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Half-Sandwich Chromium(III) Catalysts Bearing Hydroxyindanimine Ligands for Ethylene Polymerization

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A series of novel half-sandwich chromium(III) complexes bearing hydroxyindanimine ligands, $[Cp^*Cr[ArN{=}CC_2H_3(CH_3)C_6HR_1R_2O]Cl$ (Ar = Ph, R_1 = H, R_2 = Me (**2a**), R_2 = Cl (**2c**); Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$, R_1 = H, R_2 = Me (**2b**), R_2 = Cl (**2d**); Ar = Ph, R_1 = ^{t}Bu, R_2 = Me (**2e**))], were synthesized by the reaction of $Cp^*CrCl_2(THF)$ and the sodium salts of the hydroxylindanone-imine ligands in THF at −78 °C. Complex **2c** has been confirmed by single-crystal X-ray analysis. The complex adopts a three-legged piano stool geometry with a pseudo-octahedral coordination environment. After activation with only a small amount of $AlEt_3$, these catalytic precursors exhibit high activities (up to 1.68×10^5 g PE (mol Cr)$^{-1}$ h^{-1}) for ethylene polymerization to afford high molecular weight PE ((5.45−9.23) × 10^5 g mol^{-1}). The catalytic activities of the chromium complexes increase with decreasing steric hindrance on the nitrogen atom of the hydroxyl-indanone-imine ligand. The introduction of the bulky *ortho*-^{t}Bu group and the *para*-chlorine atom on the phenol hydroxyl improved the activity for the polymerization.

Introduction

Group IV metallocene catalysts, as homogeneous single-site catalysts, can produce a variety of high-performance polyolefins with high activity.[1] However, a large amount of high-cost cocatalyst such as MAO (methylaluminoxane) is need, which also raises the high ash content (Al_2O_3) of the polymers and limits the application of the metallocene catalysts.[1] The chromium-based heterogeneous Phillips catalysts systems, which do not need cocatalysts, are widely used in the large-scale industrial production of polyolefins.[2] The ill-defined nature of these paramagnetic chromium catalysts with respect to coordination environment and oxidation state, however, has prompted considerable efforts to synthesize well-defined homogeneous single-site Cr-based catalysts.[2,3] Consequently, this prompted the search for new polymerization catalysts that can provide high activity with no need for large amounts of expensive cocatalyst.[3] Activation of the non-Cp (cyclopentadienyl)-based chromium precatalysts bearing salicylaldimine and β-diketiminate ligands with MAO leads generally to much lower activities compared to those activated with alkylaluminum chlorides.[3a,4] This phenomenon indicates that the propagating centers are neutral, rather than cationic alkyls, since the mode of action of MAO is the abstraction of an alkyl anion from the metal precatalyst to give a cationic active site.[3a] Cp-based homogeneous chromium catalysts appear to be close structural models of the active site proposed for the Union Carbide heterogeneous catalyst[2,3b] and have attracted intensive research interest.[2,5−12] Complexes $[Cp^*CrL_2R]^+A^-$ (L = py, 1/2dppe, THF, MeCN; R = Me, Et; A = PF_6, BPh_4; Cp* = pentamethylcyclopentadienyl) have been reported to exhibit catalytic activity for ethylene polymerization.[6] A $Cp^*Cr(acac)Cl/Et_3Al$ system showed a catalytic activity of 4.2×10^4 g PE (mol Cr)$^{-1}$ h^{-1} under 50 atm of

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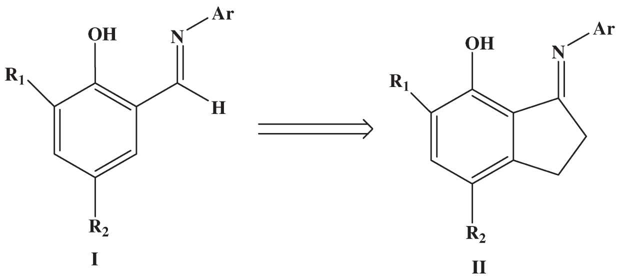
Chart 1. Ligand Evolution from Salicylaldimine to Hydroxyindanimine



