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2-Benzimidazolyl-*N*-phenylquinoline-8-carboxamide Chromium(III) Trichlorides: Synthesis and Application for Ethylene Oligomerization and Polymerization

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S Supporting Information

ABSTRACT: A series of chromium(III) complexes, LCrCl₃ (C1–C6: L = 2-(1*H*-benzo-[*d*]imidazol-2-yl)-*N*-(2,6-R¹-4-R²-phenyl)quinoline-8-carboxamide; C1: R¹ = ^{*i*}Pr, R² = H; C2: R¹ = Et, R² = H; C3: R¹ = Me, R² = H; C4: R¹ = Me, R² = Me; C5: R¹ = H, R² = H; C6: R¹ = F, R² = H), was synthesized and characterized by IR spectroscopy, elemental analysis, mass spectra, and magnetic moments. The X-ray crystallographic analysis of complexes C2 and C3 reveals distorted octahedral geometries around the chromium atoms. Upon activation with MAO, these



complexes exhibit high activities for ethylene oligomerization (up to $1.28 \times 10^7 \text{ g} \cdot \text{mol}^{-1}(\text{Cr}) \cdot h^{-1}$) and ethylene polymerization (up to $6.30 \times 10^6 \text{ g} \cdot \text{mol}^{-1}(\text{Cr}) \cdot h^{-1}$). The oligomers were produced with high selectivity for α -olefins (>99%), and the distribution closely resembled the Schultz–Flory rule. Various reaction parameters were investigated in detail, and the results revealed that both the steric and electronic effects of the ligands effect the catalytic activities of these chromium complexes as well as the distribution of the products formed.

1. INTRODUCTION

Polyolefins are by far the most important and the most produced synthetic polymers today.¹ Along with the fast development of coordination and organometallic chemistry, polyolefins remain highly technology-driven and are indeed the fastest growing segment of the polymer industry.² The ever-growing demand for high-performance polyolefins has inspired extensive industrial and academic research into developing new catalysts for polyolefin production.³ While the Cr-based Phillips catalyst accounts for more than one-third of the polyethylene sold worldwide,⁴ recently Cp-free chromium complexes have attracted attention as efficient homogeneous catalysts.3d,f,5 In particular, interest has focused on the selective trimerization^{5d,6} or tetramerization⁷ of ethylene by chromium catalysts, producing 1-hexene or 1-octene as comonomers in the production of linear low-density polyethylene (LLDPE). On the other hand, homogeneous chromium catalysts provide the opportunity of understanding both the nature of the active species and the mechanism of the polymerization/oligomerization process, which in turn might well be helpful in designing new advanced catalysts.^{6h,n,8} Recently, considerable attention has been paid to designing homogeneous catalyst systems based on chromium complexes through developing and utilizing multidentate ligand sets, such as N^{N} , ${}^{6g,7a,9}_{c,1}$, N^{O} , ${}^{9b,10}_{c,1}$, P^{P} or $P^{N}N^{P}6^{a,b,n,q,11}_{c,1}$, $P^{P}P^{12}_{c,1}$, $N^{P}N$, ${}^{9f,13}_{c,1}$, $S^{N}N^{S}$, ${}^{6i,p,14}_{c,1}$, $N^{S}N$, ${}^{15}_{c,1}$, $C^{N}N^{C}$, ${}^{16}_{c,1}$, $N^{N}N$, ${}^{6c,17d,18}_{c,1}$, and $N^{N}N^{N}N^{19}_{c,1}$ ligands.

Over the past few years, our group has studied chromium complexes bearing tridentate ligands such as 2-imino-1,

10-phenanthrolines (**A**, Scheme 1),²⁰ 2,6-bis(benzimidazolyl)pyridines (**B**, Scheme 1),²¹ 2-quinoxalinyl-6-iminopyridines (**C**, Scheme 1),²² 2-benzimidazolyl-6-aryliminopyridines (**D**, Scheme 1),²³ 2-benzazole-1,10-phenanthrolines (X = N, O, or S) (**E**, Scheme 1),²⁴ and 2-benzoxazolyl-6-aryliminopyridines (**F**, Scheme 1).²⁵ During the course of this research, it became clear that careful tuning of the environments of the ligands, namely, incorporation of different substituents or heteroatoms in the framework of the ligands, can tremendously affect the observed catalytic activities and resulting properties of the products. Therefore, we are continuing our program of designing new catalyst models. In our earlier work, we studied the 2-benzimidazolyl-*N*-phenylquinoline-8-carboxamide titanium complexes, which exhibited high activity for ethylene polymerization and ethylene/higher α -olefin copolymerization.²⁶ In extending this research, the chromium complexes bearing the same ligands have now been prepared herein and applied as procatalysts for ethylene oligomerization and polymerization.

