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Chromium(III) complexes ligated by 2-(1-isopropyl-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines: Synthesis, characterization and their ethylene oligomerization and polymerization

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Abstract

A series of chromium(III) complexes bearing 2-(1-isopropyl-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines were synthesized and characterized by IR spectroscopic and elemental analysis. The X-ray crystallographic analysis revealed a distorted octahedral geometry of the chromium complexes. When activated by Et_2AlCl, MAO or MMAO, these chromium complexes exhibited catalytic activities for ethylene oligomerization and polymerization; while the good to high activities (up to 3.95×10^6 g mol^{-1} (Cr) h^{-1}) were observed in the catalytic systems with MMAO. Therefore, various reaction parameters of the catalytic system with MMAO were investigated in detail. The steric and electronic effects of ligands affected the catalytic activities and the distribution of the products predominantly. Interestingly, sometimes their distributions of oligomers did not resemble the rules of Schulz-Flory or Poisson due to the hexenes produced in low yield.

Keywords: Chromium complexes; 2-(Benzimidazolyl)-6-iminopyridine; Ethylene oligomerization; Polymerization

1. Introduction

Among all of the synthetic polymers, polyolefins have the largest production volumes [1]. The growing demand for high performance polyolefins has inspired extensively industrial and academic researches in developing new catalysts for polyolefins [2]. Metallocene catalysts, based upon metal complexes, have shown some advantages of producing polyolefins with unique properties [3–6]. Recently common metal complexes as catalysts for olefin polymerization and oligomerization have been attractive of both academic and industrial considerations [6,7].

Chromium-based catalysts have played important roles in commercial polymerization [8] and selective trimerization of ethylene [9,10], which is also an ongoing scale-up process for 1-hexene in Chinese SINOPEC Company. The rapid progress has recently been focused on synthesizing new chromium complexes and investigating their catalytic behaviors toward ethylene reactivity, the numerous chromium complexes have been explored with numerous ligands in several chelate models such as N^O [11,12], N^N [13–15], N^N^N [16,17], P^P^P or P^N^P [18–22], S^N^S [21], C^N^C [23], N^S^N [24], N^N^N^N [25] along with half-metallocene [26]. In order to understand the active species and alternative intermediates of chromium complexes, some chromium complexes containing O^N^N [27] and N^N^N [28] ligands were investigated in our group as the extensive researches of late-transition metal analogues as catalysts in ethylene reactivity [29]. In

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general, the chromium complexes coordinated with N^N^N ligands performed good to high catalytic activities toward ethylene oligomerization and polymerization [28], moreover, their oligomers are highly selected in α-olefins formations even their polyethylenes with vinyl-type characteristics. It is necessary to use MAO or MMAO in those chromium catalytic systems; and the good point is that the process of MAO is well commercialized in PetroChina Company. Indeed, the process for ethylene oligomerization is nowadays under consideration by using chromium catalysts in China. However, the technical problems are still remained with patent issue such as 2,6-bis(2-benzimidazolyl)pyridylchromium trichlorides by two individual groups [27,28a] and scale-up in synthesizing suitable ligands as chromium(III) complexes ligated by 2-imino-1,10-phenanthrolines [28b]. Recently 2-(benzimidazole)-6-(1-arylimino-ethyl)pyridines were synthesized for their late-transition-metal complexes as highly active catalysts toward ethylene oligomerization and polymerization [30], in further extensive research, their chromium analogues were prepared. Our detail investigation revealed that the titled chromium complexes gave good catalytic activities toward ethylene oligomerization and polymerization. Uncommonly, sometimes the distributions of oligomers did not resemble the rules of Schulz-Flory or Poisson, especially for an extraordinary observation of low yield of hexenes. Herein, the syntheses, characterizations of these chromium complexes were reported, and their catalytic properties for ethylene oligomerization and polymerization were investigated under various reaction conditions.

2. Results and discussion

2.1. Synthesis and characterization of 2-(1-isopropyl-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines and their chromium complexes

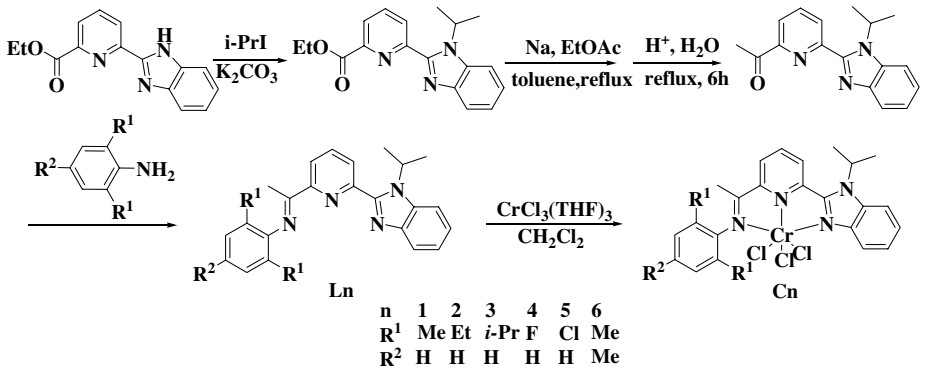
In preparation of 2-(1-isopropyl-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines and their chromium complexes (Scheme 1), the important substance is 2-(2-benzimidazolyl)-6-acetylpyridine, which was made from 2-(carboethoxy)-6-(2-benzimidazolyl)pyridine according to our reported procedure [30a]. The difference is having an isopropyl group in current work as 2-(1-isopropyl-2-benzimidazolyl)-6-acetylpyridine instead of previous one, 2-(1-methyl-2-benzimidazolyl)-6-acetylpyridine [30a]. The 2-(1-isopropyl-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines (**L1**–**L4** and **L6**) were easily prepared in satisfactory yields (51–80%) through the condensation reactions of 2-(1-isopropyl-2-benzimidazolyl)-6-acetylpyridine with the appropriate substituted anilines in the presence of *p*-toluenesulfonic acid as the catalyst. The analogue **L5** with chloride substituents on the phenyl ring, however, was synthesized with adding ethyl silicate as water absorber. All the synthesized organic compounds were well characterized and confirmed by elemental analysis, ^{1}H and ^{13}C NMR and IR. The IR spectra of the N^N^N ligands showed that the C=N stretching frequencies appeared in the range of 1643–1658 cm^{-1} with the typical absorption.

The chromium complexes **C1**–**C6** were prepared by the stoichiometric reaction of $CrCl_3(THF)_3$ with the corresponding ligands **L1**–**L6** in dichloromethane at room temperature (Scheme 1). The obtained complexes were precipitated from the reaction solution after adding diethyl ether and separated as green powders in proper yields (52–82%).

These complexes could be soluble in dichloromethane, THF and DMF at room temperature. Compared to the IR spectra of the free ligands with C=N stretching frequencies, the C=N stretching vibrations in complexes **C1**–**C6** were shifted to lower frequencies in the range of 1588–1593 cm^{-1}, indicating an effective coordination interaction between the imino nitrogen atom and the chromium center. The identity of the complexes **C1**–**C6** was established on the basis of element analysis and X-ray diffraction studies for complexes **C2** and **C3**.

Crystals of complex **C2** suitable for X-ray diffraction experiment were grown from its *N*,*N*-dimethylformamide (DMF) solutions layered with diethyl ether, in which the slow diffusion of diethyl ether happened to result a saturated solution. The molecular structure of complex **C2** is shown in Fig. 1, and selected bond lengths and angles are listed in Table 1.

The crystal structure of **C2** confirms its geometry as a slightly distorted octahedron with a tridentate N^N^N ligand and three chlorides. The N–Cr–N angles are



Scheme 1. Synthesis of 2-(1-isopropyl-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines and their chromium complexes.

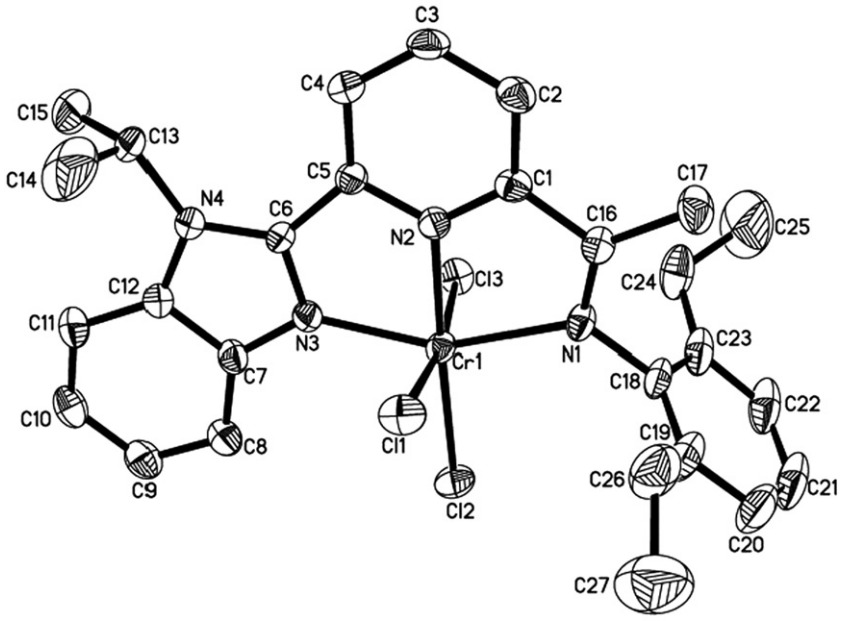


Fig. 1. Molecular structure of complex **C2**. Thermal ellipsoids are shown at 30% probability; hydrogen atoms and solvent have been omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for complexes **C2** and **C3**