ethylene.[5a] Half-sandwich salicylaldiminato chromium(III) catalysts, Cp*Cr[2,4-^{t}Bu$_2$-6-(CH=NR)-C$_6$H$_2$O]Cl/AlR'$_3$ [R = ^{t}Bu, Ph, 2,6-^{i}Pr$_2$C$_6$H$_3$; R' = Me, Et, ^{i}Bu], were reported, and they can catalyze ethylene polymerization to produce linear high molecular weight PE.[11] Recently we synthesized a series of half-sandwich chromium complexes with β-ketoiminato and β-diketiminate ligands. Upon activation with a small amount of triethylaluminum, these chromium complexes exhibited high activity for ethylene polymerization to produce linear high molecular weight PE.[12]

Salicylaldiminato ligands (**I**) (Chart 1), which were used for high performance olefin polymerization catalysts, are of wide interest in academic and industrial fields.[3a] Grubbs reported neutral nickel catalysts bearing salicylaldiminato ligands that showed high activity for ethylene homopolymerization and copolymerization.[13] Fujita and Coates independently developed a family of highly active non-metallocene group IV catalysts with bis(salicylaldiminato) ligands.[14,15] Carlini studied nickel and copper complexes bearing bis(salicylaldiminato) ligands for the polymerization of olefin and polar monomers.[16] Our group also synthesized a series of nickel and group IV catalysts based on salicylaldiminato ligands for ethylene and norbornene polymerization.[17] Gibson reported a series of non-metallocene chromium catalysts bearing salicylaldiminato ligands for ethylene oligomerization.[18]

Recently, our group designed and synthesized a series of nickel, copper, and iridium complexes based on hydroxyindanimine ligands (**II**) (Chart 1), which have the same basic fragment as salicylaldimine for norbornene, MMA, and styrene polymerization with high activity.[19] Herein we report the half-sandwich chromium(III) complexes bearing hydroxyindanimine ligands, which show high activity for ethylene polymerization to produce high molecular weight PE activated with only a small amount of triethylaluminum (Scheme 1).

Results and Discussion

The ligands **1a**−**1e** were synthesized according to the literature.[19,20] Reactions of Cp*Cr(THF)Cl$_2$ with the corresponding sodium salts of the hydroxyindanimine ligands **1a**−**1e** (Scheme 1) in THF at −78 °C resulted in the green-colored half-sandwich Cr(III) complexes **2a**−**2e** in ca. 50−70% yields. In a similar synthesis method, we also synthesized the Cp (cyclopentadienyl)-based chromium complex **2f** bearing ligand **1e** for comparing to complex **2e**, which contains a Cp* ligand. All the chromium complexes **2a**−**2f** are soluble in common solvents such as CH$_2$Cl$_2$, THF, toluene, diethyl ether, and hexane. These Cr(III) complexes were characterzed by IR and elemental analysis. ^{1}H NMR analysis indicated the paramagnetic character of the Cr(III) complexes.[21] Crystals of **2c** suitable for X-ray diffraction were obtained by recrystallization from CH$_2$Cl$_2$/hexane solution at low temperature. The molecular structure of **2c** along with selected bond lengths and angles is depicted in Figure 1.

X-ray crystallographic analysis shows that the crystal of **2c** contains one CH$_2$Cl$_2$ solvent per molecule. Complex **2c** adopts a three-legged piano stool geometry with a pseudo-octahedral coordination environment, containing a hydroxyindanimine ligand, a Cp* ligand, and chloride, which is similar to the Cp*Cr(acac)Cl, half-sandwich salicylaldiminato and β-ketoiminato and β-diketiminate chromium complexes.[5a,11,12] In complex **2c**, the bond length of Cr−O (1.935(2) Å) is longer than that of the half-sandwich salicylaldiminato (1.9185(16)−1.927(3) Å) and β-ketoiminato (1.922 (13) Å) complexes; the Cr−N bond length (2.082(3) Å) is in the range of the salicylaldiminato complexes (2.049(4)−2.097(2) Å), but longer than that of chromium complexes bearing β-ketoiminato (2.042(4) Å) and β-diketiminate (1.995(3)−2.001(3) Å) ligands. The O(1)−Cr(1)−N(1) angle