2. RESULTS AND DISCUSSIONS

2.1. Synthesis and Characterization of 2-(Benzimidazol-2yl)-*N*-phenylquinoline-8-carboxamide Chromium Trichlorides. A series of 2-(benzimidazol-2-yl)-*N*-phenylquinoline-8carboxamide derivatives (L1–L6) was prepared following

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Scheme 1. Representative Procatalysts of Chromium Complexes



Scheme 2. Synthesis of Complexes C1-C6



Figure 1. ORTEP view of the molecular structure of $C2 \cdot CH_3OH$ (ellipsoids enclose 30% electronic density; H atoms are omitted for clarity).

previously reported procedures.²⁶ The chromium complexes C1-C6 (Scheme 2) were synthesized as green solids by the stoichiometric reactions of $[CrCl_3(THF)_3]$ and the corresponding ligands in THF in high yields (91–97%). All complexes are air-stable powders, and elemental analysis confirmed that the complexes are of the LCrCl₃ composition. According to their IR spectra, the C=O stretching frequencies of C1-C6 are shifted to lower values (1618–1625 cm⁻¹) compared to those of the free ligands (1639–1665 cm⁻¹). In addition to the mononuclear structures of $C2 \cdot CH_3OH$ and $C3 \cdot DMF$ confirmed by the single-crystal X-ray diffraction, the mass spectra of complexes



Figure 2. ORTEP view of the molecular structure of $C3 \cdot DMF$ (ellipsoids enclose 30% electronic density; H atoms are omitted for clarity).

showed the mononuclear feature with the main fragments of $[M - 2Cl - H + CH_3OH]^+$ ions in their methanol solutions. Their magnetic moments were typically between 3.73 and 4.22 $\mu_{\rm B}$, which are measured in methanol- d_4 by the Evans method,²⁷ which indicate the three unpaired electrons and are consistent with observations of the paramagnetic mono-chromium(III) complexes.^{9f,i,28}

Single crystals of complexes $C2 \cdot CH_3OH$ and $C3 \cdot DMF$ suitable for X-ray diffraction analysis were grown by slow layering of diethyl ether into a methanol solution of C2 and a DMF solution of C3, respectively. The molecular structures are illustrated in Figures 1 and 2, with selected bond lengths and angles collected in Table 1. Complex $C2 \cdot CH_3OH$ exhibits a distorted octahedral coordination geometry at the Cr center. One chloride atom *trans* to the quinoline-N is replaced by one methanol molecule and acts as a counterion, which is also found for the Ni complexes.²⁹ The tridentate ligand is situated around the chromium center in a *meridional* manner (N^N^O) and adopts a puckered chelating style with the dihedral angle 6.21° defined by the two chelating rings (Cr1–N1–C7–C8–N3, Cr1–N3–Cl6–Cl5–C17–O1), which is much smaller than that of an analogous titanium complex.²⁶ The phenyl ring linked to the

Table 1. Selected Bond Lengths and Angles for $C2 \cdot CH_3OH$ and $C3 \cdot DMF$

	C2·CH ₃ OH	C3 · DMF				
	Bond Lengths (Å)					
Cr1-O1	1.956(3)	1.945(2)				
Cr1-O2	1.993(3)	1.993(2)				
Cr1-N1	2.017(4)	2.015(3)				
Cr1-N3	2.061(4)	2.055(2)				
Cr1-Cl1	2.321(1)	2.3179(1)				
Cr1-Cl2	2.306(1)	2.3177(1)				
O1-C17	1.254(5)	1.255(4)				
N4-C17	1.341(5)	1.320(4)				
Bond Angles (deg)						
Cl1-Cr1-Cl2	178.98(5)	175.79(4)				
Cl1-Cr1-O2	89.55(1)	93.40(8)				
O1-Cr1-O2	92.73(1)	92.57(9)				
N1-Cr1-N3	80.49(1)	81.08(1)				
O1-Cr1-N3	90.72(1)	90.68(1)				
N1-Cr1-O2	95.68(1)	96.26(1)				
O1-Cr1-N1	170.36(1)	171.69(1)				
O2-Cr1-N3	175.38(1)	176.53(1)				