	C2	**C3**
Bond lengths		
Cr(1)–N(1)	2.126(3)	2.138(4)
Cr(1)–N(2)	2.009(3)	2.019(4)
Cr(1)–N(3)	2.051(3)	2.039(4)
Cr(1)–Cl(1)	2.3308(1)	2.3248(2)
Cr(1)–Cl(2)	2.2875(1)	2.2965(2)
Cr(1)–Cl(3)	2.3159(1)	2.3151(2)
N(1)–C(16)	1.284(5)	1.293(6)
N(1)–C(18)	1.470(5)	1.476(6)
N(2)–C(1)	1.326(5)	1.340(6)
N(2)–C(5)	1.358(5)	1.343(6)
N(3)–C(6)	1.326(5)	1.332(6)
N(3)–C(7)	1.370(5)	1.381(6)
Bond angles		
N(2)–Cr(1)–N(3)	77.36(1)	76.92(2)
N(2)–Cr(1)–N(1)	77.37 (1)	77.34(2)
N(3)–Cr(1)–N(1)	154.73(1)	154.26(2)
N(2)–Cr(1)–Cl(3)	88.44(1)	90.46(1)
N(3)–Cr(1)–Cl(3)	87.26(1)	86.30 (1)
N(1)–Cr(1)–Cl(3)	91.60(1)	93.75 (1)
N(2)–Cr(1)–Cl(2)	176.94(1)	177.17(1)
N(3)–Cr(1)–Cl(2)	105.42(9)	105.91(1)
N(1)–Cr(1)–Cl(2)	99.85(9)	99.83(1)
Cl(3)–Cr(1)–Cl(2)	92.93(5)	89.77(6)
N(2)–Cr(1)–Cl(1)	86.27(1)	87.34(1)

77.36(1)°, 77.36(1)°, 154.73(1)°, which are bigger than those angles found in iron(II) [30a], cobalt(II) [30a] and nickel(II) analogues [30b]. The Cr–N(pyridine) bond distance (2.009(3) Å (Cr1–N2)) is about 0.04 Å shorter than that of the Cr–N(imidazole) bond (2.051(3) Å (Cr1–N3)), and the Cr–N(imino) bond distance (2.126(3) Å (Cr1–N1)) is the longest among the length of the Cr–N bond. In addition, the double-bond characters of the imidazole linkage (N3–C6 (1.326(5) Å) and imino linkage (N1–C16 (1.284(5) Å)) retained after the coordination. The two chelating rings Cr1–N3–C6–C5–N2 and Cr1–N1–C16–C1–N2 were almost in the same plane with the dihedral angle of 1.0°. The planes of benzimidazole ring and pyridine are almost coplanar with the dihedral angle defined at 5.6°, while the substituted phenyl group is situated approximately perpendicular to the chelating ring(Cr1–N1–C16–C1–N2) with the dihedral angle of 98.5°. Nonetheless, the phenyl plane lies almost perpendicular to the pyridyl ring (97.1°). It is worthy to mention that the bond lengths between the chromium and the mutually trans-disposed chlorine atoms are different. The bond length of Cr1–Cl1 (2.3159(1) Å) is shorter than the bond length of Cr1–Cl2 (2.3308(1) Å), while the bond length of Cr1–Cl3 (2.2875(1) Å) is the shortest of these three Cr–Cl bonds. In addition, the bond angles of Cl(3)–Cr(1)–Cl(1), Cl(3)–Cr(1)–Cl(2), Cl(2)–Cr(1)–Cl(1) are 171.48(5)°, 92.93(5)°, 92.68(5)°, also indicating that the three chlorides are not equally situated.

Similarly, the complex **C3** (Fig. 2) also shows a slightly distorted octahedron geometry. The selected bond distances and angles were collected in Table 1. The imino linkage (N1–C16 (1.293(6) Å)) and the imidazole linkage (N4–C6 (1.332(6) Å) retain the typical double-bond character after the coordination. The substituted phenyl group is also situated nearly perpendicular to the chelating ring (Cr1–N1–C16–C1–N2) with the dihedral angle of 96.6°. However, comparing with complex **C2**, some differences were observed in the structure of complex **C3**. The dihedral angles between two chelating rings (Cr1–N3–C6–C5–N2 and Cr1–N1–C16–C1–N2) and between benzimidazole ring and pyridyl ring are respectively, 2.2° and 7.9°, which are bigger than those of complex **C2**. In addition, the Cr–N

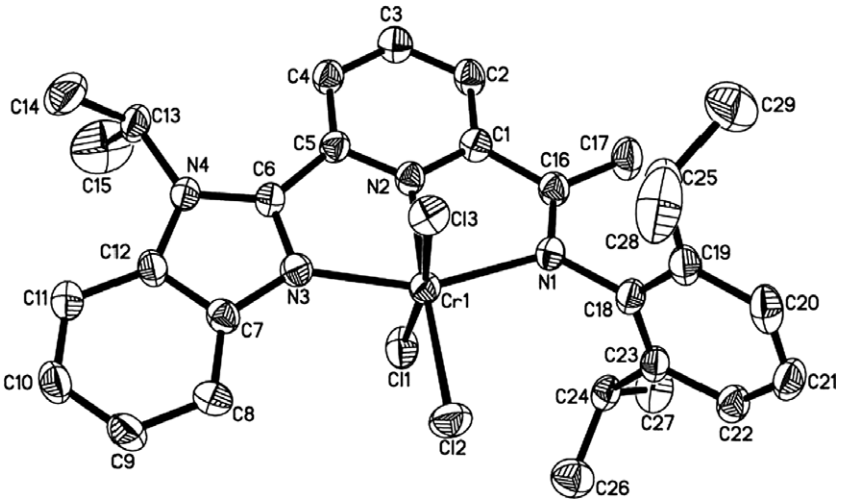


Fig. 2. Molecular structure of complex **C3**. Thermal ellipsoids are shown at 30% probability; hydrogen atoms and solvent have been omitted for clarity.

(imino) bond length of **C3** is obviously longer than that of complex **C2**. This effect is due to the relatively bulkier groups at the ortho positions of the phenyl ring in **C3**.

2.2. Ethylene oligomerization and polymerization

2.2.1. Cocatalyst selection

The effects of various cocatalysts on the productivity for ethylene activation were first studied. The chromium(III) complex **C1** for catalytic behaviors was evaluated in the presence of different cocatalysts such as methylaluminoxane (MAO), modified methylaluminoxane (MMAO), and Et_2AlCl at both 1 atm and 10 atm; and the results are collected in Table 2. At 1 atm of ethylene pressure, the catalytic system with Et_2AlCl produced butenes in lower oligomerization activities and a trace of polymer. When activated by MAO, the catalyst showed increased activity, giving both oligomers and polymers in the ratio of about 1:2. The activities for both oligomerization and polymerization were further increased when MMAO was employed as cocatalyst. In addition, olefins with much longer chain were produced compared to C1/MAO system under the same conditions. A similar trend could be observed when ethylene pressure was increased to 10 atm, and noteworthy, the polymerization activity obtained by **C1**/MMAO system was nearly 20 times greater than that generated by **C1**/MAO system. So the further investigations were carried out with MMAO as cocatalyst. What's more, from the results in Table 2, it can be found that the main product was polymer, which indicated that chain termination might be suppressed by the propagation process for this chromium complex. This is inconsistent with our previous observations in 2,6-bis(2-benzimidazolyl)pyridylchromium trichlorides and 2-carbethoxy-6-iminopyridine chromium trichlorides [27,28a], where oligomers dominated the polymerization products. In addition, long chain olefins were produced and the percentage of these longer chain olefins ($\geqslant C_{10}$) could achieve 49.9%. Surprisingly, the yield of hexenes was very low. Take the C1/MMAO with ratio of 1000 as the example (entry 2 in Table 3), the content of obtained C_6 (4.4 wt%) was much less than that of C_4 (26.6 wt%) and C_8 (19.1 wt%). Repeated trying and experiments under other conditions or with other complexes revealed the same results. This observation was different from those found in

Table 2
Catalytic system of C1 with various cocatalysts[a]

Entry	P/atm	Cocatalyst	Al/Cr	Oligomer		Polymer
				Activity[d]	Distribution[e]	Activity[d]
1[b]	1	Et_2AlCl	200	0.36	C_4	trace
2	1	MAO	1000	0.55	C_4–C_{12}	1.20
3	1	MMAO	1000	0.93	C_4–Cl_2	3.70
4[c]	10	Et_2AlCl	200	0.88	C_4	2.0
5	10	MAO	1000	2.26	C_4–C_{16}	6.76
6	10	MMAO	1000	27.0	C_4–C_{16}	114.5

[a] Reaction conditions: 5 μmol of catalyst; 20 °C.
[b] 60 min, 30 ml of toluene for entries 1–3.
[c] 30 min, 100 ml of toluene for entries 4–6.
[d] In units of 10^4 g (mol of Cr)$^{-1}$ h^{-1}.
[e] Determined by GC and GC–MS.

