

Synthesis, Characterization, and Ethylene Oligomerization and Polymerization of [2,6-Bis(2-benzimidazolyl)pyridyl]chromium Chlorides

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A series of [2,6-bis(2-benzimidazolyl)pyridyl]chromium chlorides have been synthesized and characterized by elemental analysis and IR spectroscopy, along with X-ray diffraction analysis for the structures of **C1** and **C7**. When methylaluminoxane (MAO) was employed as the cocatalyst, the chromium complexes showed high activity for ethylene oligomerization and polymerization. Oligomers were produced with high selectivity for α -olefins, and polyethylenes were generated with extremely broad molecular weight distributions. In the presence of diethylaluminum chloride (Et_2AlCl), these chromium complexes showed moderate activity for ethylene polymerization and produced high-molecular-weight linear polyethylene.

1. Introduction

In ethylene oligomerization and polymerization, increasing interest has been focused on the exploration and development of homogeneous transition-metal catalysts.¹ Chromium catalysts have played important roles in both ethylene polymerization and oligomerization.² The Cr-based heterogeneous catalysts (Phillips catalyst) for ethylene polymerization produce polyethylenes with broad molecular weight distributions as a unique property, which are significantly more useful than other polyolefins or their blends produced by Ziegler–Natta catalysts for application in blow-molding products.³ Meanwhile, the Cr-based catalysts also play a central role in the oligomerization of ethylene such as trimerization⁴ and tetramerization.⁵ In addition, chromium complexes as homogeneous catalysts for ethylene oligomerization and polymerization have recently drawn much

attention, with the expectation of being highly effective catalysts for industrial application and yielding an understanding of the catalytic mechanism.^{2,4d} Tridentate chromium complexes ligated with $\text{S}\wedge\text{N}\wedge\text{S}$,⁶ $\text{P}\wedge\text{N}\wedge\text{P}$,^{4g} $\text{O}\wedge\text{N}\wedge\text{N}$,⁷ or $\text{N}\wedge\text{N}\wedge\text{N}$ ^{4d,8} have shown great potential in ethylene oligomerization and polymerization. For example, chromium complexes coordinated with $\text{N}\wedge\text{N}\wedge\text{N}$ species such as bis(imino)pyridine,⁹ (2-pyridylmethyl)amines,¹⁰ and β -diketimate and pyrrolide-imine ligands¹¹ have been reported to polymerize or oligomerize ethylene when activated by methylaluminoxane (MAO). The 2,6-bis(2-benzimidazolyl)pyridine ligand derivatives have been reported to coordinate to transition metals in order to prepare various complexes for structure and property investigations,^{12–14} but without consideration of their catalytic properties in ethylene oligomerization

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(1) (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. (b) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (c) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283.

(2) Groppo, E.; Lamberti, C.; Bordiga, S.; Spoto, G.; Zecchina, A. *Chem. Rev.* **2005**, *105*, 115.

(3) Pullukat, T. J.; Hoff, R. E. *Catal. Rev. Sci. Eng.* **1999**, *41*, 389.

(4) (a) Briggs, J. R. *J. Chem. Soc., Chem. Commun.* **1989**, 674. (b) Emrich, R.; Heinemann, O.; Jolly, P. W.; Krueger, C.; Verhovnik, G. P. *J. Organometallics* **1997**, *16*, 1511. (c) Köhn, R. D.; Haufe, M.; Mihan, S.; Lilje, D. *Chem. Commun.* **2000**, 1927. (d) Köhn, R. D.; Haufe, M.; Kociok-Köhn, G.; Grimm, S.; Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 4337. (e) Carter, A.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F. *Chem. Commun.* **2002**, 858. (f) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Morgan, D.; Dixon, J. T.; Bollmann, A.; Maumela, H.; Hess, F.; Englert, U. *J. Am. Chem. Soc.* **2003**, *125*, 5272. (g) McGuinness, D. S.; Wasserscheid, P.; Morgan, D. H.; Dixon, J. T. *Organometallics* **2005**, *24*, 552. (h) Doebling, A.; Jensen, V. R.; Jolly, P. W.; Thiel, W.; Weber, J. C. *Organometallics* **2001**, *20*, 2234.

(5) Bollmann, A.; Blann, K.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M.; Slawin, A. M. Z.; Wasserscheid, P.; Kuhlmann, S. *J. Am. Chem. Soc.* **2004**, *126*, 14712.

(6) (a) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Hu, C.; Englert, U.; Dixon, J. T.; Grove, C. *Chem. Commun.* **2003**, 334. (b) Agapie, T.; Schofer, S. J.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 1304.

(7) Jones, D. J.; Gibson, V. C.; Green, S. M.; Maddox, P. J. *Chem. Commun.* **2002**, 1038.

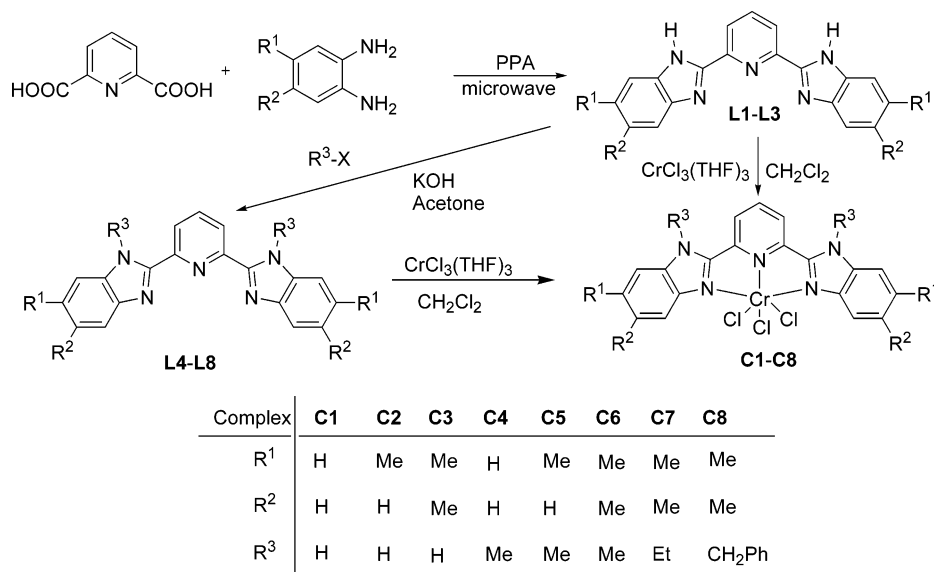
(8) (a) Wills, A. R.; Edwards, P. G. *J. Chem. Soc., Dalton Trans.* **1989**, 1253. (b) Wasserscheid, P.; Grimm, S.; Köhn, R. D.; Haufe, M. *Adv. Synth. Catal.* **2001**, *343*, 814. (c) Rüther, T.; Cavell, K. J.; Braussaud, N. C.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2002**, 4684.

(9) (a) Small, B. L.; Carney, M. J.; Holman, D. M.; O'Rourke, C. E.; Halfen, J. A. *Macromolecules* **2004**, *37*, 4375. (b) Esteruelas, M. A.; López, A. M.; Méndez, L.; Oliván, M.; Oñate, E. *Organometallics* **2003**, *22*, 395. (c) Nakayama, Y.; Sogo, K.; Yasuda, H.; Shiono, T. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3368.

(10) Carney, M. J.; Robertson, N. J.; Halfen, J. A.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2004**, *23*, 6184.

(11) (a) Gibson, V. C.; Maddox, P. J.; Newton, C.; Redshaw, C.; Solan, G. A.; Andrew, J. P. W.; Williams, D. J. *Chem. Commun.* **1998**, 1651. (b) Kim, W.-K.; Fevola, M. J.; Liable-Sands, L. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1998**, *17*, 4541.

(12) (a) Breslow, R.; Hunt, J. T.; Smiley, R.; Tamowski, T. *J. Am. Chem. Soc.* **1983**, *105*, 5337. (b) Beer, R. H.; Tolmann, W. B.; Bott, S. G.; Lippard, S. J. *Inorg. Chem.* **1989**, *28*, 4557. (c) Wu, F.-J.; Kurtz, D. M., Jr.; Hagen, K. S.; Nyman, P. D.; Debrunner, P. G.; Vankai, V. A. *Inorg. Chem.* **1990**, *29*, 5174. (d) Kimblin, C.; Allen, W. E.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1995**, 1813. (e) Sorrell, T. N.; Allen, W. E.; White, P. S. *Inorg. Chem.* **1995**, *34*, 952.

Scheme 1. Synthesis of 2,6-Bis(2-benzimidazolyl)pyridine Derivatives **L1–L8** and Chromium Complexes **C1–C8**

and polymerization. As an extension of our investigation of transition-metal complexes with $\Lambda\Lambda\Lambda$ ligands,¹⁵ bis(benzimidazolyl)pyridine derivatives were prepared and coordinated to iron(II) chloride. However, the bis(benzimidazolyl)pyridyl ferrous complexes showed low activity for ethylene polymerization. Therefore, chromium complexes ligated by bis(benzimidazolyl)pyridine were synthesized (Scheme 1). Very recently, the Gibson group reported a mechanism study of ethylene oligomerization by **C1**.¹⁶ In this study, the chromium complexes ligated by bis(benzimidazolyl)pyridine derivatives showed good activities for the combined oligomerization and polymerization of ethylene with MAO as cocatalyst, while the ethylene polymerization only proceeds in the presence of diethylaluminum chloride (Et_2AlCl). Here the synthesis and characterization of chromium complexes bearing bis(benzimidazolyl)pyridine ligands are reported along with single-crystal X-ray structural analyses. The ethylene reactivity and their product properties have also been investigated.