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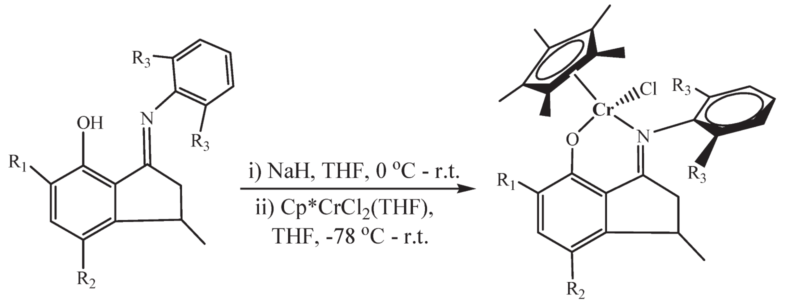
Scheme 1. Synthesis of Complexes 2a−2e



1a: $R_1 = H$, $R_2 = CH_3$, $R_3 = H$;
1b: $R_1 = H$, $R_2 = CH_3$, $R_3 =$ *iso*-Pr;
1c: $R_1 = H$, $R_2 = Cl$, $R_3 = H$;
1d: $R_1 = H$, $R_2 = Cl$, $R_3 =$ *iso*-Pr;
1e: $R_1 =$ *tert*-Bu, $R_2 = CH_3$, $R_3 = H$.

2a: $R_1 = H$, $R_2 = CH_3$, $R_3 = H$;
2b: $R_1 = H$, $R_2 = CH_3$, $R_3 =$ *iso*-Pr;
2c: $R_1 = H$, $R_2 = Cl$, $R_3 = H$;
2d: $R_1 = H$, $R_2 = Cl$, $R_3 =$ *iso*-Pr;
2e: $R_1 =$ *tert*-Bu, $R_2 = CH_3$, $R_3 = H$.

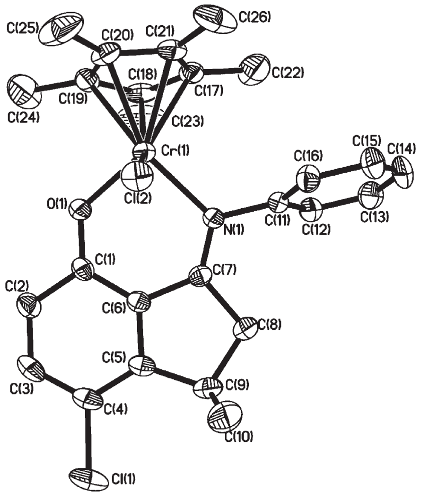


Figure 1. Thermal ellipsoid figure of complex **2c** (30% probability thermal ellipsoids). Hydrogen atoms and uncoordinated CH_2Cl_2 molecule are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Cr(1)−O(1) = 1.935(2), Cr(1)−N(1) = 2.082(3), Cr(1)−Cl(2) = 2.3101(14), C(1)−O(1) = 1.297(4), C(7)−N(1) = 1.293(4), C(1)-(6) = 1.403(5), C(6)−C(7) = 1.445(5), Cl(1)−C(4) = 1.745(4), O(1)−Cr(1)−N(1) = 92.12(10), O(1)−Cr(1)−Cl(2) = 94.78(8), N(1)−Cr(1)−Cl(2) = 91.14(8), Cr(1)−O(1)−C(1) = 125.8(2), C(1)−C(6)−C(7) = 126.6(3), C(6)−C(7)−N(1) = 125.2(3), C(7)−N(1)−Cr(1) = 121.0(2), C(7)−N(1)−C(11) = 116.4(3).