Table 3
Oligomerization and polymerizatiom with C1/MMAO at 1 atm ethylene[a]

Entry	Al/Cr	T[b] (°C)	t[c] (min)	Productivity[d]	Oligomers (wt%)	PE (wt%)	T_m^e (°C)				Oligomer distribution (%)[f]				
							1	2	3	4	$C_4/\sum C$	$C_6/\sum C$	$C_8/\sum C$	$\geqslant C_{10}/\sum C$	α-Olefin (%)
1	500	20	60	0.22	24.0	76.0	–	92.0	106.6	130.0	10.0	3.7	13.0	73.3	92.1
2	1000	20	60	0.47	20.8	79.2	72.8	86.9	104.8	125.3	26.6	4.4	19.1	49.9	92.6
3	1500	20	60	0.51	24.9	75.1	68.9	86.3	103.0	126.0	27.9	4.1	9.3	58.7	93.5
4	2000	20	60	0.67	25.2	74.8	71.5	85.6	102.5	126.4	23.7	3.3	6.7	66.3	90.8
5	3000	20	60	1.31	12.2	87.8	–	93.2	104.7	123.7	29.5	3.9	7.7	58.9	87.8
6	1500	40	60	0.35	63.8	36.2	70.0	–	101.9	126.9	25.2	4.4	14.0	56.4	89.9
7	1500	60	60	0.28	65.2	34.8	74.0	–	101.9	127.7	48.2	19.5	14.1	18.2	83.9
8	1500	80	60	0.06	$\geqslant$99	$\leqslant$1.0	nd				47.4	8.0	34.0	10.6	80.2
9	1500	20	15	0.38	46.4	53.6	75.2	91.7	103.8	125.0	15.9	3.6	9.1	71.4	94.7
10	1500	20	30	0.46	25.2	74.8	74.6	90.6	103.4	126.4	25.9	4.9	23.2	46.0	96.8
11	1500	20	90	0.39	25.6	74.4	70.9	–	102.9	127.0	25.0	5.0	15.3	54.7	91.8
12	1500	20	120	0.30	26.6	73.4	–	83.8	104.3	127.7	21.0	4.2	11.9	62.9	91.9

[a] Reaction conditions: 5 μmol of catalyst; 30 ml of toluene.
[b] Reaction temperature.
[c] Reaction time.
[d] In units of 10^5 g (mol of Cr)$^{-1}$ h^{-1}.
[e] Determined by DSC.
[f] Determined by GC.

other chromium complexes [17,31,32], and the reason was hitherto unclear.

2.2.2. Ethylene oligomerization and polymerization at ambient pressure

2.2.2.1. Effects of the molar ratio of Al/Cr and reaction temperature. The amount of cocatalyst was found to have significant influences on the catalytic behaviors of C1/MMAO system. Increasing the Al/Cr molar ratio from 500 to 3000 led to an enhancement of the productivity (entries 1–5 in Table 3). When the ratio of Al/Cr is 3000, the catalytic system displayed high productivity up to 1.31×10^5 g (mol of Cr)$^{-1}$ h^{-1}. However, the distribution of oligomers and the selectivity for α-olefins were not strongly affected by the Al/Cr ratio, which can be observed in Fig. 3. 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 molar ratio of Al/Cr 1500. DSC analysis revealed the presence of several compositions of the obtained polymers, and the DSC curves included a main peak at around 125 °C and broad shoulders ranged from 40 to 110 °C. Unusually two or three small peaks could be found from the wide shoulders. Under different Al/Cr molar ratios, the profile of DSC curves were similar except for the various shoulder peaks. These phenomena demonstrated polyethylenes

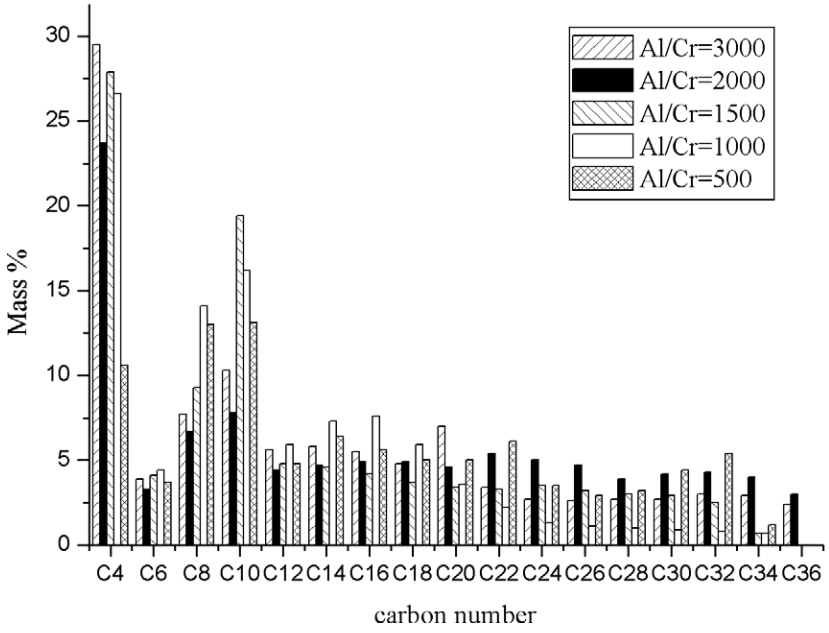


Fig. 3. Oligomer distribution obtained with **C1** at different Al/Cr ratios at 1 atm.

containing different components had broad molecular weight distributions, which were concurrent with the results observed for chromium(III) complexes supported by bis(2-pyridylmethyl)amines [33]. Such phenomena of multiple endothermic peaks in polyolefin have also observed in our previous research [28] and literatures [34–38]. The broad molecular weight distribution of polymers was in agreement with that of oligomers.

As the ethylene oligomerization and polymerization are highly exothermic reactions, the reaction temperature significantly affects the catalytic activity. To understand this influence, the catalytic system of **C1** with 1500 equiv. of MMAO at 1 atm of ethylene was investigated with changing reaction temperature. Elevation of the reaction temperature from 20 to 80 °C resulted in a sharp decrease of catalytic activity, which can be explained as the decomposition of some active species and lower ethylene solubility at higher temperature [39]. At the same time, increasing the temperature results in a decrease of PE proportion (entries 3 and 6–8, Table 3), which was due to an increase in the rate of the β-hydrogen elimination relative to the rate of propagation at higher temperature [40]. In addition, increasing the temperature from 20 to 80 °C led to a rapid decrease of α-olefin selectivity from 93.5% to 80.2%. This can be attributed to the faster chain transfer or isomerization at high temperature. It was noteworthy that the oligomer distribution showed an unprecedented small amount of C_6. This is similar to the reported observation [41], in which the chromium system showed much lower activity towards ethylene trimerization. The reaction temperature had an obvious effect on the thermal property of the resultant polyethylenes. DSC curves of polyethylenes produced at different temperatures were similar with one obvious peak and a broad shoulder at low temperature. However, elevating the temperature from 20 to 60 °C has increased the melting points (judging from the main peak of DSC curves) of the polyethylenes (entries 3 and 6–8, Table 3). In general, the suitable active sites were formed at temperature 20 °C for the high activity and good selectivity of α-olefins, therefore, more investigations were carried out at 20 °C.

2.2.2.2. Effect of the reaction time. The catalyst lifetime is one significant factor in industrial considerations. The effect of reaction time on catalytic activity was also studied using the **C1**/MMAO system with an Al/Cr molar ratio of 1500 at 20 °C. When the reaction time was increased from 15 min to 120 min, the catalytic productivity initially increased and then decreased, with the optimum activity being at reaction time of 60 min (entries 3, and 9–12, Table 3), indicating that there may be an induction period at the initial stage of reaction and the active species of **C1** were deactivated with the prolonged reaction time. All the DSC curves gave one obvious peak and a broad shoulder. Increasing the reaction time from 15 to 120 min, the main peak on the DSC curves of the resultant polyethylene increased from 125.0 to 127.7 °C.

2.2.2.3. Effect of the ligand environments. The data listed in Table 4 (entries 1–6) showed that the structure of the ligands considerably affected the catalytic behaviors of the complexes. It is evident to find that the steric hindrance of ligands affected the ethylene activities of chromium complexes. Comparing **C3** (with *i*-Pr), **C2** (with Et) and **C1** (with Me) (entries 1, 2 and 3, Table 4), an increase of the bulkiness of the groups in the ortho positions of the anilines renders a less active catalyst. Complex **C1** bearing 2,6-dimethyl substituents on the imino-N aryl ring, showed the highest activity at 0.51×10^5 g (mol of Cr)$^{-1}$ h^{-1}. This could be explained that in this catalytic system with MMAO, the reaction speed mostly depended on the insertion of ethylene at the active species, so a more bulky group caused slower insertion reaction and consequently lower activity. Meanwhile, with more bulkiness, the content of oligomers is obviously increased, which might be attributed that the catalysts with less steric bulkiness facilitate the reaction of propagation not the β-hydrogen elimination reaction. The electronic effect of ligands on the activities of chromium complexes was also observed. Complexes **C4** ($R^1 = F$) and **C5** ($R^1 = Cl$) bearing halogen groups exhibited relatively higher activities with better selectivity of α-olefin than the corresponding complexes bearing alkyl groups at the *ortho*-positions of the imino-N aryl ring. In addition, products obtained by **C4**/MMAO systems comprised of more proportions of oligomers than those by alkyl-substituted systems. The improved catalytic activity

Table 4
Ethylene reactivity with C1–C6/MMAO at ambient pressure[a]