2. Results and Discussion

2.1. Synthesis and Characterization of 2,6-Bis(2-benzimidazolyl)pyridine Derivatives (L1–L8). The 2,6-bis(2-benzimidazolyl)pyridine derivatives **L1–L3** were prepared by condensation reactions of the corresponding 1,2-phenylenediamines and pyridine-2,6-dicarboxylic acid in the presence of phosphoric acid (PPA) in the microwave oven (Scheme 1). Among these compounds, **L1** has been synthesized by refluxing the corresponding reactants in solution for several hours.¹⁷ To significantly shorten the reaction time, the condensation reactions were carried out under microwave radiation.¹⁸ The ligands **L4–L7** were prepared in high yields through simple N-

alkylation of **L1–L3** in acetone at room temperature,¹⁹ while the alkylation for **L8** proceeds at higher temperature (60 °C). The stretching frequencies of all ligands fall within the following ranges: $\nu(\text{N–H})$ is about 3055 cm^{-1} for **L1–L3**, $\nu(\text{C=C})$ is between 1584 and 1600 cm^{-1} , and $\nu(\text{C=N})$ is between 1567 and 1572 cm^{-1} . All of the 2,6-bis(2-benzimidazolyl)pyridine derivatives synthesized were confirmed by elemental analysis and NMR spectra.

2.2. Synthesis and Characterization of the Chromium Complexes C1–C8. The six-coordinated [2,6-bis(2-benzimidazolyl)pyridyl]chromium(III) trichlorides **C1–C8** were prepared in high yields through the treatment of 2,6-bis(2-benzimidazolyl)pyridine derivatives with 1 equiv of $\text{CrCl}_3(\text{THF})_3$ in CH_2Cl_2 at room temperature (Scheme 1). According to their IR spectra, the typical stretching frequency of $\nu(\text{N–H})$ shift to a band at around 3064 cm^{-1} for **C1–C3**, and the frequencies of $\nu(\text{C=C})$ and $\nu(\text{C=N})$ shift to bands between 1603 and 1613 cm^{-1} and between 1568 and 1590 cm^{-1} , respectively. On the other hand, the strong ligand bands at around 1313 cm^{-1} (**L1–L3**) and 1325 cm^{-1} (**L4–L8**) shift to higher frequencies around 1323 cm^{-1} (**C1–C3**) and 1335 cm^{-1} (**C4–C8**), indicating coordination through the pyridine nitrogen. All of the complexes were consistent with their elemental analyses.

Complexes **C1** and **C7** were further characterized by X-ray crystallography. Crystals of complex **C1** suitable for an X-ray structure determination were grown from an *N,N*-dimethylformamide (DMF) solution layered with diethyl ether. It is the first crystal structure determined by X-ray crystallography of a chromium(III) complex bearing 2,6-bis(2-benzimidazolyl)pyridine. The molecular structure is shown in Figure 1, and selected bond lengths and angles are given in Table 1. The geometry around the six-coordinated chromium atom could be described as a distorted octahedron with a tridentate $\Lambda\Lambda\Lambda$ ligand and three chlorines. The Cl–Cr–Cl and N–Cr–N angles are $77.55(10)$, $77.56(10)$, $155.09(10)^\circ$ and $92.07(4)$, $93.17(4)$, $174.71(4)^\circ$ respectively. The $\text{Cr–N}(\text{pyridine})$ bond distance ($\text{Cr1–N3} = 2.040(2)\text{ \AA}$) is about $0.03\text{ \AA}$ shorter than the $\text{Cr–N}(\text{imidazole})$ bond distance ($(2.072(3)\text{ \AA})$ (Cr1–N1) and $2.084(3)\text{ \AA}$ (Cr1–N4)), with the formal double-bond character

(13) (a) Chatlas, J.; Kaizaki, S.; Kita, E.; Kita, P.; Sakagami, N.; Van Eldik, R. *J. Chem. Soc., Dalton Trans.* **1999**, 91. (b) Winter, J. A.; Caruso, D.; Shepherd, R. E. *Inorg. Chem.* **1988**, 27, 1086. (c) Bocarsly, J. R.; Chiang, M. Y.; Bryant, L.; Barton, J. K. *Inorg. Chem.* **1990**, 29, 4898.

(14) Cenicer-Gómez, A. E.; Barba-Behrens, N.; Quiroz-Castro, M. E.; Bernès, S.; Nöth, H.; Castillo-Blum, S. E. *Polyhedron* **2000**, 19, 1821.

(15) (a) Wang, L.; Sun, W.-H.; Han, L.; Yang, H.; Hu, Y.; Jin, X. *J. Organomet. Chem.* **2002**, 658, 62. (b) Ma, Z.; Sun, W.-H.; Li, Z.-L.; Shao, C.-X.; Hu, Y.-L. *Chin. J. Polym. Sci.* **2002**, 20, 205.

(16) Tomov, A. K.; Chirinos, J. J.; Jones, D. J.; Long, R. J.; Gibson, V. C. *J. Am. Chem. Soc.* **2005**, 127, 10166.

(17) (a) Addison, A. W.; Burke, P. J. *J. Heterocycl. Chem.* **1981**, 18, 803. (b) Muller, G.; Bu1nzli, J.-C. G.; Schenk, K. J.; Piguet, C.; Hopfgartner, G. *Inorg. Chem.* **2001**, 40, 2642.

(18) (a) Cui, Y.; Tang, X.; Shao, C.; Li, J.; Sun, W.-H. *Chin. J. Chem.* **2005**, 23, 589. (b) Yang, H.; Sun, W.-H.; Li, Z.; Wang, L. *Synth. Commun.* **2002**, 32, 2395.

(19) Kikugawa, Y. *Synthesis* **1981**, 124.

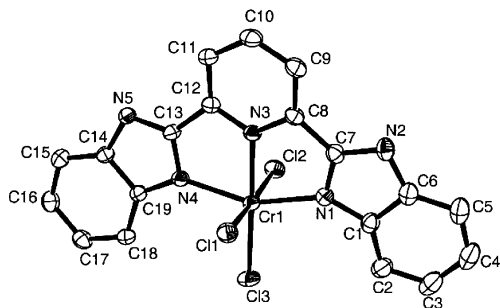


Figure 1. Molecular structure of complex **C1**. Thermal ellipsoids are shown at 30% probability; hydrogen atoms and solvent have been omitted for clarity.

Table 1. Selected Bond Lengths and Bond Angles for Complexes **C1** and **C7**

C1		C7	
Bond Lengths (Å)			
Cr1–N3	2.040(2)	Cr1–N18	2.044(4)
Cr1–N1	2.072(3)	Cr1–N1	2.050(4)
Cr1–N4	2.084(3)	Cr1–N38	2.069(4)
Cr1–Cl3	2.2945(10)	Cr1–Cl1	2.3003(16)
Cr1–Cl2	2.3270(11)	Cr1–Cl2	2.3036(14)
Cr1–Cl1	2.3488(11)	Cr1–Cl3	2.3717(16)
N4–C13	1.334(4)	N18–C10	1.340(6)
N4–C19	1.386(4)	N18–C17	1.383(6)
N1–C7	1.337(4)	N38–C30	1.329(6)
N1–C1	1.397(4)	N38–C37	1.380(6)
Bond Angles (deg)			
N3–Cr1–N1	77.55(10)	N18–Cr1–N1	77.28(15)
N3–Cr1–N4	77.56(10)	N18–Cr1–N38	154.24(14)
N1–Cr1–N4	155.09(10)	N1–Cr1–N38	77.16(15)
N3–Cr1–Cl3	178.70(8)	N18–Cr1–Cl1	88.94(12)
N1–Cr1–Cl3	103.53(8)	N1–Cr1–Cl1	93.28(11)
N4–Cr1–Cl3	101.37(7)	N38–Cr1–Cl1	89.36(12)
N3–Cr1–Cl2	88.65(8)	N18–Cr1–Cl2	100.99(11)
N1–Cr1–Cl2	89.10(8)	N1–Cr1–Cl2	173.53(12)
N4–Cr1–Cl2	89.47(8)	N38–Cr1–Cl2	104.77(11)
Cl3–Cr1–Cl2	92.07(4)	Cl1–Cr1–Cl2	92.92(6)
N3–Cr1–Cl1	86.11(8)	N18–Cr1–Cl3	89.46(12)
N1–Cr1–Cl1	89.00(8)	N1–Cr1–Cl3	85.04(11)
N4–Cr1–Cl1	90.18(8)	N38–Cr1–Cl3	91.49(12)
Cl3–Cr1–Cl1	93.17(4)	Cl1–Cr1–Cl3	177.89(6)
Cl2–Cr1–Cl1	174.71(4)	Cl2–Cr1–Cl3	88.73(6)

of the imidazole linkages (N4–C13 (1.334(4) Å) and N1–C7 (1.337(4) Å)) having been retained. The two benzimidazole rings and the pyridine ring in the ligand are nearly coplanar: the average deviations from the plane C13–N4–C19–C18–C17–C10–C15–C4–N5 and the plane N1–C7–N2–C6–C5–C4–C3–C2–C1 are 0.09 and 0.0088 Å, respectively, and the dihedral angle between these two benzimidazole planes is 3.1°. It is worthwhile to mention that the bond lengths between the chromium and the mutually trans-disposed chlorine atoms are significantly different. The bond length of Cr1–Cl2 (2.3270(11) Å) is shorter than the bond length of Cr1–Cl1 (2.3488(11) Å), while the bond length of Cr1–Cl3 (2.2945(10) Å) is the shortest of the three Cr–Cl bonds.