amide group orients nearly perpendicularly to the coordination plane with a dihedral angle of 70.8°. Similar phenomena have been observed in reported chromium complexes ligated by bis(imino)pyridine,^{17d,18b,22} 2-carbethoxy-6-iminopyridines,^{17b} 2-imino-1,10-phenanthrolines,²⁰ 2-quinoxalinyl-6-iminopyridine,²² and 2-benzimidazolyl-6-aryliminopyridine.²³ Compared to the half-titanocene analogue, this angle is slightly smaller due to more congestion.²⁶ The chromium atom and the mutually *trans*-disposed chlorines are almost in one line [Cl1-Cr1-Cl2 = $178.98(5)^{\circ}$ with N1, N3, O1, and O2 atoms located in an equatorial plane. Most of the bond angles in the equatorial plane are close to a right angle $[O1-Cr1-N3 = 90.72(1)^{\circ};$ $O1-Cr1-O2 = 92.73(1)^{\circ}; N1-Cr1-N3 = 80.49(1)^{\circ};$ N1-Cr1-O2 = $95.68(1)^{\circ}$]. The coordination sphere contains six bonds of three types, for which the bond lengths of the same type are very similar [Cr1-O1 = 1.956(3) Å; Cr1-O2 =1.993(3) Å; Cr1-N1 = 2.017(4) Å; Cr1-N3 = 2.061(4) Å; Cr1-Cl1 = 2.321(1) Å; Cr1-Cl2 = 2.306(1) Å]. The O1-C17 bond length [1.254(5) Å] is slightly longer than the characteristic C=O bond (1.19–1.23 Å), indicating partial electron donation by oxygen to the central metal, but this is shorter than the corresponding one found in 2-benzimidazolyl-N-phenylquinoline-8-carboxamide half-titanocenes [1.330(4) Å], which exhibit a conjugated feature within the carboximidate group.²⁶ Similar phenomena are also observed in our other reported systems containing the carboximidate group as a ligand.³

Complex C3·DMF (Figure 2) possesses similar coordination features to C2·CH₃OH; selected structural parameters for both complexes are presented in Table 1. Given the lack of structural deviation between C2·CH₃OH and C3·DMF, we believe that the other complexes will possess similar coordination characteristics. In C3·DMF, one DMF molecule coordinates to the Cr metal center, while the chloride atom *trans* to the quinoline-N is dissociated as a counterion. The C–O bond length (O1–C17 = 1.255(4) Å) of the amidate group is almost equal to that in C2·CH₃OH and displays partial conjugated features. However,

Table 2. Effect of Co-catalyst on Ethylene Reactivity with $C3^a$

			oligomers ^c			
entry	cocatalyst	Al/Cr	activity ^b	distribution	Κ	waxes activity ^b
1	MAO	1500	3.05	$C_4 - C_{28}$	0.73	1.39
2	MMAO	1500	1.37	$C_4 - C_{28}$	0.64	0.650
3	Et ₂ AlCl	200	0.105	C_4		
4	Et ₃ Al	200				
¹ Condi	tions: 2 <i>u</i> n	nol of C	r: 1 atm o	of ethvlene: 2	20 °C.	30 min. toluene

(total volume 50 mL). ^b In units of $10^6 \text{ g} \cdot \text{mol}^{-1} \cdot (\text{Cr}) \cdot \text{h}^{-1}$. ^c Determined by GC.

some interesting differences can be observed between C2· CH₃OH and C3·DMF. The dihedral angle defined by the two chelating rings (Cr1–N1–C7–C8–N3, Cr1–N3–Cl6– Cl5–C17–O1) is 2.0°, which is smaller than that in C2· CH₃OH. In contrast, the dihedral angle between the phenyl ring and the coordination plane is 88.6°, which is much larger than the corresponding one found in C2·CH₃OH. In turn, these differences also influence their catalytic behavior during olefin polymerization, which will be discussed in the next section.

2.2. Ethylene Oligomerization and Polymerization. The effects of various cocatalysts, such as methylaluminoxane (MAO), modified methylaluminoxane (MMAO), Et₂AlCl, and Et₃Al, on the activity toward ethylene reactivity were first studied in detail with C3. The results are collected in Table 2 and indicate that the ethylene reactivity is strongly influenced by the chosen cocatalyst. The catalytic system with Et_2AlCl (entry 3, Table 2) produced only butenes with low oligomerization activities, and it is inactive when Et₃Al was employed as the cocatalyst. However, high activity could be achieved by the catalytic system of complex C3 when combined with MAO or MMAO (entries 1 and 2, Table 2). Further investigations were carried out with MAO as cocatalyst, and all the complexes were found to exhibit high catalytic activities for ethylene oligomerization and polymerization with high α -olefin selectivity (>99%). The distributions of obtained oligomers closely resemble the Schulz-Flory rules, which is characteristic of the constant K, where K represents 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)).³¹ The K values in this context are determined by the molar ratio of C_{12} and C_{14} .