Entry	Complex	Productivity[b]	Oligomers (wt%)	PE (wt%)	T_m^c (°C)				Oligomer distribution (%)[d]				
					1	2	3	4	$C_4/\sum C$	$C_6/\sum C$	$C_8/\sum C$	$\geqslant C_{10}/\sum C$	α-Olefin (%)
1	**C1**	0.51	24.9	75.1	68.9	86.3	103.0	126.0	27.9	4.1	9.3	58.7	93.5
2	**C2**	0.46	27.3	72.7	69.8	85.6	101.9	127.0	34.0	5.5	19.2	41.3	93.2
3	**C3**	0.19	55.3	44. 7	67.9	88.6	102.1	125.4	31.8	3.6	17.2	47.4	89.4
4	**C4**	2.10	82.5	17.5	66.7	–	102.7	123.4	81.6	5.9	5.8	6.7	99.6
5	**C5**	1.47	36.5	63.5	64.9	–	–	124.6	15.3	11.1	14.2	59.4	97.5
6	**C6**	2.03	11.5	88.5	65.2	–	102.8	125.7	11.6	4.2	9.6	74.6	96.8

[a] Reaction conditions: 5 μmol of catalyst; Al/Cr = 1500; 20 °C; 60 min; 30 ml of toluene.
[b] In units of 10^5 g (mol of Cr)$^{-1}$ h^{-1}.
[c] Determined by DSC.
[d] Determined by GC and GC–MS.

was attributed to the more electrophilic nature of the chromium center after the introduction of the electron-withdrawing substituents on the *ortho*-positions of phenyl group. Comparing **C4** and **C5**, the fluoro-substituted complex **C4** showed much higher activity than **C5** and produced more oligomers in the final products, which can be explained as the combined result of the electronic and steric effects. Therefore, less bulky ligands with electron-withdrawing substituents would be helpful in increasing the catalytic activity of the tridentate chromium complexes with the MMAO as the activator. All these chromium complexes especially complexes **C4** and **C5** bearing electron-withdrawing substituents displayed the high α-olefin selectivity for ethylene oligomerization at 1 atm. The distribution of oligomers produced by complex **C4** resembles Schulz-Flory rules with $K = 0.73$, where K represented the probability of chain propagation (K = rate of propagation/((rate of propagation) + (rate of chain transfer)) = (moles of C_{n+2})/(moles of C_n)) [42]. However, the distribution of oligomers, which contained a small portion of C_6 by complex **C1**–**C3**, **C5** and **C6**, did not resemble neither Schulz-Flory rules or Poisson distribution (entries 1–3, 5 and 6 in Table 4). The oligomer distributions achieved by **C2**, **C3** and **C5** were shown in Fig. 4.

In addition, the introduction of a methyl group in the *para*-position has exerted obvious influences on the catalytic behaviors. For example, complex **C6** exhibited much higher activity than the corresponding complexes **C1** and produced more polymers in the final products compared with other systems. Furthermore, complex **C6** bearing 2,4,6-trimethyl substituents on the imino-N aryl ring exhibited exceptionally higher activity than complexes **C2** and **C3**. This may be caused by the changed net charge on the transition metal due to the presence of the methyl group in the *para*-position. This phenomenon is in agreement with the results observed for the chromium(III) catalysts with bis(imino)pyridyl ligands [43].

These findings indicated that the ligand environments had dramatic effect on the ethylene oligomerization and polymerization. Less bulky ligands with electron-withdrawing substituents can be helpful in enhancing the catalytic activity of the tridentate chromium complexes. In addition, both products of oligomers and polyethylenes were obtained in current catalytic systems at ambient pressure, while chromium complexes with bis(imino)pyridines favorably performed ethylene polymerization in combination with MMAO [34,43], and [2,6-bis(2-benzimidazolyl)pyridyl] chromium complexes gave oligomers as main products [28a]. This may be attributed to the geometry of the complexes. In the molecular structures of bis(imino)pyridyl chromium(III) complexes, the planes of the phenyl rings are oriented essentially orthogonal to the pyridyl plane [34,43], while benzimidazole rings are almost coplanar with pyridyl rings in [2,6-bis(2-benzimidazolyl)pyridyl]chromium complexes [28a]. Comparing with imino groups in chromium complexes, the introduction of benzimidazole groups coplanar with pyridyl rings favor β-hydrogen elimination reaction during ethylene activation, while the existence of imino groups favor chain propagation reaction. So the titled complexes which contain both benzimidazole groups and imino groups produce both polymers and oligomers.

All the DSC curves obtained by **C1**–**C6** showed one main peak around 125 °C and a broad shoulder at lower temperature ranges, which indicated that all samples had broad distribution of molecular weights. These phenomena were commonly observed among complexes containing pyridyl ligands [44]. Under the same condition, the ligand environment showed only little effect on the thermal properties of the resulting polymer. In addition, the T_m of the polymers obtained by complexes **C4** (R^1 = F) and **C5**

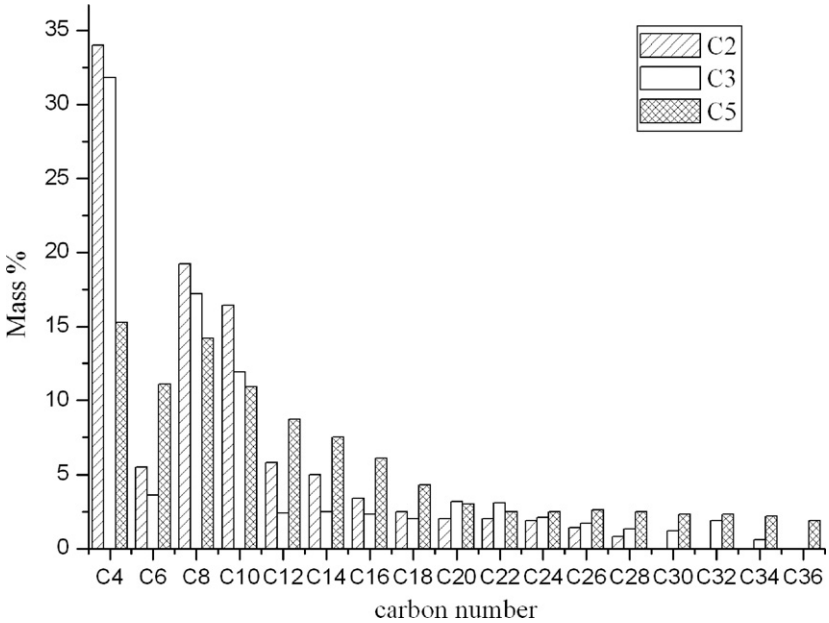


Fig. 4. Oligomer distribution obtained in entries **2**, **3** and **5** in Table 4.

($R^1 = Cl$) bearing halogen groups were lower than those obtained by their analogues bearing alkyl groups at *ortho*-positions of the imino-N aryl ring (entries 4 and 5, Table 5). IR spectra recorded using a KBr disk in the range of 4000–400 cm^{-1} revealed only four obvious peaks at 2920, 2850, 1464, and 720 cm^{-1}, suggesting the linear structure of the obtained polyethylenes. This is in line with what we observed in our previous models [28a]. The oligomer distribution behavior and DSC analysis indicate that the obtained polymers have a very broad molecular weight distribution.

2.2.3. Ethylene oligomerization and polymerization at 10 atm of ethylene

2.2.3.1. Effect of the ethylene pressure. The results of polymerization performed under 10 atm pressure employing **C1**–**C6** are summarized in Table 5. The data indicated that the ethylene pressure significantly affected the catalytic behavior of all the complexes including activities, product distributions and polymer properties. Comparing with the catalytic behavior at ambient pressure (Table 4), the higher catalytic activities could be obtained with increasing the ethylene pressure and the catalytic activities for both oligomerization and polymerization increased by nearly one order of magnitude at 10 atm of ethylene. However, the increase of ethylene pressure did not significantly change the weight ratios between oligomers and polymers of the products compared with the results obtained at 1 atm.

2.2.3.2. Effect of the ligand environment. Upon activation with modified methylaluminoxane (MMAO), all the chromium complexes exhibited good catalytic activities for oligomerization and polymerization at 10 atm of ethylene. The detailed results are listed in Table 5 (entries 1–6). The ligand environment has exerted similar influences on

Table 5
Ethylene reactivity with C1–C6/MMAO at 10 atm[a]

Entry	Complex	Productivity[b]	Oligomers (wt%)	PE (wt%)	T_m^c (°C)				Oligomer distribution (%)[d]				
					1	2	3	4	$C_4/\sum C$	$C_6/\sum C$	$C_8/\sum C$	$\geqslant C_{10}/\sum C$	α-Olefin
1	**C1**	1.42	23.9	76.1	69.6	89.2	101.7	121.7	14.1	9.5	9.0	67.4	96.1
2	**C2**	0.57	35.0	65.0	68.9	88.7	102.2	125.7	22.2	18.8	16.9	42.1	97.5
3	**C3**	0.48	46.1	53.9	71.3	89.4	102.5	124.0	38.6	18.4	14.4	28.6	97.5
4	**C4**	3.95	88.4	11.6	65.2	–	98.1	119.5	81.0	9.3	3.5	6.2	99.2
5	**C5**	1.49	66.2	33.8	61.8	–	–	120.7	21.9	18.4	14.9	44.8	98.7
6	**C6**	1.70	22.3	77.7	60.9	89.1	100.7	120.7	9.8	8.2	14.4	67.6	100

[a] Reaction conditions: 5 μmol of catalyst; Al/Cr = 1500; 20 °C; 60 min; 30 ml of toluene.
[b] In units of 10^6 g (mol of Cr)$^{-1}$ h^{-1}.
[c] Determined by DSC.
[d] Determined by GC and GC–MS.