Crystals of complex **C7** suitable for an X-ray structure determination were grown by diffusion of diethyl ether into a dichloromethane solution. Its molecular structure is shown in Figure 2, and selected bond lengths and angles are given in Table 1. Its structure is very similar to that of **C1**. The basal plane consists of the three nitrogen atoms from the pyridine and imidazole and one equatorial chloride, with the remaining chloride occupying the apical position. In this geometry, the Cr1–N1(pyridine) distance (2.050(4) Å) is about the same as the Cr1–N(imino) bond length (Cr1–N38 = 2.069(4) Å, Cr1–N18 = 2.044(4) Å) and Cl1–Cr1–Cl3 = 177.89-

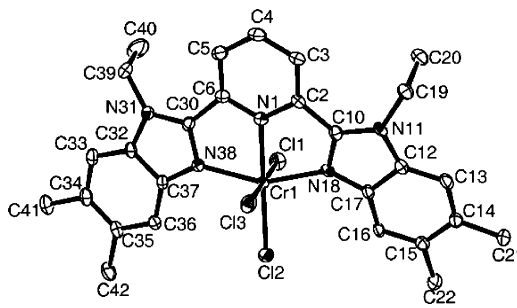


Figure 2. Molecular structure of **C7**. Thermal ellipsoids are shown at 30% probability; hydrogen atoms and solvent have been omitted for clarity.

Table 2. Effect of Cocatalyst and Solvent on Ethylene Reactivity^a

entry	com-plex	cocat.	Al/Cr	solvent	oligomer		polymer activity ^b
					activity ^b	distribn ^c	
1	C1	MAO	1000	toluene	32.0	C ₄ –C ₂₈	7.45
2	C1	MMAO	1000	toluene	8.49	C ₄ –C ₂₀	2.28
3	C1	AlEt ₃	1000	toluene	7.95	C ₄	trace
4	C1	AlMe ₃	1000	toluene	6.76	C ₄	trace
5	C1	MAO	1000	C ₂ H ₄ Cl ₂	4.14	C ₄ , C ₆	trace
6	C1	MAO	1000	CH ₂ Cl ₂	3.25	C ₄ –C ₁₆	trace
7	C1	Et ₂ AlCl	150	toluene	0		1.50

^a General conditions: 5 μmol of complex; ethylene pressure 1 atm; temperature 20 °C; 1 h; volume 30 mL. ^b In units of 10⁴ g (mol of Cr)^{–1} h^{–1}. ^c Determined by GC and GC-MS.

(6)°. The bond distance Cr1–Cl2 = 2.3036(14) Å is as long as the distance Cr1–Cl1 (2.3003(16) Å), which is much shorter than the bond length of Cr1–Cl3 (2.3717(16) Å). The two benzimidazole rings are slightly distorted from the coordination plane by three nitrogen atoms with dihedral angles of 5 and 3°. The average deviations from the plane of the benzimidazole C10–N11–C12–C13–C14–C15–C16–C17–N18 and the other benzimidazole ring are 0.0224 and 0.0141 Å, respectively. The dihedral angle between these two planes is 15.7°, which is much larger than that in **C1** (3.1°), indicating that the greater substitution leads to more distortion of the benzimidazole ring.

2.3. Ethylene Oligomerization and Polymerization. 2.3.1. Selecting a Suitable Solvent and Cocatalyst. The effects of various cocatalysts on the productivity for ethylene reactivity were first studied in detail with **C1**, and the results are collected in Table 2. The results indicate that the ethylene reactivity is strongly influenced by the chosen cocatalysts. The **C1**/MAO system shows remarkably higher catalytic activity than the other systems activated with MMAO, AlEt₃, AlMe₃, and Et₂AlCl. Among them, the distribution of oligomers with MAO and MMAO activation resembles Schulz–Flory rules.²⁰ The lower activity with MMAO could be traced to the presence of triisobutylaluminum (TIBAO), and the species generated therefrom hinder the insertion reaction of ethylene, due to their steric bulkiness.²¹ When **C1** is activated by Et₂AlCl, ethylene polymerization is observed without oligomerization in the process. Under the same reaction parameters, the **C1**/MAO

(20) (a) Flory, P. J. *J. Am. Chem. Soc.* **1940**, 62, 1561. (b) Schulz, G. V. *Z. Phys. Chem., Abt. B* **1935**, 30, 379. (c) Schulz, G. V. *Z. Phys. Chem., Abt. B* **1939**, 43, 25. (d) Meurs, M. V.; Britovsek, G. J. P.; Gibson, V. C.; Cohen, S. A. *J. Am. Chem. Soc.* **2005**, 127, 9913. (e) Britovsek, G. J. P.; Cohen, S. A.; Gibson, V. C.; Meurs, M. V. *J. Am. Chem. Soc.* **2004**, 126, 10701.

(21) (a) Chen, E. Y.; Marks, T. J. *Chem. Rev.* **2000**, 100, 1391. (b) Karam, A. R.; Catarí, E. L.; López-Linares, F.; Agrifoglio, G.; Albano, C. L.; Díaz-Barrios, A.; Lehmann, T. E.; Pekerar, S. V.; Albornoz, L. A.; Atencio, R.; González, T.; Ortega, H. B.; Joskowics, P. *Appl. Catal. A: Gen.* **2005**, 280, 165.

Table 3. Oligomerization and Polymerization under 1 atm of Ethylene with C1–C8/MAO^a

entry	complex	Al/Cr	T (°C)	oligomer distribn ^c (%)				productivity ^b	oligomers (wt %)	% PE (wt %)
				C ₄ /ΣC	C ₆ /ΣC	≥C ₈ /ΣC	α-olefin (%)			
1	C1	500	20	34.7	13.9	51.4	>99.9	2.80	78.6	21.4
2	C2	500	20	40.4	12.0	47.6	98.6	0.96	91.1	8.9
3	C3	500	20	56.6	8.5	34.9	98.5	0.61	96.0	4.0
4	C4	500	20	89.7	3.1	7.2	100	0.53		
5	C5	500	20	59.9	11.8	28.3	95.4	0.36	100	
6	C6	500	20	100			100	0.38	100	
7	C7	500	20	86.7	5.01	8.3	90.4	0.71	100	
8	C8	500	20	74.9	11.6	13.5	97.1	0.43	100	
9	C1	100	20	100			100	0.56	100	
10	C1	300	20	17.6	13.2	69.3	96.4	2.45	83.3	16.7
11	C1	700	20	15.4	16.7	67.8	94.5	3.52	80.1	19.9
12	C1	1000	20	13.9	16.0	70.1	97.2	3.94	81.1	18.9
13	C1	1500	20	12.5	16.5	71.0	95.5	4.62	83.5	16.5
14	C1	1000	0	47.9	9.6	42.5	100	1.12	65.5	34.5
15	C1	1000	40	9.4	14.9	75.7	91.4	5.59	72.4	27.6
16	C1	1000	50	7.4	12.5	80.1	82.1	9.26	75.8	24.2
17	C1	1000	60	6.1	13.2	80.7	77.8	14.3	72.2	27.8
18	C1	1000	80	13.6	14.4	72.0	66.8	10.3	97.1	2.8
19 ^d	C1	1000	20	11.7	13.3	75.0	95.0	3.02	77.8	22.1

^a General conditions: 5 μmol of complex; 30 mL of toluene; 1 h; MAO cocatalyst. ^b In units of 10⁵ g (mol of Cr)^{−1} h^{−1}. ^c Determined by GC and GC-MS. ^d Reaction time 2 h.

shows better ethylene reactivity in toluene (entry 1) than in dichloromethane or 1,2-dichloroethane (entries 5 and 6). It has been suggested that chloro solvents act as effective chain termination agents.²² Therefore, further detailed investigations have been carried out in toluene while changing the catalytic parameters with cocatalysts of MAO and Et₂AlCl.

2.3.2. Ethylene Oligomerization and Polymerization with MAO as Cocatalyst. The chromium complexes were studied in detail for their catalytic activities in ethylene oligomerization and polymerization using methylaluminoxane (MAO) as cocatalyst. The results at 1 atm of ethylene are summarized in Table 3.