2.2.1. Effect of Reaction Parameters. The catalytic system of C3/MAO was typically investigated with varying reaction conditions, such as the reaction temperature, the molar ratio of Al/Cr, and the reaction time. Elevating the reaction temperature from 0 to 20 °C speeds the combined catalytic reactions of oligomerization and polymerization (entries 1 and 2, Table 3). However, further increasing the reaction temperature to 40 °C leads to a decrease of catalytic activity (entry 4, Table 3), which could be attributed to the decomposition of the active species and lower ethylene solubility in the reaction solution at higher temperature.³² This is consistent with the chromium complexes ligated by 2-benzimidazolyl-6-aryliminopyridine, which also showed the best activity at 20 °C.^{23a} Although the activities of the C3/MAO system were affected by various reaction temperatures, the reaction temperatures did not significantly change the distributions of oligomers, for which the K values fall in the range 0.70 to 0.74 (entry 1-4, Table 3). Fewer polyethylene waxes were produced at elevated temperatures (entries 1 vs 4, Table 3)

Table 3. Oligomerization and Polymerization of Ethylene with $C3/MAO^a$

		Т				oligomers ^b		waxes	
	entry	$(^{\circ}C)$	Al/Cr	$t(\min)$	activity ^c	(wt %)	Κ	(wt %)	
	1	0	1500	30	2.78	68.0	0.73	32.0	
	2	20	1500	30	4.44	68.7	0.73	31.3	
	3	30	1500	30	2.62	74.0	0.70	26.0	
	4	40	1500	30	1.97	74.5	0.74	25.5	
	5	20	500	30	0.256	100	0.76	trace	
	6	20	1000	30	2.61	73.6	0.74	26.4	
	7	20	2000	30	3.68	73.1	0.74	26.9	
	8	20	2500	30	2.15	72.6	0.78	27.4	
	9	20	1500	10	4.88	68.9	0.78	31.1	
	10	20	1500	20	4.76	68.1	0.76	31.9	
	11	20	1500	60	3.11	67.2	0.73	32.8	
ι,	Condit	iona 2	umal of	Cr. 1 at	n of oth	ulana, talua	na (tat	al vialum	

^{*a*} Conditions: 2 μ mol of Cr; 1 atm of ethylene; toluene (total volume 50 mL). ^{*b*} Determined by GC. ^{*c*} In units of 10⁶ g·mol⁻¹·(Cr)·h⁻¹.

Table 4. Oligomerization and Polymerization of 1 atm of Ethylene with $C1-C6/MAO^a$

entry	complex	activity ^c	oligomers ^b (wt %)	Κ	waxes (wt %)
1	C1	2.86	81.8	0.71	18.2
2	C2	3.38	74.0	0.71	26.0
3	C3	4.44	68.7	0.73	31.3
4	C4	4.66	68.9	0.75	31.1
5	C5	1.48	69.6	0.73	30.4
6	C6	1.05	71.0	0.70	29.0

^{*a*} Conditions: 2 μ mol of Cr; 20 °C, 30 min, Al/Cr = 1500, toluene (total volume 50 mL). ^{*b*} Determined by GC. ^{*c*} In units of 10⁶ g·mol⁻¹·(Cr)·h⁻¹.

because of faster β -hydrogen elimination than chain propagation, which is consistent with the observation for [2,6-bis(2-benzimidazolyl)pyridyl]chromium trichlorides.^{21,33} It is notable that increasing the temperature does not lead to a decrease in the selectivity for α -olefins.

The amount of cocatalyst was found to have significant influence on the catalytic behavior of the C3/MMAO system. Increasing the Al/Cr molar ratio from 500 to 1500 leads to an enhancement of the ethylene oligomerization and polymerization activities (see entries 2, 5, 6, Table 3). When the ratio of Al/Cr is 1500, the catalytic system displays the highest activity of $4.44 \times 10^6 \text{ g} \cdot \text{mol}^{-1} \cdot (\text{Cr}) \cdot \text{h}^{-1}$ (entry 2, Table 3). A further increase in the Al/Cr molar ratio to 2000 or 2500 leads to decreased catalytic activity (entries 7 and 8, Table 3). Similar phenomena were observed in previously reported chromium complexes, and the deactivation might be caused by the impurities present in commercial MAO such as alkyl aluminum, which can react with the active species.^{20,24,25}

With regard to the lifetime of the C3/MAO system, the ethylene polymerization was conducted over different time periods, namely, 10, 20, 30, and 60 min (entries 2, 9-11, Table 3). The activities were almost maintained over the initial 30 min, but decreased somewhat on extending the runs to 60 min, indicating that the active species slowly deactivated over prolonged reaction times.