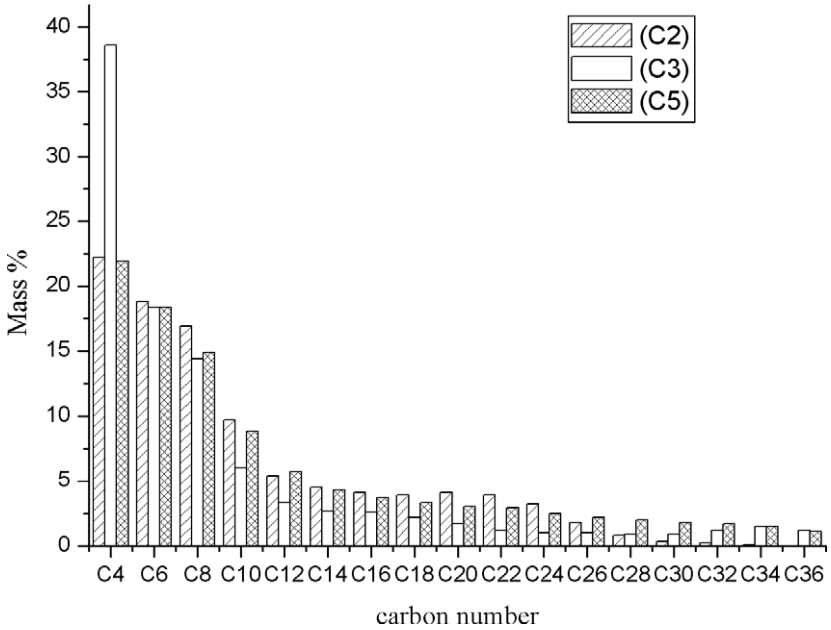


Fig. 5. Oligomer distribution obtained in entries **2**, **3**, **5** in Table 5.

catalytic behaviors as those found at 1 atm of ethylene pressure. For example, the introduction of electron-withdrawing halogen groups on the imino-N aryl ring resulted in increased catalytic activities, higher α-olefin selectivity together with higher oligomer fraction in the polymerization products. In addition, for the three alkyl-substituted complexes (**C1**–**C3**), greater bulky substituents at the *ortho*-positions of the imino-N aryl ring led to decrease of catalytic activity and lower proportion of polymers.

At ambient pressure, complex **C6** made an exception for ethylene oligomerization and polymerization. Similarly, at 10 atm of ethylene, complex **C6** showed higher productivity with much more polymers than the corresponding alkyl-substituted analogues (entry 6, Table 5).

In addition, the distribution of olefin oligomers obtained by **C1**–**C5** deviated more from the Schulz-Flory rule, and the oligomer distributions achieved by complexes**C2**, **C3** and **C5** at 10 atm were shown in Fig. 5. In addition, GC analysis of the oligomers indicated that the selectivity for linear α-olefins in the range of 96.1–99.2% are a little higher than those found at 1 atm. Polymers obtained by complex **C1** at 10 atm are also mainly linear-olefins through the characterization by the IR spectrum.

At 10 atm, the effects of the ligand environments on the T_m accorded with the results at 1 atm. However, the main T_m peak of the resultant polymers obtained at 10 atm ranged from 119.5 to 120.7 °C, which are lower than those of polyethylenes (range from 123.4 to 127.0 °C) at 1 atm.

3. Conclusion

Inspired by the success of 2,6-bis(2-benzimidazolyl)pyridyl chromium trichlorides [28a] and 2-(1-methyl-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridyl iron and cobalt complexes [30] as highly active catalysts toward ethylene activation, a family of octahedral chromium(III) complexes ligated by the 2-(1-isopropyl-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines were prepared and characterized. Upon activation with modified methylalumoxane (MMAO), these tridentate chromium complexes afforded moderate to high activity for ethylene oligomerization and polymerization with broad oligomer distributions from C_4 to C_{36} and some complexes got special distributions of oligomers. In most cases, polyethylene was the main product and higher carbon number olefins usually accounted for the majority of the oligomers. The obtained polymers were confirmed to be vinyl-terminal long-chain alkenes. Reaction conditions including cocatalyst, temperature, ethylene pressure and reaction time were found to have significant influences on the catalytic behaviors. Increasing the Al/Cr molar ratio led to an enhancement of the productivity, however, exerted little influences on the α-olefin selectivity and the product compositions. Elevation of the reaction temperature resulted in the decreased activity, reduced polymer content and less α-olefin selectivity. The electronic nature of the aromatic substituents has also a marked influence on the activity. Less bulky ligand with electron-withdrawing substituent produce an positive influence on increasing the catalytic activity of the tridentate chromium complexes with the MMAO as the activator. In addition, complexes bearing electron-withdrawing substituents produced much more oligomers than polymers in the products at 10 atm of ethylene. Higher ethylene pressure favors increased catalytic activities and higher α-olefin selectivity. In some cases, the polymers have been obtained and confirmed to be vinyl-terminal long-chain alkenes. Finally, we can conclude that these tridentate chromium complexes could be promising catalysts with technological application in ethylene oligomerization and polymerization.

4. Experimental

4.1. General considerations

All manipulations of air- and moisture-sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium-benzophenone and distilled under nitrogen prior to use. Methylaluminoxane (MAO) was purchased from Albemarle as a 1.4 M solution in toluene. Modified methylaluminoxane (MMAO, 1.93 M in heptane) was purchased from Akzo Corp. Diethylaluminum chloride (Et_2AlCl, 1.7 M in hexane) was purchased from Acros Chemicals. All other reagents were purchased from Aldrich or Acros Chemicals; the boiling range of light petroleum is 60–90 °C and the type of silica gel used is 200–300 mesh. ^1H and ^{13}C NMR spectra were recorded on a Bruker DMX 300 MHz instrument at ambient temperature using TMS as an internal standard. 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) CP-Sil 5 CB column. The yield of oligomers was calculated by referencing to the mass of the solvent on the basis of the prerequisite that the mass of each fraction was approximately proportional to its integrated area 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 10 °C/min. The polymer sample was first equilibrated at 0 °C and then heated to 160 °C at a rate of 10 °C/min to remove thermal history. The sample was then cooled to 0 °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. Preparation of ligands

4.2.1. Preparation of (E)-N-(1-(6-(1-isopropyl-1H-benzo[d]imidazol-2-yl)pyridin-2-yl)ethylidene)-2,6-dimethylbenzenamine (*L1*)

2-(1-Isopropyl-2-benzimidazolyl)-6-acetylpyridine (167 mg, 0.6 mmol) and 2,6-dimethylaniline (72.7 mg, 0.6 mmol) were refluxed in toluene (20 ml) in the presence of *p*-toluenesulfonic. After solvent evaporation, the crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5/1 v/v) as eluent to afford the product as a yellow powder in 65% yield. M.p.: 143–145 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 8.47 (d, 1H, $J = 7.9$ Hz, Py), 8.38 (d, 1H, $J = 7.7$ Hz, Py), 7.99 (t, 1H, $J = 7.9$, 7.7, Py), 7.87 (m, 1H, Ph), 7.70 (m, 1H, Ph), 7.33 (m, 2H, Ph), 7.09 (d, 2H, $J = 7.5$ Hz, Ph), 6.96 (t, 1H, $J = 6.9$, 7.2 Hz, Ph), 6.06 (m, 1H, CH), 2.20 (s, 3H, CH_3), 2.06 (s, 6H, CH_3), 1.75 (d, 6H, $J = 6.9$ Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 165.2, 154.0, 148.9, 148.6, 147.3, 142.3, 136.3 (2C), 133.25, 126.7 (2C), 125.5, 124.1, 121.9, 121.6, 121.0, 119.9, 119.4, 111.7, 47.7, 20.2 (2C), 16.7 (2C), 15.3. IR (KBr; cm^{-1}): 2972, 2937, 1654 ($\nu_{C=N}$), 1589, 1570, 1455, 1398, 1207, 825, 754. Anal. Calc. for $C_{25}H_{26}N_4$ (382.5): C, 78.50; H, 6.85; N, 14.65. Found: C, 78.32; H, 6.98; N, 14.76%.

4.2.2. (E)-2,6-Diethyl-N-(1-(6-(1-isopropyl-1H-benzo[d]imidazol-2-yl)-pyridin-2-yl)ethylidene)benzenamine (*L2*)

Using the same procedure as for the synthesis of **L1**, **L2** was obtained as a yellow powder in 79% yield. M.p.: 130–132 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 8.45 (d, 1H, $J = 7.9$ Hz, Py), 8.38 (d, 1H, $J = 7.8$ Hz, Py), 7.99 (t, 1H, $J = 7.9$, 7.8 Hz, Py), 7.85 (m, 1H, Ph), 7.61 (m, 1H, Ph), 7.32 (m, 2H, Ph), 7.28 (d, 2H, $J = 7.1$ Hz, Ph), 7.07(m, 1H, Ph), 6.10 (m, 1H, CH), 2.40 (m, 4H, CH_2), 2.22 (s, 3H, CH_3), 1.75 (d, 6H, $J = 6.0$ Hz, CH_3) 1.15 (t, 6H, $J = 7.5$, 7.5 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 165.0, 154.1, 148.6, 148.5, 146.4, 142.3, 136.3, 133.3, 129.9 (2C), 125.4, 124.7 (2C), 122.2, 121.6, 120.9, 119.9, 119.4, 111.7, 47.7, 23.4 (2C), 20.2 (2C), 15.7, 12.4 (2C). IR (KBr; cm^{-1}): 2970, 2934, 1654 ($\nu_{C=N}$), 1587, 1568, 1455, 1397, 1384, 827, 748. Anal. Calc. for $C_{27}H_{30}N_4$ (410.6): C, 78.99; H, 7.37; N, 13.65. Found: C, 78.74; H, 7.31; N, 13.44%.