2.3.2.1. Effect of the Ligand Environment. These complexes exhibit moderate catalytic activities for ethylene oligomerization and polymerization at 1 atm of ethylene pressure. The products obtained by C1–C3 with MAO are comprised of oligomers with a distribution that closely resembles Schulz–Flory rules²⁰ and waxlike polyethylene. However, complexes C4–C8 produced the major product butene and a trace of polymer. The ethylene reactivity greatly depends on the ligand environment. It is observed that, for the same reaction conditions, the productivity decreased in the orders C1 > C2 > C3 and C4 > C5, which indicates that the more substituted the phenyl group, the lower the ethylene reactivity. This can perhaps be attributed to the increasing nucleophilicity of the metal center by the greater number of methyl groups on the phenyl ring, which weakens the interaction between the chromium atom and the π-electrons of the ethylene monomer and decreases the rate of ethylene insertion in the chain-growth steps.²³

On the other hand, the incorporation of an alkyl group on the N atom of imidazole into the complexes leads to a dramatic decrease in ethylene reactivity and greatly affects the distribution of the oligomers. As shown in Table 3, the complexes C4–C8 showed lower productivity than C1–C3, especially in their polymer yields which decrease to traces. For example, the productivity of C1 is much higher than that of C4 (Table 3, entries 1 and 4), and the same is true for the other complexes in a similar order of C2 > C5 and C3 > C6. The complexes

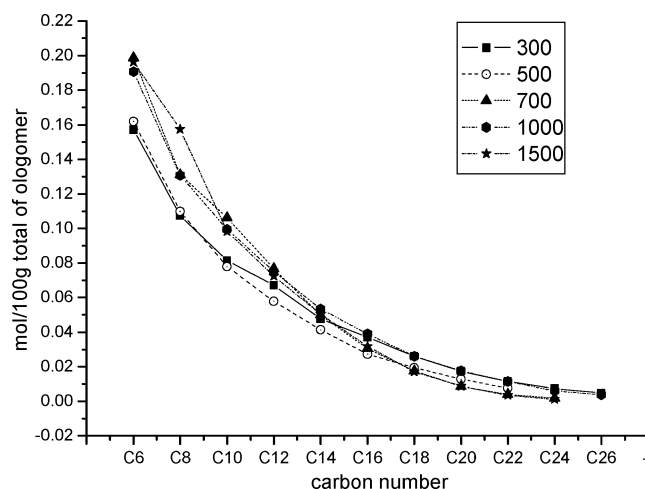


Figure 3. Oligomer molar distribution obtained with C1 at different Al/Cr ratios at 1 atm.

C1–C3, containing N–H groups, show relatively high catalytic activities compared with other analogues. This could be possibly caused by their deprotonation to give anionic amide ligands when activated by MAO (or residual AlMe₃). The anionic amide ligands could be free or form N–Al species (anion–cation pair) to increase their catalytic activity. Though the mechanism is not clear, the fact that complexes C4–C8, containing N-alkyl groups, have low catalytic activities indicates that alkylation of N–H groups plays a negative role in ethylene reactivity. These results are in agreement with the literature.^{4b}

2.3.2.2. Effects of Al/Cr Molar Ratio and Reaction Temperature. The influences of the Al/Cr molar ratio and the reaction temperature on ethylene activation were investigated in detail with C1. Increasing the Al/Cr molar ratio from 100 to 1500 led to a significant increase of the productivity (entries 1 and 9–13 in Table 3). When the ratio of Al/Cr is 1500, the catalytic system displayed high productivity of up to 4.62 × 10⁵ g (mol of Cr)^{−1} h^{−1}. However, the molar distribution of oligomers and the selectivity for α-olefins were not strongly affected by Al/Cr ratio, which can be observed in Figure 3 and is verified by the small variability in their selectivities, with all values higher than 94.5% (entries 9–13 in Table 3), individually. In particular, when the Al/Cr ratio is 100, the productivity was

(22) Robertson, N. J.; Carney, M. J.; Halfen, J. A. *Inorg. Chem.* **2003**, 42, 6876.

(23) Oouchi, K.; Mitani, M.; Hayakawa, M.; Yamada, T. *Macromol. Chem. Phys.* **1996**, 197, 1545.

Table 4. Polymerization and Oligomerization of 10 atm of Ethylene with C1–C8/MAO^a

entry	complex	T (°C)	α -olefin ^c (%)	K	productivity ^b	oligomer (wt %)	PE (wt %)
1 ^d	C1	75	91.7		13.00	65.7	34.3
2	C1	80	93.6	0.70	11.60	65.8	34.2
3	C1	40	95.8		23.70	59.0	41.0
4	C2	40	100	0.62	8.20	78.6	21.3
5	C3	40	100	0.67	2.77	78.0	22.0
6	C4	40	98.5	0.67	3.82	84.5	15.4
7	C5	40	100		0.56	84.7	15.3
8	C6	40	94.5	0.70	1.40	93.6	6.4
9	C7	40	97.0	0.67	0.67	93.2	6.8
10	C8	40	100	0.75	0.58	91.7	8.3

^a General conditions: 2 μ mol of complex; 100 mL of toluene; 1 h; MAO cocatalyst, Al/Cr = 1000. ^b In units of 10^6 g (mol of Cr)⁻¹ h⁻¹. ^c Determined by GC and GC-MS. ^d 5 μ mol of complex.

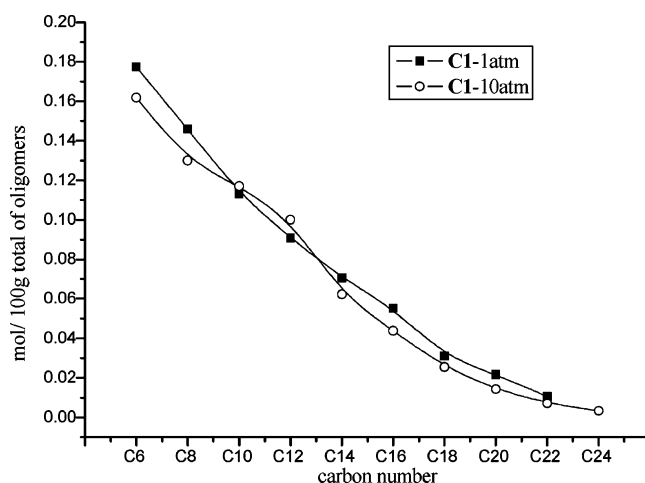
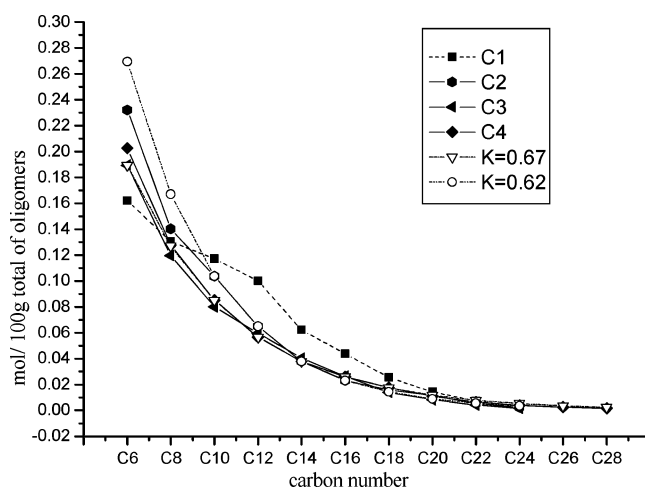
very low, which may be attributed to consumption of the MAO by impurities in the solvent.

Elevating the reaction temperature from 0 to 60 °C sped up the combined catalytic reactions of oligomerization and polymerization. A sharp increase in the production of oligomers and polymer was observed. However, a further increase of the reaction temperature to 80 °C results in a sharp decrease in productivity due to the deactivation of some active centers.²⁴ At the same time, increasing the temperature results in a decrease of PE proportion (see Table 3, entries 14–18), which is due to an increase in the rate of the β -hydrogen elimination relative to the rate of propagation at higher temperature.^{25,26} In addition, increasing the temperature leads to a rapid decrease in the selectivity for α -olefins. For example, the selectivity for α -olefins decreased from 100% at 0 °C to 66.8% at 80 °C.

The catalyst lifetime is one significant factor in industrial considerations. The effect of reaction time on catalytic activity was also studied using the C1/MAO system with a Al/Cr molar ratio of 1000/1 at 20 °C. The productivity obviously decreases with prolonged reaction time (compare entry 12 with entry 19, Table 3), suggesting that the active species of C1 were deactivated as the time of the catalytic reaction increased.

2.3.2.3. Ethylene Pressure Effects. Ethylene oligomerization and polymerization with complexes C1–C8 were also studied at 10 atm of ethylene with MAO as cocatalyst, and the results are listed in Table 4. The results show that ethylene pressure significantly affects the catalytic behavior of the complexes. This observation of increased productivity at elevated ethylene pressure is in accordance with the previously reported results for a homogeneous chromium catalyst.²⁷ Among those precursors, C1 shows the highest activity of up to 2.37×10^7 g (mol of Cr)⁻¹ h⁻¹, which is more than 40 times greater than the result at 1 atm of ethylene (entry 3 in Table 4 vs entry 15 in Table 3). At 10 atm of ethylene, the effect of the ligand environments on the productivity activity is similar to the results at 1 atm.