2.2.2. Effect of the Ligand Environment. On the basis of the results observed with the C3/MAO system, the title complexes C1-C6 were investigated with an MAO/Cr molar ratio of 1500

Table 5. Oligomerization and Polymerization of 10 atm of Ethylene with $C1-C6/MAO^a$

		Т			oligomers ^b		waxes
entry	complex	$(^{\circ}C)$	Al/Cr	activity ^c	(wt %)	Κ	(wt %)
1	C1	20	1500	15.0	61.5	0.74	38.5
2	C2	20	1500	15.9	63.5	0.73	36.5
3	C3	20	1500	18.8	67.0	0.73	33.0
4	C4	20	1500	19.1	67.0	0.73	33.0
5	C5	20	1500	4.80	65.6	0.72	34.4
6	C6	20	1500	1.89	66.7	0.74	33.3
7	C3	30	1500	8.14	72.0	0.74	38.0
8	C3	40	1500	4.81	87.6	0.72	12.4
9	C3	20	1000	16.0	65.6	0.76	34.4
10	C3	20	2000	11.2	74.5	0.74	25.5
11^d	C3	20	1500	18.9	66.7	0.74	33.6
12^e	C3	20	1500	18.1	66.9	0.73	32.5
' Condi	tions: 2 μ	umol o	f Cr; 30) min, to to 10^6 of 10^6	luene (total \cdot	volume r) $\cdot h^{-1}$	100 mL). ^d Toluene

^o Determined by GC. ^o In units of 10^o g·mol ^(Cr) (Cr)·h ^{$(Cr)} (total volume 200 mL). ^e 1 <math>\mu$ mol of Cr.</sup></sup>

at 20 °C under 1 atm of ethylene. The data listed in Table 4 show that the structures of the ligands have a considerable effect on the catalytic behavior of the complexes. It is evident that an electrondonating effect positively influences the activities of the chromium complexes. Complexes C1-C4, containing electron-donating groups, namely, 'Pr, Et, and Me on the anilines, exhibit much higher activity comparing to complex C6, which bears electron-withdrawing groups. On the other hand, increasing the steric hindrance at the ortho positions of the anilines renders a less active catalyst (C3 ($R^1 = Me$) > C2 ($R^1 = Et$) > C1 ($R^1 =$ ⁱPr)). This could be explained in terms of the reaction rate, which depends on the insertion of ethylene at the active species, and so a bulkier group would cause a slower insertion reaction and consequently lower activity. Meanwhile, with increased bulk, the content of longer chain oligomers and polyethylene is decreased, which might be attributed on the basis that the catalysts with more steric bulkiness facilitate the β -hydrogen elimination reaction and not the reaction of propagation.

2.2.3. Ethylene Oligomerization and Polymerization of 10 atm of Ethylene. Kinetic studies have shown that the rate of oligomerization increases with increasing ethylene concentration.^{7e,34} Therefore, ethylene oligomerization and polymerization with complexes C1-C6 were also carried out at 10 atm of ethylene with MAO as cocatalyst, and the results are listed in Table 5. The results show that the ethylene pressure significantly affects the catalytic behavior of the complexes. This observation of increased activity at elevated ethylene pressure is in accordance with previously reported results for homogeneous chro-mium catalysts.^{14b,21,23a} Among the catalytic systems herein, the C4/MAO system shows the highest activity of up to 1.91×10^7 $g \cdot mol^{-1} \cdot (Cr) \cdot h^{-1}$ (entry 4, Table 5). At 10 atm of ethylene, the effect of the ligand environments and the reaction parameters (the reaction temperature and the molar ratio of Al/Cr) on the activity is similar to the results obtained at 1 atm of ethylene. In comparison with the results with 1 atm of ethylene, the percentages of polyethylene waxes increased remarkably, which can be explained by the rate of propagation being faster than that of hydrogen elimination at higher pressure. The distributions of the oligomers achieved by the C1-C3/MAO systems (entries 1-3,



Figure 3. Plot of the molar amount of oligomers formed by C1–C3/MAO (entries 1–3 in Table 5) versus carbon number (C_6-C_{28}) and the calculated distribution for a K value of 0.73.