4.2.3. (E)-2,6-Diisopropyl-N-(1-(6-(1-isopropyl-1H-benzo[d]imidazol-2-yl)pyridin-2-yl)ethylidene)benzenamine (*L3*)

Using the same procedure as for the synthesis of **L1**, **L3** was obtained as a yellow powder in 80% yield. M.p.: 179–180 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 8.44 (d, 1H, $J = 7.9$ Hz, Py), 8.38 (d, 1H, $J = 7.3$ Hz, Py), 7.99 (t, 1H, $J = 7.9$, 7.3 Hz, Py), 7.73 (m, 1H, Ph), 7.62 (m, 1H, Ph), 7.32 (m, 2H, Ph), 7.18 (m, 2H, Ph), 7.14 (m, 1H, Ph), 6.07 (m, 1H, CH), 2.76 (m, 2 H, CH), 1.75 (d, 6H, $J = 7.0$ Hz, CH_3), 1.16 (d, 12H, $J = 6.8$ Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 166.5, 155.5, 150.3, 150.0, 146.4, 143.7, 137.7, 135.8 (2C), 134.6, 126.7, 123.8, 123.2 (2C), 122.9, 122.4, 121.4, 120.7, 113.1, 49.1, 28.5 (2C), 23.3 (2C), 22.9 (2C), 21.6 (2C), 17.4. IR (KBr; cm^{-1}): 2960, 2868, 1650 ($\nu_{C=N}$), 1588, 1570, 1454, 1398, 824, 782, 750. Anal. Calc. for $C_{29}H_{34}N_4$ (438.6): C, 79.41; H, 7.81; N, 12.77. Found: C, 79.37; H, 7.91; N, 12.48%.

4.2.4. (E)-2,6-Difluoro-N-(1-(6-(1-isopropyl-1H-benzo[d]imidazol-2-yl)pyri-dine-2-yl)ethylidene)-benzenamine (*L4*)

Using the same procedure as for the synthesis of **L1**, **L4** was obtained as a yellow powder in 51% yield. M.p.: 94–95 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS):δ 8.48 (d, 1H, $J = 7.9$ Hz, Py), 8.39 (d, 1H, $J = 7.8$ Hz, Py), 7.99 (t, 1H, $J = 7.9$, 7.8, Py), 7.88 (m, 1H, Ph), 7.71 (m, 1H, Ph), 7.33 (m, 2H, Ph), 7.08 (m, 2H, Ph), 6.99 (m, 2H, Ph), 6.05 (m, 1H, CH), 2.43 (s, 3H, CH_3), 1.75 (d, 6H, $J = 6.9$ Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 171.9, 154.7, 151.4, 149.9, 149.8, 143.5, 137.7 (2C), 134.5, 127.2 (2C), 124.3, 122.9, 122.3, 121.9, 120.6, 113.0, 111.8, 111.5, 49.0, 21.4 (2C), 17.7. IR (KBr; cm^{-1}): 2969, 1643 ($\nu_{C=N}$), 1588, 1453, 824, 745. Anal. Calc. for $C_{23}H_{20}F_2N_4$ (390.4): C, 70.75; H, 5.16; N, 14.35. Found: C, 70.80; H, 5.17; N, 14.41%.

4.2.5. (E)-2,6-Dichloro-N-(1-(6-(1-isopropyl-1H-benzo[d]imidazol-2-yl)pyridin-2-yl)ethylidene)-benzenamine (*L5*)

2-(1-Isopropyl-2-benzimidazolyl)-6-acetylpyridine (279 mg, 1 mmol) and 2,6-dichlorolaniline (324 mg, 2 mmol) were refluxed in ethyl silicate (4 ml) in the presence of *p*-toluenesulfonic. After solvent evaporation, the crude product was purified by column chromatography on alumina with petroleum ether/ethyl acetate (10/1 v/v) as eluent to afford the product as a yellow powder in 5% yield. M.p.: 121–122 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 8.47 (d, 1H, $J = 7.4$ Hz, Py), 8.41 (d, 1H, $J = 7.4$ Hz, Py), 8.00 (t, 1H, $J = 7.4$, 7.4, Py), 7.86 (m, 1H, Ph), 7.70 (m, 1H, Ph), 7.37 (d, 2H, $J = 7.9$, 7.9 Hz, Ph), 7.30 (m, 2H, Ph), 7.01 (t, 1H, $J = 8.3$, 7.9 Hz, Ph), 6.04 (m, 1H, CH), 2.33 (s, 3H, CH_3), 1.75 (d, 6H, $J = 6.9$ Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 170.8, 155.2, 154.6, 150.1, 145.6, 143.6, 137.9 (2C), 134.6, 128.4 (2C), 127.4, 124.7, 124.6, 123.0, 122.4, 122.1, 120.7, 113.1, 49.1, 21.6 (2C), 17.8. IR (KBr; cm^{-1}): 2970, 1658 ($\nu_{C=N}$), 1588, 1455, 1434, 1399, 824, 789, 744. Anal. Calc. for $C_{23}H_{20}Cl_2N_4$ (423.3): C, 65.25; H, 4.76; N, 13.23. Found: C, 64.93; H, 4.90; N, 12.94%.

4.2.6. (E)-2,4,6-Trimethyl-N-(1-(6-(1-isopropyl-1H-benzo[d]imidazol-2-yl)pyridin-2-yl)ethylidene)-benzenamine (*L6*)

Using the same procedure as for the synthesis of **L1**, **L6** was obtained as a yellow powder in 71% yield. M.p.: 189–190 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.49 (d, 1H, $J = 8.0$ Hz, Py), 8.37 (d, 1H, $J = 7.8$ Hz, Py), 8.00 (t, 1H,

$J = 8.0$, 7.8, Py), 7.87 (m, 1H, Ph), 7.71 (m, 1H, Ph), 7.31 (m, 2H, Ph), 6.91 (s, 2H, Ph), 6.06 (m, 1H, CH), 2.36 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.06 (s, 6H, CH_3), 1.75 (d, 6H, $J = 7.0$ Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 167.8, 155.5, 149.9, 150.2, 146.2, 143.6, 137.6 (2C), 132.5, 128.7 (2C), 126.7, 125.3 (2C), 122.9, 122.4, 121.4, 120.7, 113.1, 49.1, 21.5 (2C), 20.9, 18.0 (2C), 16.6. IR (KBr; cm^{-1}): 2970, 1651 ($\nu_{C=N}$), 1570, 1478, 1453, 1399, 824, 769, 750. Anal. Calc. for $C_{26}H_{28}N_4$ (396.5): C, 78.75; H, 7.12; N, 14.13. Found: C, 78.73; H, 7.21; N, 14.40%.

4.3. Synthesis of complexes (*C1–C6*)

4.3.1. Complex *C1*

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. A solution of $CrCl_3(THF)_3$ (0.225 g, 0.600 mmol) and **L1** (0.138 g, 0.600 mmol) in dichloromethane was stirred at room temperature for 12 h, giving a green suspension. The reaction volume was reduced, diethyl ether was added, and a green solid was obtained, which was washed repeatedly with diethyl ether and dried under vacuum. The green powder (0.151 g, 0.279 mmol) was obtained in a yield of 46.5%. IR (KBr; cm^{-1}): 2979, 1589 ($\nu_{C=N}$), 1503, 1472, 1409, 1376, 1336, 1281, 1163, 1136, 1108, 1038, 752. Anal. Calc. for $C_{25}H_{26}Cl_3CrN_4$ (540.9): C, 55.52; H, 4.85; N, 10.36. Found: C, 55.32; H, 4.90; N, 10.26%.

4.3.2. Complex *C2*

Analogous to the procedure for **C1**, ligand **L2** (0.246 g, 0.600 mmol) and $CrCl_3(THF)_3$ (0.225 g, 0.600 mmol) reacted to form 0.258 g (0.454 mmol) of a green solid in a yield of 75.7%. IR (KBr; cm^{-1}): 2968, 1588 ($\nu_{C=N}$), 1469, 1408, 1374, 1336, 1280, 1163, 1134, 1038, 855, 792, 752. Anal. Calc. for $C_{27}H_{30}Cl_3CrN_4$ (568.9): C, 57.00; H, 5.32; N, 9.85. Found: C, 57.69; H, 5.28; N, 9.86%.

4.3.3. Complex *C3*

Analogous to the procedure for **C1**, ligand **L3** (0.263 g, 0.600 mmol) and $CrCl_3(THF)_3$ (0.225 g, 0.600 mmol) reacted to form 0.213 g (0.356 mmol) of a green solid in a yield of 59.4%. IR (KBr; cm^{-1}): 2970, 1589 ($\nu_{C=N}$), 1564, 1504, 1472, 1409, 1382, 1338, 1280, 1218, 1162, 1133, 1038, 848, 806, 788, 759. Anal. Calc. for $C_{29}H_{34}Cl_3CrN_4$ (597.0): C, 58.35; H, 5.74; N, 9.39. Found: C, 58.30; H, 5.58; N, 9.30%.