In comparison with the results with 1 atm of ethylene, the distribution of oligomers formed at 10 atm of ethylene pressure shifts to higher carbon number olefins. Especially for complexes C4–C8, bearing an N-alkyl group, the percentages of PE increase remarkably, which can be explained by the rate of propagation being faster than that of hydrogen elimination at higher pressure. The oligomer distribution obtained by C1 showed a similar trend on changing the ethylene pressure (as

**Figure 4.** Oligomer distribution obtained with C1 at different ethylene pressures (entry 15 in Table 3 and entry 3 in Table 4).**Figure 5.** Oligomer distributions obtained in entries 3–6 in Table 4.

shown in Figure 4), which is in accord with the result of the Gibson group.¹⁶ Most of the oligomer distributions closely resemble the Schulz-Flory rules, and the corresponding K values are given in Table 4. Among them, the distributions obtained by C1, C5, and C7 deviated more from the Schulz-Flory distribution; perhaps their catalytic systems did not follow a simple chain growth reaction. The results indicated that the ligand environment had little effect on the chain growth reaction. The substituents, located far away from the active site due to the planar ligand structure in the complexes, will impose a slight steric influence on the ethylene reactivity. The oligomer distributions achieved by C1–C4 were shown in Figure 5, while the imitations of Schulz-Flory distributions for C2 ($K = 0.62$), C3 ($K = 0.67$) and C4 ($K = 0.67$) fit well with their experimental results (other oligomer distributions were included in the Supporting Information). In addition, GC and GC-MS analysis of the oligomers indicates that the selectivity for linear α -olefins is higher than that at 1 atm for complexes C1–C8.

2.3.2.4. Characterization of Polyethylenes. Regardless of oligomers, all catalysts at 10 atm of ethylene produced significant quantities of polyethylene coproduct. The GPC traces of polyethylenes (Figure 6) showed their bimodal and even multimodal behavior, which were also observed in the catalytic systems of the pyridinebis(imino)chromium^{9a} and [bis(pyridylmethyl)amine]chromium complexes.¹⁰

The GPC curves showed that the molecular weights of the polymers produced by these complexes are largely dependent

(24) Svejda, S. A.; Brookhart, M. *Organometallics* **1999**, *18*, 65.

(25) Huang, C.; Ahn, J.; Kwon, S.; Kim, J.; Lee, J.; Han, Y.; Kim, H. *Appl. Catal. A: Gen.* **2004**, *258*, 173.

(26) Chen, Y.; Qian, C.; Sun, J. *Organometallics* **2003**, *22*, 1231.

(27) Bluhm, M. E.; Walter, O.; Doring, M. *J. Organomet. Chem.* **2005**, *690*, 713.

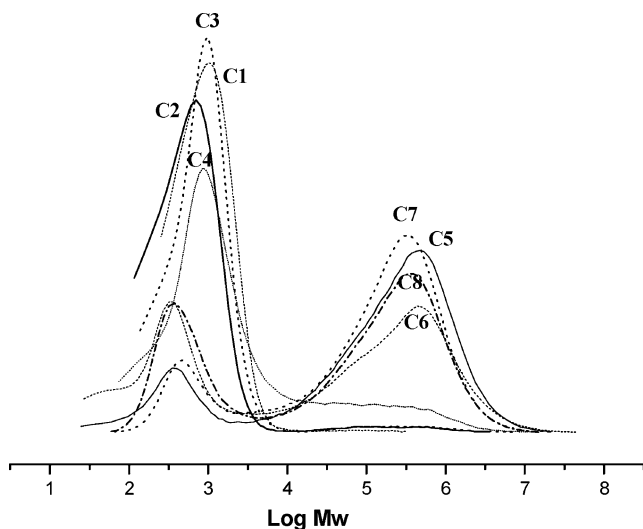


Figure 6. GPC traces of PE samples obtained by entries 3–10 in Table 4.

on the ligand environment. Precursors **C1**–**C4** produced mainly waxlike polyethylenes with low molecular weights (M_w of the largest peak ranges from 927 to 1657). The steric bulk is not sufficient to prevent associative displacement of the growing oligomeric chain, and the electron affinity of the chromium center facilitates the chromium-induced abstraction of a β -hydride from the growing alkyl chain; these combined reasons result in a rapid chain transfer process and low-molecular-weight polymer chains.^{23,28} In contrast, precatalysts **C5**–**C8** produced mainly high-molecular-weight polymer along with some low-molecular-weight polymer. The average molecular weights (M_w) range from 6.0×10^4 to 14.5×10^4 , which are much higher than those of **C1**–**C3**. Perhaps the incorporation of substituents on the nitrogen contributes to the increase in the molecular weight, but more study is needed to fully assess these molecular weight trends.

As characterized by its IR spectrum recorded using a KBr disk in the range of 4000–400 cm^{-1} , the polymer can be confirmed to be mainly linear α -olefins from the characteristic vibration absorption bands of various C–H and C=C bonds. The NMR spectra verified that all the polyethylenes are similar higher order linear α -olefins. The ^{13}C NMR spectrum of the PE obtained by complex **C1** (see Figure 7) at 10 atm of ethylene pressure demonstrated that the PE sample is strictly linear with the presence of end vinyl groups.²⁹

2.3.3. Ethylene Polymerization with Et_2AlCl as Cocatalyst. The initial study of ethylene polymerization showed that, with Et_2AlCl as activator, complexes **C1**–**C3** showed special behavior in ethylene polymerization, which differs from the result with MAO. It has been reported that chromium complexes produce high-molecular-weight PE with noticeably higher activities when Et_2AlCl was used in place of MAO as cocatalyst.³⁰ We performed a detailed study of chromium complexes with the activator Et_2AlCl for ethylene polymerization.

The polymerization results are shown in Table 5. With the activator Et_2AlCl , complexes **C1**–**C6** showed moderate activity for the polymerization of ethylene. At 1 atm of ethylene, increasing the Al/Cr ratio from 100 to 250 has little effect on

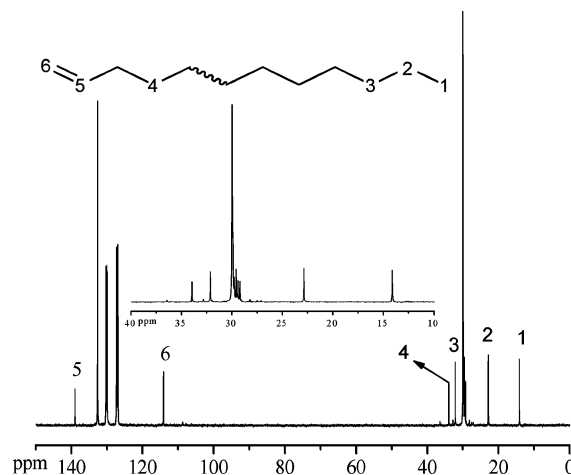


Figure 7. ^{13}C NMR spectrum of the PE sample obtained by **C1**/MAO in entry 3 in Table 4.

Table 5. Polymerization of Ethylene with Et_2AlCl as Cocatalyst^a

entry	complex	pressure (atm)	Al/Cr	activity ^b	T_m^e (°C)	$10^4 M_n^f$	$10^4 M_w^f$	M_w/M_n^f
1 ^c	C2	1	100	2.41	136.3	1.65	27.8	16.8
2	C2	1	150	2.88	136.7	1.63	28.7	17.7
3	C2	1	200	2.68	nd	nd	nd	nd
4	C2	1	250	2.63	136.2	1.44	40.4	28.0
5	C2	1	500	1.05	nd	nd	nd	nd
6 ^d	C1	10	250	3.98	nd	2.23	18.0	8.1
7	C2	10	250	3.52	136.7	4.82	36.4	7.55
8	C3	10	250	3.19	nd	3.03	25.0	8.26
9	C4	10	250	2.66	137.4	5.57	169.4	30.4
10	C5	10	250	4.07	134.2	1.05	14.1	13.4
11	C6	10	250	6.87	139.4	1.62	39.3	24.3

^a General conditions: 5 μmol of complex; temperature 20 °C; reaction time 1 h. ^b In units of $10^4 \text{ g (mol of Cr)}^{-1} \text{ h}^{-1}$. ^c 30 mL of toluene for entries 1–5. ^d 100 mL of toluene for entries 6–11. ^e Determined by DSC. ^f Determined by GPC; nd = not determined.

the polymerization activity (entries 1–5 in Table 5). However, when a ratio of 500 was used, the polymerization activity decreased significantly. Meanwhile, increasing the ethylene pressure resulted in a slight change in polymerization activities (entries 4 and 7, Table 5), which is not what was observed with MAO as cocatalyst. In addition, there was no regulation of the environment effect on the polymerization activity, which differs from the results of polymerization with MAO as cocatalyst.