Figure 4. ¹³C NMR spectrum of the waxes obtained by the C3/MAO system in entry 3 in Table 5.

Table 5) are shown in Figure 3, indicating an approximate Schulz–Flory distribution. It is worthy to mention that dilute catalyst concentration through either more solvent (entry 11, Table 5) or loading less catalyst (entry 12, Table 5) resulted in a slight decrease of the catalytic activity.

Along with the high selectivity for α -olefins, polyethylene waxes were also obtained. As characterized by IR spectra (KBr disks), the polyethylene waxes were confirmed to be composed of highly linear α -olefins by the characteristic vibration absorption bands of the C–H and C=C bonds. A ¹³C NMR spectrum (Figure 4) of the polyethylene waxes obtained by the C3/MAO system (entry 3, Table 5) was recorded at 110 °C in *o*-dichlorobenzene- d_4 using TMS as the internal standard and demonstrates that linear α -olefins of the waxes predominate in

the polymers. The resonances at about δ 138.7 (CH=) and 113.8 (CH₂=) ppm are typical for a vinyl-unsaturated chain end;³⁵ the other ethylene waxes showed very similar NMR spectra.

3. CONCLUSION

The chromium(III) complexes (LCrCl₃, C1–C6) have been synthesized and characterized, including by single-crystal X-ray diffraction for C2 and C3. All procatalysts show high activity, up to $1.91 \times 10^7 \text{ g} \cdot \text{mol}^{-1} \cdot (\text{Cr}) \cdot \text{h}^{-1}$, toward ethylene oligomerization and polymerization in the presence of MAO. The procatalysts bearing ligands with electron-donating groups give higher activity, while the activity is favored for less bulky substituents at

	C2·CH ₃ OH	C3 · DMF
formula	C ₂₇ H ₂₃ Cl ₃ CrN ₅ O·CH ₃ OH	$C_{25}H_{21}Cl_3CrN_4O \cdot DMF$
fw	623.90	610.89
Т (К)	173(2)	173(2)
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	triclinic
space group	P2(1)/c	$P\overline{1}$
a (Å)	8.7764(1)	9.4487(1)
b (Å)	20.349(4)	10.408(2)
c (Å)	21.050(4)	16.144(3)
α (deg)	90.00	84.10(3)
β (deg)	92.29(3)	73.53(3)
γ (deg)	90.00	79.76(3)
$V(\text{\AA}^3)$	3756.3(1)	1495.9(5)
Ζ	4	2
$D_{ m calcd}~(m g~ m cm^{-3})$	1.103	1.356
$\mu \ (\mathrm{mm}^{-1})$	0.545	0.681
F(000)	1284	630
heta range (deg)	1.39-27.48	1.99-27.44
limiting indices	$-11 \le h \le 11, -24 \le k \le 26, -27 \le l \le 23$	$-12 \le h \le 12, -13 \le k \le 12, -20 \le l \le 20$
no. of rflns collected	30 509	20 234
no. of unique reflns	8582	6818
completeness to θ (%)	99.6 $(\theta = 27.48^{\circ})$	99.7 ($\theta = 27.44^{\circ}$)
abs corr	numerical	numerical
no. of params	352	347
goodness of fit on F^2	1.068	1.123
final <i>R</i> indices $(I > 2\sigma(I))$	R1 = 0.0666, wR2 = 0.1711	R1 = 0.0823, wR2 = 0.1930
R indices (all data)	R1 = 0.0870, wR2 = 0.1825	R1 = 0.1085, wR2 = 0.2071
largest diff peak, hole (e ${\rm \AA}^{-3}$)	0.537 and -0.589	0.589 and -0.500

Table 6. Crystallographic Data and Refinement Details for C2 · CH₃OH and C3 · DMF

the *ortho* positions of the amidate aryl rings. The oligomers were produced with high selectivity for α -olefins (>99%), and the distributions closely resemble the Schultz–Flory rule. The polyethylene waxes were verified to be long linear olefins with vinyl end groups by their characteristic IR and ¹H and ¹³C NMR spectra.