4.3.4. Complex *C4*

Analogous to the procedure for **C1**, ligand **L4** (0.234 g, 0.600 mmol) and $CrCl_3(THF)_3$ (0.225 g, 0.600 mmol) reacted to form 0.176 g (0.321 mmol) of a green solid in a yield of 53.5%. IR (KBr; cm^{-1}): 2977, 1591 ($\nu_{C=N}$), 1567, 1505, 1474, 1409, 1376, 1338, 1289, 1164, 1109, 1137, 1033, 1008, 785, 757. Anal. Calc. for $C_{23}H_{20}Cl_3CrF_2N_4$ (548.8): C, 50.34; H, 3.67; N, 10.21. Found: C, 50.30; H, 3.62; N, 9.98%.

4.3.5. Complex *C5*

Analogous to the procedure for **C1**, ligand **L5** (0.085 g, 0.200 mmol) and $CrCl_3(THF)_3$ (0.075 g, 0.200 mmol) reacted to form 0.068 g (0.117 mmol) of a green solid in a yield of 52.1%. IR (KBr; cm^{-1}): 2976, 1589 ($\nu_{C=N}$), 1564, 1503, 1473, 1436, 1408, 1377, 1337, 1281, 1229, 1197, 1162, 1137, 1036, 857, 791, 756. Anal. Calc. for $C_{23}H_{20}Cl_5CrN_4$ (581.7): C, 47.49; H, 3.47; N, 9.63. Found: C, 47.41; H, 3.96; N, 9.45%.

4.3.6. Complex *C6*

Analogous to the procedure for **C1**, ligand **L6** (0.238 g, 0.600 mmol) and $CrCl_3(THF)_3$ (0.225 g, 0.600 mmol) reacted to form 0.202 g (0.364 mmol) of a green solid in a yield of 60.7%. IR (KBr; cm^{-1}): 2970, 1586 ($\nu_{C=N}$), 1564, 1505, 1472, 1409, 1374, 1337, 1281, 1222, 1138, 1038, 862, 809, 748. Anal. Calc. for $C_{26}H_{28}Cl_3CrN_4$ (554.9): C, 56.28; H, 5.09; N, 10.10. Found: C, 56.15; H, 5.28; N, 9.94%.

4.4. Procedure for ethylene oligomerization and polymerization at 1 atm

Ethylene oligomerization and polymerizations were carried out as follows: the catalyst precursor (chromium complex) was dissolved in toluene in a Schlenk tube stirred with a magnetic stirrer under an ethylene atmosphere (1 atm), and the reaction temperature was controlled by a water bath. The reaction was initiated by adding the desired amount of cocatalyst. After the desired period of time, a small amount of the reaction solution was collected with a syringe and was quenched by the addition of 5% hydrochloric acid in an ice-water bath in accordance with the oligomers of C_4 and C_6 produced. An analysis by gas chromatography (GC) was carried out to determine the distribution of oligomers obtained. The remaining solution was quenched with HCl–acidified ethanol (5%), and the precipitated polyethylene was collected by filtration, washed with ethanol, dried under vacuum at 60 °C to constant weight, weighed, and finally characterized.

4.5. Procedure for ethylene oligomerization and polymerization at higher pressure

Ethylene oligomerization and polymerization were performed in a 250 ml autoclave stainless steel reactor equipped with a mechanical stirrer and a temperature controller. A 100 ml amount of toluene containing the catalyst precursor was transferred to the fully dried reactor under a nitrogen atmosphere. The required amount of cocatalyst (MAO, MMAO, or Et_2AlCl) was then injected into the reactor via a syringe. At the reaction temperature, the reactor was sealed and pressurized to high ethylene pressure, and the ethylene pressure was maintained with feeding of

Table 6
Crystal data and refinement details for **C2** and **C3**

	C2 · DMF	**C3**
Empirical formula	$C_{30}H_{37}Cl_3CrN_5O$	$C_{29}H_{34}Cl_3CrN_4$
Formula weight	642.00	596.95
Crystal color	Green	Green
Temperature (K)	296(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$P21/c$
a (Å)	8.1681(2)	8.6022(5)
b (Å)	11.801(2)	31.5105(2)
c (Å)	32.964(7)	13.5669(7)
α (°)	90	90
β (°)	94.40(3)	126.814(3)
γ (°)	90	90
Volume (Å^3)	3168.2(1)	2944.1(3)
Z	4	4
D_{calc} (Mg m^{-3})	1.346	1.347
μ (mm^{-1})	0.645	0.686
$F(000)$	1340	1244
Crystal size (mm)	0.45 × 0.25 × 0.04	0.35 × 0.25 × 0.20
θ Range (°)	2.48–25.00	1.98–28.30
Limiting indices	$-9 \leqslant h \leqslant 9$ $-14 \leqslant k \leqslant 14$ $-39 \leqslant l \leqslant 38$	$-11 \leqslant h \leqslant 11$ $-41 \leqslant k \leqslant 41$ $-17 \leqslant l \leqslant 18$
Number of reflections collected	9197	30972
Number of unique reflections	5439	7270
R_{int}	0.0443	0.2034
Completeness to θ (%)	96.0 ($\theta = 25.00$)	99.1 ($\theta = 28.30$)
Absorption correction	Empirical	Empirical
Data/restraints/parameters	5349/173/380	7270/0/335
Goodness-of-fit on F^2	1.050	0.959
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0577$, wR2 = 0.1427	$R_1 = 0.0747$, $wR_2 = 0.1504$
R indices (all data)	$R_1 = 0.0899$, $wR_2 = 0.1557$	$R_1 = 0.2113$, $wR_2 = 0.2073$
Largest difference in peak, hole (e Å^{-3})	0.637, −0.354	0.379, −0.327

ethylene. After the reaction mixture was stirred for the desired period, the pressure was released and a small amount of the reaction solution was collected, which was then analyzed by gas chromatography (GC) for determining the composition and mass distribution of oligomers obtained. Then the residual reaction solution was quenched with 5% hydrochloric acid in ethanol. The precipitated low-molecular-weight waxes were collected by filtration, washed with ethanol and water, and dried under vacuum to constant weight.

4.6. X-ray crystallographic studies

Single-crystal X-ray diffraction studies for **C2** and **C3** were collected on a Rigaku R-AXIS Rapid IP diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 296(2) K. Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package [45]. Crystal data and processing parameters for **C2** and **C3** are summarized in Table 6.

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Appendix A. Supplementary material

CCDC 660792 and 660793 contain the supplementary crystallographic data for **C2** and **C3**. 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.2007.11.049.

References

[1] L.L. Böhm, Angew. Chem., Int. Ed. 42 (2003) 5010–5030.
[2] (a) R.F. Service, Science 278 (1997) 33–34;
(b) E.J. Beckman, Science 283 (1999) 946–947;
(c) T.R. Younkin, E.F. Connor, J.I. Henderson, S.K. Friedrich, R.H. Grubbs, D.A. Bansleben, Science 287 (2000) 460–462;
(d) K.A. Chaffin, J.S. Knutsen, P. Brant, F.S. Bates, Science 288 (2000) 2187–2190.
[3] (a) M. Enders, P. Fernandez, G. Ludwing, H. Pritzkow, Organometallics 20 (2001) 5005–5007;
(b) L. Resconi, R.L. Jones, A.L. Rheingold, G.P.A. Yap, Organometallics 15 (1996) 998–1005.
[4] (a) N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, Macromolecules 19 (1986) 2464–2465;
(b) G. Xu, D. Cheng, Macromolecules 33 (2000) 2825–2831.
[5] (a) K.H. Theopold, Acc. Chem. Res. 23 (1990) 263–270;
(b) K.H. Theopold, Chemtech 27 (1997) 26–32;
(c) C. Pariya, K.H. Theopold, Curr. Sci. 78 (2000) 1345–1351.
[6] K.H. Theopold, Eur. J. Inorg. Chem. (1998) 15–24.
[7] (a) V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283–315;
(b) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem., Int. Ed. 38 (1999) 428–447.
[8] (a) J.P. Hogan, R.L. Banks, US A2 825 721, 1958;
(b) E. Groppo, C. Lamberti, S. Bordiga, G. Spoto, A. Zecchina, Chem. Rev. 105 (2005) 115–184.
[9] (a) W.K. Reagen, Am. Chem. Soc. Symp., Div. Petrol. Chem. 34 (1989) 583–588;
(b) W.K. Reagen, EP 0417477, 1991 (to Phillips Petroleum Company);
(c) W.K. Reagen, B.K Conroy, US 5, 288, 823, 1994 (to Phillips Petroleum Company);
(d) W.K. Reagen, T.M. Pettijohn, J.W. Freeman, US Patent 5523507, 1996 (to Phillips Petroleum Company).
[10] (a) D.F. Wass, Dalton Trans. (2007) 816–819;
(b) J.T. Dixon, M.J. Green, F.M. Hess, D.H. Morgan, J. Organomet. Chem. 689 (2004) 3641–3668.
[11] V.C. Gibson, S. Mastroianni, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans. (2000) 1969–1971.