(92.12(10)°) of complex **2c** is bigger than the angles of 87.44(14)−89.98(15)° for salicylaldiminato and *β*-ketoiminato chromium complexes,[11,12] but the angle C(6)−C(7)−N(1) (125.2(3)°) is smaller than that of the salicylaldiminato chromium complex (128.4(2)−128(7)°).[11]

Like the hydroxyindanimine nickel, copper, and iridium complexes,[19] the five-remembered ring is not completely in the plane of the phenoxy ring in complex **2c** (Figure 2). The six atoms [Cr1−O1−C1−C6−C7−N1] form one six-membered ring, which however, is not in a plane (Figure 2). The [ON] skeleton plane is almost in the plane of phenoxy, which deviates by 0.0245 Å from the ideal plane. The dihedral angle of the [ON] skeleton plane and the plane formed by the Cr, O, and N atoms is 21.8°. The chromium atom deviates by 0.5417 Å from the plane formed by the phenoxy skeleton plane. The dihedral angle of the Cp* ring and the plane through Cr, O, and N atoms is 126.6°, while the dihedral angle between the Cp* and the plane of phenoxy is 105.5°. Both of the dihedral angles are larger than that of the salicylaldiminato chromium(III) complexes Cp*Cr[2,4-^{t}Bu$_2$-6-(CH=NR)-C_6H_2O]Cl (48.2−56.5° and 5.5−83.7°, respectively.).[11] The N-substituted phenyl ring is steeply inclined (123.3°) to the plane formed by the Cr, O, and N atoms. Hydrogen bonds between Cl(2) and H(3), which is a C−H from a neighboring phenoxy group, between Cl(2) and H25A, which is a C−H of a Cp* in the same molecule, and between Cl(2) and CH_2Cl_2 (Cl2···H3 = 2.746 Å, Cl2···H25A = 2.874 Å, Cl2···H27B = 2.910 Å) play an important role in constructing complex **2c** and further stabilize the network structure. Compared to the differences between the half-sandwich hydroxyindanimine chromium complexes and the salicylaldiminato chromium complexes, it indicated that the orientation of the nitrogen atom in the space is limited due to the introduction of a five-membered ring, which may affect the polymerization results.

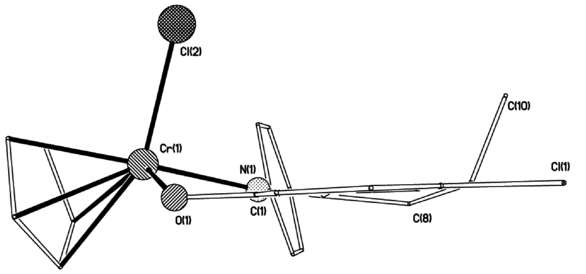


Figure 2. Side-on view of complex **2c**. The hydrogen atoms, CH_2Cl_2 molecule, and CH_3 of the Cp* rings are ommited for clarity.

As observed in half-sandwich *β*-ketoiminato and *β*-diketiminate chromium complexes,[12] after activation with a small amount of $AlEt_3$, the green complexes **2a**−**2f** changed color to light yellow and show good activity (up to 1.68×10^5 g PE (mol Cr)$^{-1}$ h^{-1}) for ethylene polymerization under 1 bar, producing high molecular weight ((5.45−9.23) × 10^5 g mol^{-1}) PE. A summary of the ethylene polymerization tests for **2a**−**2f** is shown in Table 1. The DSC results of some obtained PE are shown in Table 2. The melt transition temperatures (T_m) of the obtained PE are in the range 133.7−134.5 °C, and the crystallinity of these PE is in the range 46.4−53.7%. The steric hindrance of the ligands remarkably affected the catalyst activity and the molecular weights of PE. The catalytic activities of the complexes and the molecular weights and the crystallinity of the PE decrease with the increasing steric hindrance on the nitrogen

Table 1. Results of Ethylene Polymerization Runs Using Catalysts 2a–2f[a]

run	catalyst (5 μmol)	T (°C)	time (min)	$AlEt_3$ (μmol/ equiv)	yield (g)	activity[b]	M_v[c]
1	**2a**	25	30	125/25	0.23	0.92	8.62
2	**2b**	25	30	125/25	0.08	0.32	6.46
3	**2c**	25	30	125/25	0.34	1.36	8.96
4	**2d**	25	30	125/25	0.14	0.56	6.78
5	**2e**	25	30	125/25	0.42	1.68	9.12
6	**2f**	25	30	125/25	0.25	1.01	7.34
7	**2e**	25	30	50/10	trace		
8	**2e**	25	30	250/50	0.24	0.96	6.64
9	**2e**	25	30	500/100	0.18	0.73	5.45
10	**2e**	−15	30	125/25	0.04	0.16	7.98
11	**2e**	0	30	125/25	0.14	0.56	7.86
12	**2e**	50	30	125/25	0.11	0.44	5.47
13	**2e**	75	30	125/25	trace		
14	**2e**	25	5	125/25	0.04	1.04	5.54
15	**2e**	25	15	125/25	0.18	1.45	6.42
16	**2e**	25	60	125/25	0.61	1.22	9.23