4. EXPERIMENTAL SECTION

4.1. General Considerations. All manipulations of air- and/or moisture-sensitive compounds were performed under a nitrogen atmosphere in a glovebox or using standard Schlenk techniques. 2-(Benzimidazol-2-yl)-N-phenylquinoline-8-carboxamide derivatives were prepared as previously reported.²⁶ Tetrahydrofuran (THF) and toluene were refluxed over sodium/benzophenone and distilled under nitrogen prior to use. Methylaluminoxane (MAO, a 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane, 3A) were purchased from Akzo Nobel Corp. Diethylaluminum chloride (Et₂AlCl, 1.7 M in toluene) and triethyl aluminum (AlEt₃, 2 M in hexane) were purchased from Acros Chemicals. Other reagents were purchased from Beijing Chemicals. FT-IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using an HPMOD 1106 microanalyzer. For measuring magnetic moments by the Evans method, a solution of the chromium complex in C_6H_{12} -CD₃OD solution (3% cyclohexane in CD₃OD, v/v) was prepared along with the reference C₆H₁₂-CD₃OD solution (3% cyclohexane in CD₃OD, v/v).²⁷ The ESI-MS spectrum was obtained with a LC-MS 2010 (constant infusion 6 mL h⁻¹, needle voltage 4.6 kV, capillary voltage 50 V). GC analyses were performed with a Varian CP-3800 gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μ m film thickness) CP-Sil 5 CB column. The yield of oligomers was calculated by referencing with the mass of the solvent on the basis of the prerequisite that the mass of each fraction was approximately proportional to its integrated areas in the GC trace. Selectivity for the linear α -olefin was defined as (amount of linear α -olefin of all fractions)/(total amount of oligomer products) in percent. ¹H NMR and ¹³C NMR spectra of the polyethylene waxes were recorded on a Bruker DMX-300 MHz instrument at 110 °C in deuterated 1,2-dichlorobenzene with TMS as an internal standard.

4.2. General Procedure. Solid $[CrCl_3(THF)_3]$ was added to a solution of the ligand in THF (20 mL) to slowly give a green suspension, which was stirred for 6 h. The solvent was removed under vacuum, affording a green powder, which was washed with diethyl ether (2 \times 20 mL) and dried *in vacuo* overnight. All of the complexes were prepared in high yield following this same procedure.

2-(1*H*-Benzo[*d*]imidazol-2-yl)-*N*-(2,6-diisopropylphenyl)quinoline-8-carboxamide CrCl₃ (**C1**). Obtained as a green powder in 95.0% yield. FT-IR (KBr, cm⁻¹): 3436m, 3210w, 3065m, 2966m, 2868w, 1623s, 1604s, 1570s, 1540m, 1442m, 1363w, 1339m, 1232w, 1146m, 1013w, 997m, 856w, 765m. *m*/z 566.1, $[M - 2Cl - H + CH_3OH]^+$ (ESI-MS). $\mu_{eff.} = 3.82 \ \mu_B$. Anal. Calcd for C₂₉H₂₈Cl₃CrN₄O: C, 57.39; H, 4.65; N, 9.23. Found: C, 57.13; H, 4.55; N, 9.11.

2-(1H-Benzo[d]imidazol-2-yl)-N-(2,6-diethylphenyl)quinoline-8-carboxamide $CrCl_3$ (**C2**). Obtained as a green powder in 94.5% yield. FT-IR (KBr, cm⁻¹): 3416m, 3198m, 3065w, 2970m, 1623s, 1600s, 1565s,

1532m, 1501m, 1457w, 1340w, 1233w, 1141m, 1012m, 860m, 760m. m/z 538.1, $[M - 2Cl - H + CH_3OH]^+$ (ESI-MS). $\mu_{eff} = 3.73 \mu_B$. Anal. Calcd for C₂₇H₂₄Cl₃CrN₄O: C, 56.02; H, 4.18; N, 9.68. Found: C, 55.98; H, 4.09; N, 9.65.

2-(1H-Benzo[d]imidazol-2-yl)-N-(2,6-dimethylphenyl)quinoline-8carboxamide CrCl₃ (**C3**). Obtained as a green powder in 97.0% yield. FT-IR (KBr, cm⁻¹): 3428m, 3185m, 3064w, 2925m, 1624s, 1601s, 1566s, 1538m, 1474w, 1440w, 1341w, 1303w, 1228w, 1150m, 1092m, 857m, 761m. *m*/*z* 510.1, [M – 2Cl – H + CH₃OH]⁺ (ESI-MS). $\mu_{\rm eff}$ = 3.91 $\mu_{\rm B}$. Anal. Calcd for C₂₅H₂₀Cl₃CrN₄O: C, 54.51; H, 3.66; N, 10.17. Found: C, 54.50; H, 3.33; N, 10.10.