2.3.3.1. Characterization of Polyethylenes. The GPC curves (Figure 8) showed that all polyethylenes obtained with AlEt_2Cl activator have broad molecular weight distributions. By using precursors **C1**–**C3**, the molecular weights of polyethylenes with Et_2AlCl are much higher than those with MAO. From the M_n and M_w/M_n data in Table 5, polyethylene with a lower molecular weight (M_n) and broader molecular weight distribution is formed at higher Al/Cr ratios (entries 1, 2, and 4 in Table 5). This may be due to chain transfer to aluminum and more active species generated in these systems. The effect of environment on the polymerization activity is not regular; however, the M_w/M_n values of polyethylenes produced by complexes **C4**–**C6** are much higher than those for **C1**–**C3** (entries 6–11).

Although the ethylene pressure has little effect on the polymerization activity, it significantly affects the M_w and M_w/M_n

(28) Cowdell, R.; Davies, C. J.; Hilton, S. J.; Maréchal, J.-D.; Solan, G. A.; Thomas, O.; Fawcett, J. *Dalton Trans.* **2004**, 3231.

(29) (a) Kokko, E.; Lehmus, P.; Leino, R.; Luttikhedde, H. J. G.; Ekholm, P.; Näslman, J.; Seppälä, J. V. *Macromolecules* **2000**, *33*, 9200. (b) Galland, G. B.; Quijada, R.; Bazan, G.; Komon, Z. J. A. *Macromolecules* **2002**, *35*, 339.

(30) (a) Kim, W. K.; Fevola, M. J.; Liable-Sands, L. M.; Rheingold, A. L.; Thepold, K. H. *Organometallics* **1998**, *17*, 4541. (b) Gibson, V. C.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Eur. J. Inorg. Chem.* **2001**, 1895.

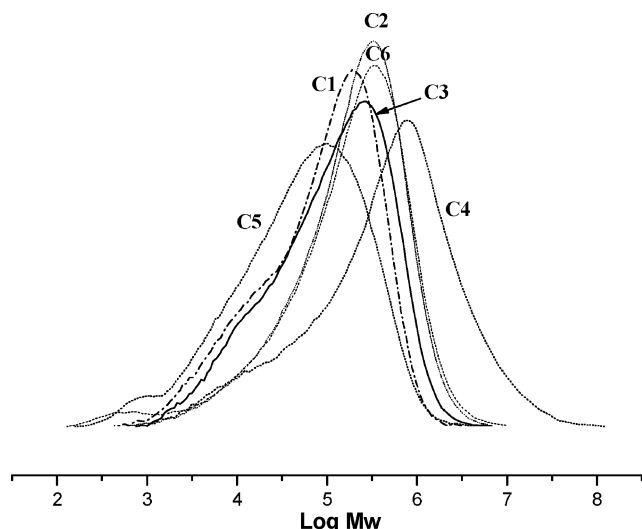


Figure 8. GPC traces of samples obtained by entries 6–11 in Table 5.

values. A higher M_n value and a narrower molecular weight distribution (M_w/M_n) were observed when the ethylene pressure increased from 1 to 10 atm (compare entry 4 with entry 7 in Table 5), which suggests that the chain transfer process was depressed due to the faster insertion of ethylene because of the higher monomer concentration.

The melting points (T_m) of the resulting PEs were determined by differential scanning calorimetry analysis (DSC), and the results are given in Table 5. For different catalysts and various catalytic conditions, the melting point ranges between 134 and 139 °C with enthalpies between 210 and 225 J/g. These values are in line with values given for HDPE.³¹

NMR analyses of the polyethylenes also confirmed the high linearity of polymers obtained with Et_2AlCl as cocatalyst. This is based upon the observation of only one signal from the methylene group ($-\text{CH}_2-$) in the ^1H and ^{13}C NMR spectra, which is clear evidence of the high linearity of the polymer.

3. Conclusion

In summary, the described chromium(III) complexes reveal differences in their behavior as precatalysts for oligomerization and polymerization of ethylene. When using MAO as the cocatalyst, the complexes show high activity for ethylene oligomerization and polymerization, and the resulting polyethylenes obtained at 10 atm have broad molecular weight distributions. They were verified to be long linear olefins with vinyl end groups by ^1H NMR and ^{13}C NMR. The complexes with N-alkyl substitution show lower activities than the complexes with N-H. Under activation by Et_2AlCl , the chromium complexes show moderate activity for polymerization of ethylene, and the polyethylene obtained was a highly linear polymer with a high molecular weight.

4. Experimental Details

4.1. General Considerations. All manipulations of air- and/or moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques. Melting points (mp) were measured with a digital electrothermal apparatus without calibration. ^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 analyses were performed on a Flash EA 1112 instrument. GC analysis was performed with a Carlo Erba Strumentazione gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) DM-1 silica capillary column. GC-MS analysis was performed with a HP 5890 Series II and a HP 5971 Series mass detector. The yields of oligomers were calculated by referencing with the mass of the solvent on the basis of the prerequisite that the mass of each fraction is approximately proportional to its integrated areas in the GC trace. The selectivity for linear α -olefin is defined as (amounts of linear α -olefin of all fractions)/(total amounts of oligomer products) $\times 100$. ^1H and ^{13}C NMR spectra of the PE samples were recorded on a Bruker DMX 400 MHz instrument at 135 °C in 1,2-dichlorobenzene- d_4 using TMS as an internal standard. Molecular weights and polydispersity indices (PDI) of PE were determined by a PL-GPC220 instrument at 150 °C with 1,2,4-trichlorobenzene as the eluent. 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. A microwave oven, the Midea PJ21B-A (800 W, 21 L), was used for microwave-assisted condensation reactions.¹⁸

Toluene was refluxed over sodium-benzophenone until the purple color appeared and distilled under nitrogen prior to use. Dichloromethane was distilled under nitrogen from CaH_2 . 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. Trimethylaluminum (2 M in toluene) and diethylaluminum chloride (Et_2AlCl , 1 M in hexane) were purchased from Acros Chemicals. Other reagents were purchased from Aldrich or Acros Chemicals. All other chemicals were obtained commercially and used without further purification unless stated otherwise.

4.2. Synthesis of Ligands. 4.2.1. 2,6-Bis(benzimidazol-2-yl)-pyridine (L1). Pyridine-2,6-dicarboxylic acid (0.720 g, 4.28 mmol), *o*-phenylenediamine (0.931 g, 8.58 mmol), and phosphoric acid (8 mL) were mixed together and irradiated in the microwave oven (450 W) three times for 2 min. The dark green solution of the reactants was poured into the ice-water mixture after cooling, and a green solid precipitated. A NaHCO_3 solution was added to adjust the mixture pH value to 9–10, and the precipitate was filtrated and washed with water. After drying, it was recrystallized from an ethanol solution, and a yellow powder (0.631 g, 4.03 mmol) was obtained.^{17a} Yield: 47.0%. IR (KBr; cm^{-1}): 3186, 3055 ($\nu_{\text{N-H}}$), 1599 ($\nu_{\text{C=C}}$), 1573 ($\nu_{\text{C=N}}$), 1458 ($\delta_{\text{N-H}}$), 1436, 1318, 741 ($\delta_{\text{N-H}}$). ^1H NMR (300 MHz, acetone- d_6): δ (ppm) 11.11–11.17 (2H, N-H), 8.48 (d, 2H, $J = 7.57$ Hz, Py H), 8.20 (t, 1H, $J = 7.45$ Hz, Py H), 7.75 (d, 4H, $J = 7.80$ Hz, Ph H), δ 7.32 (s, 4H, Ph H).

4.2.2. 2,6-Bis(5'-methylbenzimidazol-2'-yl)-pyridine (L2). Using the same procedure as for the synthesis of L1, L2 (1.08 g, 3.21 mmol) was obtained as a yellow powder by the reaction of pyridine-2,6-dicarboxylic acid (0.800 mg, 4.79 mmol) and 4-methyl-*o*-phenylenediamine (1.20 g, 9.84 mmol) in a yield of 67.0%. IR (KBr; cm^{-1}): 3196, 3056 ($\nu_{\text{N-H}}$), 1599 ($\nu_{\text{C=C}}$), 1572 ($\nu_{\text{C=N}}$), 1457 ($\delta_{\text{N-H}}$), 1315, 737 ($\delta_{\text{N-H}}$). ^1H NMR (300 MHz, CDCl_3): δ (ppm) 11.11–11.17 (2H, N-H), 8.34 (d, 2H, $J = 9.00$ Hz, Py H), 7.82 (d, 1H, $J = 6.02$, Ph H), 7.75 (s, 2H, Ph H), 7.12 (d, 4H, $J = 9.00$ Hz, Ph H), 2.46 (s, 6H, CH_3). ^{13}C NMR (75.45 MHz, CDCl_3): δ (ppm) 149.5, 145.9, 137.6, 136.5, 135.7, 131.9, 124.7, 119.5, 113.9, 112.8, 20.3. Anal. Calcd for $\text{C}_{21}\text{H}_{17}\text{N}_5$: C, 74.32; H, 5.05; N, 20.63. Found: C, 74.44; H, 5.60; N, 20.33.

(31) Elias, H. G. *An Introduction to Polymer Science*; VCH: Weinheim, Germany, 1997.

4.2.3. 2,6-Bis(5',6'-dimethylbenzimidazol-2'-yl)pyridine (L3).