[a] Polymerization conditions: solvent 50 mL of toluene, ethylene pressure 1 bar. [b] Units of 10^5 g PE (mol Cr)$^{-1}$ h^{-1}. [c] Measured in decahydronaphthalene at 135 °C, units of 10^5 g mol^{-1}.

Table 2. DSC Results of PE Obtained by 2a–2f[a]

complex	T_m[a] (°C)	Xc[b] (%)
2a (run 1, Table 1)	133.8	52.2
2b (run 2, Table 1)	133.7	46.6
2c (run 3, Table 1)	134.3	53.7
2d (run 4, Table 1)	134.5	46.7
2e (run 5, Table 1)	133.9	49.5
2f (run 6, Table 1)	134.3	46.4

[a] Determined by DSC at a heating rate of 10 °C min^{-1}. [b] Crystallinity $X_c = \triangle H_f/\triangle H_f^o$, $\triangle H_f^o = 273$ J/g for completed crystal PE.[11]

atom of the hydroxyindanimine ligands (the order of the activities: **2a** > **2b**; **2c** > **2d**, runs 1–4, Table 1). These results may be relevant to the dihedral angles of the Cp* ring with the plane of phenoxy, which indicated that the small steric opening degree in front of the chromium atom in the complexes was unfavorable for ethylene access.[11,12] However, introduction of the bulky *ortho*-*tert*-butyl group on the phenoxy enhanced the activity and the molecular weight of the polymer (**2e** > **2a**), up to the highest activity (1.68×10^5 g PE (mol Cr)$^{-1}$ h^{-1}). This phenomenon was similar to the neutral nickel catalysts[13] and FI catalysts.[14,15] The reason may be that a bulky steric group on the *ortho*-position of the phenoxy can prevent the coordination of excess $AlEt_3$, promote the separation of the bridged heterobimetallic chromium–aluminum species, and allow more space for ethylene to coordinate the chromium center and for its insertion into the carbon–chromium bond, which promotes the balance point to the production of polyethylene.[3,11,14a] The complexes **2c** and **2d**, bearing *para*-chlorine substitution of the ligands, exhibited greater activity than the methyl-substituted complexes **2a** and **2b**, respectively. It is indicated that the remote electron-withdrawing electronic effects also increased activity for the polymerization.[13–15] Complex **2e**, containing a Cp* fragment, showed higher activity (1.68×10^5 g PE (mol Cr)$^{-1}$ h^{-1}) than the corresponding Cp-containing complex **2f** (1.01×10^5 g PE (mol Cr)$^{-1}$ h^{-1}). The reason may be that the electron-donating methyl group can stabilize the active center.[2,3]

The amount of cocatalyst $AlEt_3$ was found to have a dramatic effect on catalyst activity and molecular weights of the polymer. When the Al/Cr ratio was 10, there was almost no PE product. This indicated that the impurities of the system should be cleaned up by the cocatalyst $AlEt_3$.[1] When the Al/Cr ratio increased to 25, the highest catalytic activity of complex **2e** was observed; when the Al/Cr ratio was increased further, the activity and the molecular weight decreased. These interesting phenomena were similar to the $Cp^*Cr(C_6F_5)(\eta^3\text{-Bz})/Et_3Al$,[8a] half-sandwich salicylaldiminato, and β-ketoiminato chromium(III) catalyst systems.[11,12] On the basis of the results that the activity decreased when the Al/Cr ratio increased and as previous literature[11,12] suggested, we proposed that the half-sandwich hydroxyindanimine chromium system may form a heterobimetallic chromium–aluminum intermediate. The effect of $AlEt_3$ concentration on the catalytic activity suggests an equilibrium between the bridged heterobimetallic chromium–aluminum species and the ethylene-coordinated mononuclear intermediate, which promotes formation of the catalytic cycle for ethylene polymerization.