2-(1H-Benzo[d]imidazol-2-yl)-N-(2,4,6-trimethylphenyl)quinoline-8-carboxamide CrCl₃ (**C4**). Obtained as a green powder in 96.2% yield. FT-IR (KBr, cm⁻¹): 3399m, 3256m, 3057w, 2971m, 1625s, 1602s, 1570s, 1534m, 1476w, 1441w, 1422w, 1378w, 1337w, 1223w, 1147m, 1045m, 853m, 763m. *m*/*z* 524.1, [M – 2Cl – · H + CH₃OH]⁺ (ESI MS). $\mu_{\text{eff.}} = 3.95 \ \mu_{\text{B}}$. Anal. Calcd for C₂₆H₂₂Cl₃CrN₄O: C, 55.29; H, 3.93; N, 9.92. Found: C, 54.97; H, 3.77; N, 9.68.

 $\begin{array}{l} 2-(1H\text{-}Benzo[d]\text{imidazol-2-yl}\text{)-}N\text{-}phenylquinoline-8-carboxamide}\\ CrCl_3 (\textbf{C5}). Obtained as a green powder in 91.0% yield. FT-IR (KBr, cm^{-1}): 3408m, 3201m, 3022w, 2951m, 1620s, 1602s, 1567s, 1533m, 1476w, 1440w, 1429w, 1366w, 1325w, 1221w, 1177m, 1042m, 851m, 760 m. m/z 482.1, [M - 2Cl - H + CH_3OH]^+ (ESI-MS). \mu_{eff.} = 4.09 \, \mu_{\rm B}.$ Anal. Calcd for C₂₃H₁₆Cl₃CrN₄O: C, 52.84; H, 3.09; N, 10.72. Found: C, 52.57; H, 3.08; N, 10.53.

2-(1H-Benzo[d]imidazol-2-yl)-N-(2,6-difluorophenyl)-8-carboxamide CrCl₃ (**C6**). Obtained as a green powder in 91.5% yield. FT-IR (KBr, cm⁻¹): 3448m, 3257m, 3067w, 1618s, 1601m, 1571s, 1541m, 1474s, 1441m, 1422w, 1341w, 1324w, 1227w, 1148m, 1050w, 1016s, 998m, 856m, 763m. *m*/z 518.0, $[M - 2Cl - H + CH_3OH]^+$ (ESI-MS). $\mu_{eff.} = 4.22 \,\mu_B$. Anal. Calcd for C₂₃H₁₄Cl₃CrF₂N₄O: C, 49.44; H, 2.53; N, 10.03. Found: C, 49.21; H, 2.39; N, 9.95.

4.3. Procedure for Oligomerization and Polymerization with 1 atm of Ethylene. Polymerizations were carried out as follows: the catalyst precursor (chromium complex) was dissolved in toluene in a 250 mL 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% aqueous HCl. 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, and dried under vacuum at 60 °C to constant weight.

4.4. Procedure for Oligomerization and Polymerization with 10 atm of Ethylene. Ethylene oligomerization and polymerization at 10 atm of ethylene pressure was carried out in a 500 mL autoclave stainless steel reactor equipped with a mechanical stirrer and a temperature controller. Briefly, toluene, the desired amount of cocatalyst, and a toluene solution of the catalytic precursor (the total volume was 100 mL) were added to the reactor in this order under an ethylene atmosphere. When the desired reaction temperature was reached, ethylene at 10 atm pressure was introduced to start the reaction, and the ethylene pressure was maintained by constant feeding of ethylene. After the required time, the reaction was stopped. A small amount of the reaction solution was collected, the reaction was terminated by the addition of 5% aqueous hydrogen chloride, and then this mixture was analyzed by gas chromatography (GC) to determine the distribution of oligomers obtained. The remaining solution was quenched with HCl-acidified ethanol (5%), and the precipitated polyethylene waxes were filtered, washed with ethanol, and dried under vacuum at 60 °C to constant weight.

4.5. Crystal Structure Determination. Single crystals of C2 · CH₃OH and C3 · DMF suitable for X-ray diffraction studies were

obtained by slow diffusion of diethyl ether into methanol or DMF solutions, respectively. Single-crystal X-ray diffraction studies for C2·CH₃OH and C3·DMF were carried out on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 . All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.³⁶ Crystal data and processing parameters for C2·CH₃OH and C3·DMF are summarized in Table 6.

ASSOCIATED CONTENT

Supporting Information. CIF file giving X-ray crystal structural data of nickel complexes **C2** and **C3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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