[12] (a) V.C. Gibson, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans. (1999) 827–830;
(b) D.J. Jones, V.C. Gibson, S.M. Green, P.J. Maddox, Chem. Commun. (2002) 1038–1039.
[13] (a) L.A. MacAdams, G.P. Buffone, C.D. Incarvito, A.L. Rheingold, K.H. Theopold, J. Am. Chem. Soc. 127 (2005) 1082–1083;
(b) L.A. MacAdams, W.K. Kim, L.M. Liable-Sands, I.A. Guzei, A.L. Rheingold, K.H. Theopold, Organometallics 21 (2002) 952–960.
[14] (a) V.C. Gibson, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, Eur. J. Inorg. Chem. (2001) 1895–1903;
(b) W.-K. Kim, M.J. Fevola, L.M. Liable-Sands, A.L. Rheingold, K.H. Theopold, Organometallics 17 (1998) 4541–4543;
(c) V.C. Gibson, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 1651–1652;
(d) V.C. Gibson, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans. (2002) 4017–4023.
[15] P. Wei, D.W. Stephan, Organometallics 21 (2002) 1308–1310.
[16] (a) R.D. Köhn, M. Haufe, G. Kociok-Köhn, S. Grimm, P. Wasserscheid, W. Keim, Angew. Chem., Int. Ed. 39 (2000) 4337–4339;
(b) R.D. Köhn, M. Haufe, S. Mihan, D. Lilge, Chem. Commun. (2000) 1927–1928.
[17] A.K. Tomov, J.J. Chirinos, R.J. Long, V.C. Gibson, M.R.J. Elsegood, J. Am. Chem. Soc. 128 (2006) 7704–7705.
[18] A. Carter, S.A. Cohen, N.A. Cooley, A. Murphy, J. Scutt, D.F. Wass, Chem. Commun. (2002) 858–859.
[19] R.J. Baker, P.G. Edwards, J. Chem. Soc., Dalton Trans. (2002) 2960–2965.
[20] D.S. McGuinness, P. Wasserscheid, W. Keim, C. Hu, U. Englert, J.T. Dixon, C. Grove, Chem. Commun. (2003) 334–335.
[21] (a) D.S. McGuinness, P. Wasserscheid, W. Keim, D. Morgan, J.T. Dixon, A. Bollmann, H. Maumela, F. Hess, U. Englert, J. Am. Chem. Soc. 125 (2003) 5272–5273;
(b) 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) 14712–14713.
[22] (a) M.E. Bluhm, O. Walter, M. Döring, J. Organomet. Chem. 690 (2005) 713–721;
(b) D.S. McGuinness, P. Wasserscheid, D.H. Morgan, J.T. Dixon, Organometallics 24 (2005) 552–556.
[23] D.S. McGuinness, V.C. Gibson, D.F. Wass, J.W. Steed, J. Am. Chem. Soc. 125 (2003) 12716–12717.
[24] J. Liu, Y. Li, J. Liu, Z. Li, J. Mol. Catal. A: Chem 244 (2006) 99–104.
[25] N.J. Robertson, M.J. Carney, J.A. Halfen, Inorg. Chem. 42 (2003) 6876–6885.
[26] (a) B.J. Thomas, K.H. Theopold, J. Am. Chem. Soc. 110 (1988) 5902–5903;
(b) B.J. Thomas, S.K. Noh, G.K. Schulte, S.C. Sendlinger, K.H. Theopold, J. Am. Chem. Soc. 113 (1991) 893–902;
(c) A. Döhring, J. Göhre, P.W. Jolly, B. Kryger, J. Rust, G.P.J. Verhovnik, Organometallics 19 (2000) 388–402;
(d) O. Heinemann, P.W. Jolly, C. Kruger, G.P.J. Verhovnik, J. Organomet. Chem. 553 (1998) 477–479;
(e) G. Mani, F.P. Gabbai, Angew. Chem., Int. Ed. 43 (2004) 2263–2266;
(f) R.A. Heintz, S. Leelasubcharoen, L.M. Liable-Sands, A.L. Rheingold, K.H. Theopold, Organometallics 17 (1998) 5477–5485;
(g) Y. Liang, G.P.A. Yap, A.L. Rheingold, K.H. Theopold, Organometallics 15 (1996) 5284–5286;
(h) G. Bhandari, Y. Kim, J.M. McFarland, A.L. Rheingold, K.H. Theopold, Organometallics 14 (1995) 738–745;
(i) G. Bhandari, A.L. Rheingold, K.H. Theopold, Chem. Eur. J. 1 (1995) 199–203.
[27] W. Zhang, W.-H. Sun, X. Tang, T. Gao, S. Zhang, P. Hao, J. Chen, J. Mol. Catal. A: Chem. 265 (2007) 159–166.
[28] (a) W. Zhang, W.-H. Sun, S. Zhang, J. Hou, K. Wedeking, S. Schultz, R. Fröhlich, H. Song, Organometallics 25 (2006) 1961–1969;
(b) S. Zhang, J. Jie, Q. Shi, W.-H. Sun, J. Mol. Catal. A: Chem. 127 (2007) 174–183.
[29] (a) W.-H. Sun, X. Tang, T. Gao, B. Wu, W. Zhang, H. Ma, Organometallics 23 (2004) 5037–5047;
(b) X. Tang, W.-H. Sun, T. Gao, J. Hou, J. Chen, W. Chen, J. Organomet. Chem. 690 (2005) 1570–1580;
(c) W.-H. Sun, S. Jie, S. Zhang, W. Zhang, Y. Song, H. Ma, J. Chen, K. Wedeking, R. Fröhlich, Organometallics 25 (2006) 666–677;
(d) W.-H. Sun, S. Zhang, S. Jie, W. Zhang, Y. Li, H. Ma, J. Chen, K. Wedeking, R. Fröhlich, J. Organomet. Chem. 691 (2006) 4196–4203;
(e) S. Jie, S. Zhang, K. Wedeking, W. Zhang, H. Ma, X. Lu, Y. Deng, W.-H. Sun, C.R. Chim. 9 (2006) 1500–1509.
[30] (a) W.-H. Sun, P. Hao, S. Zhang, Q. Shi, W. Zuo, X. Tang, Organometallics 26 (2007) 2720–2734;
(b) P. Hao, S. Zhang, W.-H. Sun, Q. Shi, S. Adewuyi, X. Lu, P. Li, Organometallics 26 (2007) 2439–2446.
[31] P.R. Elowe, C. McCann, P.G. Pringle, S.K. Spitzmesser, J.E. Bercaw, Organometallics 25 (2006) 5255–5260.
[32] M. Ganesan, F.P. Gabba, Organometallics 23 (2004) 4608–4613.
[33] M.J. Carney, N.J. Robertson, J.A. Halfen, L.N. Zakharov, A.L. Rheingold, Organometallics 23 (2004) 6184–6190.
[34] Y. Nakayama, K. Sogo, H. Yasuda, T. Shiono, J. Polym. Sci. Part A: Polym. Chem. 43 (2005) 3368–3375.
[35] R.T. Mathers, K. Damodaran, J. Polym. Sci. Part A: Polym. Chem. 45 (2007) 3150–3165.
[36] U. Subramanyam, S. Sivaram, J. Polym. Sci. Part A: Polym. Chem. 45 (2007) 120–191.
[37] H. Zou, F.M. Zhu, Q. Wu, J.Y. Ai, S.A. Lin, J. Polym. Sci., Part A: Polym. Chem. 43 (2005) 1325–1330.
[38] Q. Wang, L. Li, Z. Fan, J. Polym. Sci., Part A: Polym. Chem. 43 (2005) 1599–1606.
[39] (a) G.J.P. Britovsek, M. Bruce, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S. Mastroianni, S.J. McTavish, C. Redshaw, G.A. Solan, S. Strömberg, A.J.P. White, D.J. Williams, J. Am. Chem. Soc. 121 (1999) 8728–8740;
(b) G.J.P. Britovsek, S. Mastroianni, G.A. Solan, S.P.D. Baugh, C. Redshaw, V.C. Gibson, A.J.P. White, D.J. Williams, M.R.J. Elsegood, Chem. Eur. J. 6 (2000) 2221–2231.
[40] C. Huang, J. Ahn, S. Kwon, J. Kim, J. Lee, Y. Han, H. Kim, Appl. Catal. A: Gen. 258 (2004) 173–181.
[41] H.-K. Luo, D.-G. Li, S. Li, J. Mol. Catal. A: Chem. 221 (2004) 9–17.
[42] (a) P.J. Flory, J. Am. Chem. Soc. 62 (1940) 1561–1565;
(b) G.V. Schulz, Z. Phys. Chem., Abt. B 30 (1935) 379–398;
(c) G.V. Schulz, Z. Phys. Chem., Abt. B 43 (1939) 25–46;
(d) M.V. Meurs, G.J.P. Britovsek, V.C. Gibson, S.A. Cohen, J. Am. Chem. Soc. 127 (2005) 9913–9923;
(e) G.J.P. Britovsek, S.A. Cohen, V.C. Gibson, M.V. Meurs, J. Am. Chem. Soc. 126 (2004) 10701–10702.
[43] M.A. Esteruelas, A.M. López, L. Méndez, M. Oliván, E. Oñate, Organometallics 22 (2003) 395–406.
[44] (a) D. Reardon, F. Conan, S. Gambarotta, G. Yap, Q. Wang, J. Am. Chem. Soc. 121 (1999) 9318–9325;
(b) J. Scott, S. Gambarotta, I. Korobkov, Q. Knijnenburg, B. de Bruin, P.H.M. Budzelaar, J. Am. Chem. Soc. 127 (2005) 17204–17206;
(c) I. Vidyaratne, J. Scott, S. Gambarotta, R. Duchateau, Organometallics 26 (2007) 3201–3211.
[45] G.M. Sheldrick, SHELXTL-97, Program for the Refinement of Crystal Structures, University of Gottingen, Germany, 1997.