Sun, J. Organomet. Chem. 693 (2008) 750.
[62] W.-H. Sun, P. Hao, S. Zhang, Q. Shi, W. Zuo, X. Tang, Organometallics 26 (2007) 2720.
[63] P. Hao, S. Zhang, W.-H. Sun, Q. Shi, S. Adewuyi, X. Lu, P. Li, Organometallics 26 (2007) 2439.
[64] Y. Chen, P. Hao, W. Zuo, K. Gao, W.-H. Sun, J. Organomet. Chem. 693 (2008) 1829.
[65] L. Xiao, R. Gao, M. Zhang, Y. Li, X. Cao, W.-H. Sun, Organometallics 28 (2009) 2225.
[66] G.M. Sheldrick, SHELXTL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.