Using the same procedure as for the synthesis of **L1**, **L3** (0.741 g, 2.02 mmol) was obtained as a yellow powder by the reaction of pyridine-2,6-dicarboxylic acid (0.600 g, 3.59 mmol) and 4,5-dimethylbenzene-1,2-diamine (1.00 g, 7.35 mmol) in a yield of 56.5%. IR (KBr; cm^{-1}): 3200, 3052 ($\nu_{\text{N-H}}$), 1599 ($\nu_{\text{C=C}}$), 1572 ($\nu_{\text{C=N}}$), 1457 ($\delta_{\text{N-H}}$), 1313, 815, 736 ($\delta_{\text{N-H}}$). ^1H NMR (300 MHz, acetone- d_6): δ (ppm) 11.11–11.17 (2H, N–H), 8.31 (d, 2H, J = 6.00 Hz, Py H), 8.07 (t, 1H, J = 6.01 Hz, Py H), 7.42 (s, 4H, Ph H), 2.46 (s, 12H, CH_3). ^{13}C NMR (75.45 MHz, CDCl_3): δ (ppm) 150.0, 147.5, 138.1, 132.8, 120.8, 119.2, 112.2, 20.6. Anal. Calcd for $\text{C}_{23}\text{H}_{21}\text{N}_5$: C, 75.18; H, 5.76; N, 19.06. Found: C, 74.92; H, 5.80; N, 18.65.

4.2.4. 2,6-Bis(1'-methylbenzimidazol-2'-yl)pyridine (L4).

Powdered potassium hydroxide (0.280 g, 4.98 mmol) was added to a stirred suspension of **L1** (0.311 g, 1.00 mmol) in acetone. After a few minutes, methyl iodide (1.00 mL, 16.0 mmol) was added to the reaction mixture with vigorous stirring. After 6 h, the mixtures were added to the water, the precipitate was filtered and was recrystallized from methanol, and yellow crystals (0.26 g, 0.77 mmol) were obtained in a yield of 76.7%. Mp: 196–197 °C (lit.^{17b} mp 197 °C). IR (KBr; cm^{-1}): 3050 ($\nu_{\text{C-H}}$), 2941 ($\nu_{\text{C-H}}$), 1585 ($\nu_{\text{C=C}}$), 1571 ($\nu_{\text{C=N}}$), 1420, 1328, 745 ($\delta_{\text{C-H}}$). ^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.42 (d, 2H, J = 8.01 Hz, Py H), 8.07 (t, 1H, J = 7.83 Hz, Py H), 7.88 (d, 2H, J = 7.82, Ph H), 7.44 (d, 2H, J = 7.56, Ph H), 7.38 (m, 4H, Ph H), 4.26 (s, 6H, N– CH_3).

4.2.5. 2,6-Bis(1'-methyl-5'-methylbenzimidazol-2'-yl)pyridine (L5).

Using the same procedure as for the synthesis of **L4**, **L5** (0.300 g, 0.83 mmol) was obtained as a yellow powder by the reaction of **L2** (0.340 g, 1 mmol), powdered potassium hydroxide (0.280 g, 4.98 mmol), and methyl iodide (1.00 mL, 16.0 mmol) in a yield of 83.0%. IR (KBr; cm^{-1}): 3019 ($\nu_{\text{C-H}}$), 2942 ($\nu_{\text{C-H}}$), 1585 ($\nu_{\text{C=C}}$), 1568 ($\nu_{\text{C=N}}$), 1455 ($\delta_{\text{C-H}}$), 1330, 739 ($\delta_{\text{C-H}}$). ^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.37 (d, 2H, J = 7.82 Hz, Py H), 8.02 (t, 1H, J = 7.82 Hz, Py H), 7.75 (d, 1H, J = 8.41 Hz, Ph H), 7.65 (s, 1H, Ph H), 7.35 (d, 1H, J = 8.10 Hz, Ph H), 7.26 (s, 1H, Ph H), 7.19 (t, 2H, J = 8.10 Hz, Ph H), 4.22 (s, 6H, N– CH_3), 2.55 (d, 6H, J = 8.12 Hz, CH_3). Anal. Calcd for $\text{C}_{23}\text{H}_{21}\text{N}_5$: C, 75.18; H, 5.76; N, 19.06. Found: C, 74.87; H, 5.80; N, 18.65.

4.2.6. 2,6-Bis(1'-methyl-5',6'-dimethylbenzimidazol-2'-yl)pyridine (L6).

Using the same procedure as for the synthesis of **L4**, **L6** (0.273 g, 0.68 mmol) was obtained as a yellow powder by the reaction of **L3** (0.371 g, 1 mmol), powdered potassium hydroxide (0.281 g, 4.98 mmol), and methyl iodide (1.00 mL, 16.2 mmol) in a yield of 67.8%. IR (KBr; cm^{-1}): 3019 ($\nu_{\text{C-H}}$), 2966 ($\nu_{\text{C-H}}$), 2939 ($\nu_{\text{C-H}}$), 1585 ($\nu_{\text{C=C}}$), 1567 ($\nu_{\text{C=N}}$), 1481, 1323, 998, 828, 743, 609. ^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.35 (d, 2H, J = 7.80 Hz, Py H), 8.00 (t, 1H, J = 7.82 Hz, Py H), 7.62 (s, 2H, Ph H), 7.22 (s, 2H, Ph H), 4.20 (s, 6H, N– CH_3), 2.43 (d, 12H, J = 8.11 Hz, CH_3). ^{13}C NMR (75.45 MHz, CDCl_3): δ (ppm) 149.8, 149.6, 141.3, 137.9, 135.9, 133.1, 131.9, 124.8, 120.1, 110.1, 32.5, 20.8, 20.5. Anal. Calcd for $\text{C}_{25}\text{H}_{25}\text{N}_5$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.99; H, 6.01; N, 17.42.

4.2.7. 2,6-Bis(1'-ethyl-5',6'-dimethylbenzimidazol-2'-yl)pyridine (L7).

Using the same procedure as for the synthesis of **L6**, **L7** (0.371 g, 0.880 mmol) was obtained as a yellow powder by the reaction of **L3** (0.371 g, 1 mmol), powdered potassium hydroxide (0.280 g, 4.98 mmol), and bromoethane (1.00 mL, 13.3 mmol) in a yield of 88.0%. Mp: 226–228 °C. IR (KBr; cm^{-1}): 3026 ($\nu_{\text{C-H}}$), 2967 ($\nu_{\text{C-H}}$), 2940 ($\nu_{\text{C-H}}$), 1584 ($\nu_{\text{C=C}}$), 1568 ($\nu_{\text{C=N}}$), 1481, 1325, 999, 829, 745 ($\delta_{\text{C-H}}$), 708. ^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.30 (d, 2H, J = 7.73 Hz, Py H), 8.00 (t, 1H, J = 7.72 Hz, Py H), 7.62 (s, 2H, Ph H), 7.24 (s, 2H, Ph H), 4.76 (s, 4H, – CH_2 –), 2.43 (d, J = 7.00 Hz, 12H, Ph CH_3), 1.34 (t, 6H, J = 6.80 Hz, CH_3). ^{13}C NMR (75.45 MHz, CDCl_3): δ (ppm) 150.2, 149.3, 141.7, 137.9, 134.7, 132.9, 131.8, 125.2, 120.2, 110.4, 39.8, 20.8, 20.4, 15.5.

Anal. Calcd for $\text{C}_{27}\text{H}_{29}\text{N}_5$: C, 76.56; H, 6.90; N, 16.53. Found: C, 76.80; H, 6.89; N, 16.19.

4.2.8. 2,6-Bis(1'-benzyl-5',6'-dimethylbenzimidazol-2'-yl)pyridine (L8).

The same procedure as for the synthesis of **L6** was used, except that the reaction temperature was 60 °C. **L8** (0.490 g, 0.900 mmol) was obtained as a yellow powder by the reaction of **L3** (0.369 g, 1 mmol), powdered potassium hydroxide (0.280 g, 4.98 mmol), and benzyl chloride (1.50 mL, 13.0 mmol) in a yield of 90.0%. Mp: 294–296 °C. IR (KBr; cm^{-1}): 3028 ($\nu_{\text{C-H}}$), 2966 ($\nu_{\text{C-H}}$), 1600 ($\nu_{\text{C=C}}$), 1570 ($\nu_{\text{C=N}}$), 1455, 1324, 821, 737 ($\delta_{\text{C-H}}$). ^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.30 (d, 2H, J = 7.80 Hz, Py H), 7.97 (t, 1H, J = 8.10 Hz, Py H), 7.59 (s, 2H, Ph H), 7.19 (d, 6H, J = 6.61 Hz, Ph H), 6.98 (s, 2H, Ph H), 6.82 (d, 4H, J = 7.20 Hz, Ph H), 5.50 (s, 4H, CH_2), 2.40 (s, 12H, CH_3). ^{13}C NMR (75.45 MHz, CDCl_3): δ (ppm) 149.8, 149.4, 141.5, 138.1, 137.4, 135.2, 133.3, 132.1, 128.8, 127.3, 126.2, 125.3, 120.2, 110.9, 47.8, 20.8, 20.4. Anal. Calcd for $\text{C}_{37}\text{H}_{33}\text{N}_5$: C, 81.14; H, 6.07; N, 12.79. Found: C, 81.10; H, 6.01; N, 12.48.