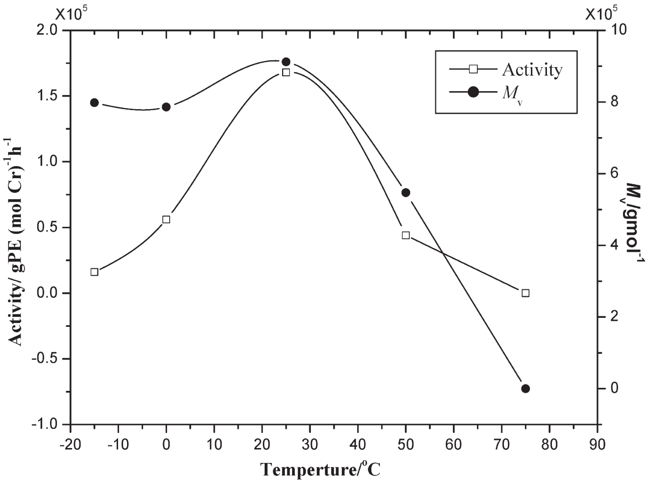


Figure 3. Dependence of the activity and the viscosity average molecular weight on temperature for complex **2e**.

The reaction temperature also affects considerably the catalytic activities and molecular weights. As can be seen from Table 1 and Figure 3, with increasing temperature from −15 to 75 °C, both the catalytic activities of complex **2e** and the M_v of polymers first increase and reach a maximum at room temperature and then sharply decrease. The results were different from the half-sandwich β-ketoiminato chromium(III) catalyst, which obtained the highest activity at low temperature.[12] This indicated that the half-sandwich hydroxyindanimine chromium catalysts showed more thermal stability. Elevated temperature will result in higher chain propagation and chain transfer rates, which would be expected to afford higher activity and lower molecular weight products. On the other hand a decrease in ethylene solubility at higher temperatures will lead to reduced productivity and results in higher rates of catalyst deactivation. A combination of these effects is likely to account for the observed temperature dependency.[3] To investigate the relationship between the polymerization time and catalytic activity and the polymer properties, the ethylene polymerizations were conducted for 5, 15, 30, and 60 min. The polymer yield and the molecular weight increased with increasing the polymerization time from 5 to 30 min (runs 5, 14, and 15, Table 1). When the polymerization time was increased further to 1 h, the polymer yield was almost constant. This indicates that the **2e**/$AlEt_3$ has a catalytic lifetime of about 30 min.

The highest activity of the hydroxyindanimine chromium catalysts (1.68 × 10^5 g PE (mol Cr)$^{-1}$ h^{-1}) was higher than that of Cp*Cr(acac)Cl/Et_3Al[5a] and β-ketoiminato and β-diketiminate complexes,[12] but lower than that of salicylaldiminato chromium(III) complexes (4.04 × 10^6 g PE (mol Cr)$^{-1}$ h^{-1}, 5 bar).[11] The molecular weights of the obtained PE produced by the hydroxyindanimine chromium catalysts ((5.45−9.23) × 10^5 g mol^{-1}) were lower than that of the salicylaldiminato chromium(III) complexes ((1.00−1.45) × 10^6 g mol^{-1}), which indicated that the introduction of a five-membered ring made the ligand more robust and limited the opening degree of the chromium center space.[19]

Conclusion

In conclusion, novel half-sandwich hydroxyindanimine chromium(III) complexes **2a**−**2f** were synthesized and employed as catalysts for ethylene polymerization to produce high molecular weight PE with good activity under mild conditions in the presence of a small amount of $AlEt_3$.