4.3. Synthesis of (L)CrCl₃ (C1–C8; L = L1–L8).

Complex C1. Complexes **C1–C8** were synthesized by the reaction of $\text{CrCl}_3(\text{THF})_3$ with the corresponding ligands in dichloromethane. A typical synthetic procedure, for **C1**, is as follows. A solution of $\text{CrCl}_3(\text{THF})_3$ (0.132 g, 0.350 mmol) and **L1** (0.109 g, 0.350 mmol) in dichloromethane was stirred at room temperature for 24 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 (0.122 g, 0.260 mmol) was obtained in a yield of 75.0%. IR (KBr; cm^{-1}): 3073 ($\nu_{\text{N-H}}$), 1609 ($\nu_{\text{C=C}}$), 1590 ($\nu_{\text{C=N}}$), 1497, 1468 ($\delta_{\text{N-H}}$), 1321, 1147, 998, 826, 754 ($\delta_{\text{N-H}}$). Anal. Calcd for $\text{C}_{19}\text{H}_{12}\text{Cl}_3\text{CrN}_5$: C, 48.59; H, 2.79; N, 14.91. Found: C, 48.30; H, 2.80; N, 14.54.

4.3.2. Complex C2. Analogous to the procedure for **C1**, ligand **L2** (0.200 g, 0.591 mmol) and $\text{CrCl}_3(\text{THF})_3$ (0.223 g, 0.590 mmol) reacted to form 0.282 g (0.570 mmol) of a green solid in a yield of 97.1%. IR (KBr; cm^{-1}): 3064 ($\nu_{\text{N-H}}$), 2956, 1612 ($\nu_{\text{C=C}}$), 1573 ($\nu_{\text{C=N}}$), 1471 ($\delta_{\text{N-H}}$), 1323, 1021, 812, 748 ($\delta_{\text{N-H}}$), 682. Anal. Calcd for $\text{C}_{21}\text{H}_{17}\text{Cl}_3\text{CrN}_5$: C, 50.67; H, 3.44; N, 14.07. Found: C, 51.17; H, 3.70; N, 13.92.

4.3.3. Complex C3. Analogous to the procedure for **C1**, ligand **L3** (0.232 g, 0.630 mmol) and $\text{CrCl}_3(\text{THF})_3$ (0.231 g, 0.624 mmol) reacted to form 0.194 g (0.360 mmol) of a green solid in a yield of 56.5%. IR (KBr; cm^{-1}): 3064 ($\nu_{\text{N-H}}$), 1613 ($\nu_{\text{C=C}}$), 1573 ($\nu_{\text{C=N}}$), 1471 ($\delta_{\text{N-H}}$), 1324, 815, 748 ($\delta_{\text{C-H}}$), 683. Anal. Calcd for $\text{C}_{23}\text{H}_{21}\text{Cl}_3\text{CrN}_5$: C, 52.54; H, 4.03; N, 13.32. Found: C, 52.31; H, 3.70; N, 13.52.

4.3.4. Complex C4. Analogous to the procedure for **C1**, ligand **L4** (0.330 g, 0.971 mmol) and $\text{CrCl}_3(\text{THF})_3$ (0.361 g, 0.970 mmol) reacted to form 0.462 g (0.931 mmol) of a green solid in a yield of 95.8%. IR (KBr; cm^{-1}): 3061, 3024, 1603 ($\nu_{\text{C=C}}$), 1589 ($\nu_{\text{C=C}}$), 1572 ($\nu_{\text{C=N}}$), 1482, 1346, 764, 749. Anal. Calcd for $\text{C}_{21}\text{H}_{17}\text{Cl}_3\text{CrN}_5$: C, 50.67; H, 3.44; N, 14.07. Found: C, 50.31; H, 3.70; N, 13.84.

4.3.5. Complex C5. Analogous to the procedure for **C1**, ligand **L5** (0.261 g, 0.710 mmol) and $\text{CrCl}_3(\text{THF})_3$ (0.262 g, 0.710 mmol) reacted to form 0.313 g (0.590 mmol) of a green solid in a yield of 83.0%. IR (KBr; cm^{-1}): 3423, 3101, 2919, 1603 ($\nu_{\text{C=C}}$), 1566 ($\nu_{\text{C=N}}$), 1485, 1344, 807, 746. Anal. Calcd for $\text{C}_{23}\text{H}_{21}\text{Cl}_3\text{CrN}_5$: C, 52.54; H, 4.03; N, 13.32. Found: C, 52.09; H, 4.40; N, 13.47.

4.3.6. Complex C6. Analogous to the procedure for **C1**, ligand **L6** (0.343 g, 0.861 mmol) and $\text{CrCl}_3(\text{THF})_3$ (0.320 g, 0.860 mmol) reacted to form 0.351 g (0.640 mmol) of a green solid in a yield of 74.2%. IR (KBr; cm^{-1}): 3033, 2922, 1602 ($\nu_{\text{C=C}}$), 1566 ($\nu_{\text{C=N}}$), 1520, 1483, 1320, 1261, 860, 806, 743. Anal. Calcd for $\text{C}_{25}\text{H}_{25}\text{Cl}_3\text{CrN}_5$: C, 54.21; H, 4.55; N, 12.64. Found: C, 53.95; H, 4.84; N, 12.65.

4.3.7. Complex C7. Analogous to the procedure for **C1**, ligand **L7** (0.350 g, 0.830 mmol) and $\text{CrCl}_3(\text{THF})_3$ (0.312 g, 0.830 mmol) reacted to form 0.252 g (0.420 mmol) of a green solid in a yield of 51.0%. IR (KBr; cm^{-1}): 3416, 2974, 1604 ($\nu_{\text{C}=\text{C}}$), 1568 ($\nu_{\text{C}=\text{N}}$), 1516, 1484, 1457, 1335, 1275, 1094, 851, 809. Anal. Calcd for $\text{C}_{27}\text{H}_{29}\text{Cl}_3\text{CrN}_5$: C, 55.73; H, 5.02, N, 12.04. Found: C, 55.44; H, 5.12; N, 11.75.

4.3.8. Complex C8. Analogous to the procedure for **C1**, ligand **L8** (0.400 g, 0.731 mmol) and $\text{CrCl}_3(\text{THF})_3$ (0.272 g, 0.730 mmol) reacted to form 0.463 g (0.651 mmol) of a green solid in a yield of 88.8%. IR (KBr; cm^{-1}): 3391, 1603 ($\nu_{\text{C}=\text{C}}$), 1568 ($\nu_{\text{C}=\text{N}}$), 1475, 1451, 1331, 1265, 1003, 733. Anal. Calcd for $\text{C}_{37}\text{H}_{33}\text{Cl}_3\text{CrN}_5$: C, 62.94; H, 4.71; N, 9.92. Found: C, 62.56; H, 5.02; N, 10.0.

4.4. 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 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 methylaluminoxane (MAO). 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, dried under vacuum at 60 °C to constant weight, weighed, and finally characterized.

4.5. Procedure for Oligomerization and Polymerization with 10 atm of 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 MAO, 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 reaction. After 1 h, the reaction was stopped. A small amount of the reaction solution was collected, the reaction was terminated by the addition of 5% aqueous HCl, and the mixture was then analyzed by 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.

4.6. X-ray Crystallographic Studies. Single-crystal X-ray diffraction measurements for **C1** were carried out on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Intensity data for **C7** were

Table 6. Crystallographic Data and Refinement Details for C1 and C7

	C1 ·2DMF	C7 ·CH ₂ Cl ₂
formula	$\text{C}_{25}\text{H}_{25.50}\text{Cl}_3\text{CrN}_7\text{O}_{2.25}$	$\text{C}_{28}\text{H}_{31}\text{Cl}_5\text{CrN}_5$
fw	618.37	666.83
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	$Pbca$
<i>a</i> (Å)	10.9720(15)	18.633(1)
<i>b</i> (Å)	11.0483(16)	15.712(1)
<i>c</i> (Å)	13.5496(19)	20.742(1)
α (deg)	88.558(2)	90
β (deg)	86.707(2)	90
γ (deg)	60.655(2)	90
<i>V</i> (Å ³)	1429.4(3)	6072.5(6)
<i>Z</i>	2	8
<i>D</i> _{calcd} (g cm ⁻³)	1.437	1.459
abs coeff, μ (mm ⁻¹)	0.717	0.844
<i>F</i> (000)	635	2744
θ range (deg)	2.56–26.22	1.96–24.99
no. of data collected	8040	10 122
no. of unique data	5688	5333
<i>R</i>	0.0414	0.0647
<i>R</i> _w	0.1015	0.1181
goodness of fit	1.070	1.025

collected with a Nonius Kappa CCD diffractometer, where the monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) is generated by a rotating anode generator. 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. Crystal data and processing parameters for complexes **C1** and **C7** are summarized in Table 6.

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Supporting Information Available: CIF files giving crystallographic data for **C1** and **C7** and text and figures giving NMR measurements of polyethylenes obtained by **C4** with activation by MAO and **C6** under the activation of Et_2AlCl at 10 atm pressure of ethylene and oligomer molar distributions and their fitting analysis by Schulz–Flory rules. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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