Experimental Section

General Procedures. All manipulations of air- and/or water-sensitive complexes were carried out under Ar using standard Schlenk techniques or a dry glovebox. Solvents were dried by refluxing with appropriate drying agents and distilled under nitrogen prior to use. $AlEt_3$ was purchased from Aldrich. Methylaluminoxane (MAO) was purchased from Aldrich as 10% weight of a toluene solution and used without further purification. ^{n}BuLi (1.6 M) was obtained from Acros Chem. Co. NMR spectra were recorded with a Varian Unity-500 spectrometer. Elemental analyses were performed on an Elementarvario EL III analyzer. FT-IR analyses were detected with a Nicolet-FT-IR-50X spectrometer. The thermal characteristics of the PE were examined using a DSC Perkin-Elmer instrument with a heating rate of 10 °C/min, in the range from 50 to 160 °C. The viscosity-average molar masses (M_v) of the polyethylene were calculated using the Mark−Houwink equation:[22] $[\eta] = (6.77 \times 10^{-4})M_v^{0.67}$. Cp*Li was prepared from Cp* and ^{n}BuLi at −78 °C.

Synthesis of Complex 2a. NaH (0.02 g, 0.86 mmol) was added to a stirred solution of ligand **1a** (0.109 g, 0.43 mmol) in THF (10 mL) at 0 °C. The mixture was slowly warmed to room temperature and stirred for 12 h; then the filtrate of the sodium salt was channeled at −78 °C to a solution of Cp*Cr(THF)Cl_2, which was prepared by the reaction of $CrCl_3(THF)_3$ (0.16 g, 0.43 mmol) and Cp*Li (0.062 g, 0.44 mmol) in THF (15 mL). The mixture was slowly warmed to room temperature and continuously stirred overnight. A green solution was obtained, and the solvent was removed under vacuum. After the residual solid was solved in CH_2Cl_2 and filtered to remove inorganic salts, the filtrate was concentrated to about 2 mL and mixed with hexane (25 mL). Cooling to −30 °C gave green crystals of **2a** (0.13 g, 64%). Anal. Calcd for $C_{27}H_{31}NOCrCl$ (472.99): C, 68.56; H, 6.61; N, 2.96. Found: C, 68.51; H, 6.58; N, 3.01. IR (cm^{-1}): 3057 (w), 2959 (m), 2919 (m), 2868 (w), 1608 (s), 1553 (m), 1480 (s), 1385 (m), 1332 (m), 1246 (m), 1204 (m), 1166 (w), 1105 (w), 1025 (w), 820 (m), 754 (m), 695 (w), 515 (w).

Synthesis of Complex 2b. Complex **2b** was synthesized the same way as for the synthesis of complex **2a**. Cooling to −30 °C gave green crystals of **2b** (0.109 g, 45%). Anal. Calcd for $C_{33}H_{43}NOCrCl$(557.15): C, 71.14; H, 7.78; N, 2.51. Found: C, 71.11; H, 7.79; N, 2.56. IR (cm^{-1}): 3056 (w), 2964 (m), 2878 (w), 1610 (s), 1565 (m), 1481 (s), 1387 (m), 1328 (m), 1261 (m), 1097 (w), 1023 (w), 863 (w), 803 (m), 764 (w), 694 (w), 538 (w).

Synthesis of Complex 2c. Complex **2c** was synthesized the same way as for the synthesis of complex **2a**. Cooling to −30 °C gave green crystals of **2c** (0.14 g, 68%). Anal. Calcd for $C_{26}H_{28}NOCrCl_2 \cdot CH_2Cl_2$ (578.32): C, 56.07; H, 5.23; N, 2.42. Found: C, 56.11; H, 5.21; N, 2.46. IR (cm^{-1}): 3061 (w), 2961 (m), 2924 (m), 2868 (w), 1619(s), 1592 (m), 1553 (m), 1465 (s), 1399 (m), 1339 (m), 1237 (m), 1212 (m), 1177 (w), 1098 (w), 1026 (w), 864 (w), 819 (m), 773 (w), 704 (w), 553 (w).

Synthesis of Complex 2d. Complex **2d** was synthesized the same way as for the synthesis of complex **2a**. Cooling to −30 °C gave green crystals of **2d** (0.098 g, 46%). Anal. Calcd for $C_{32}H_{40}NOCrCl_2$(577.57): C, 66.54; H, 6.98; N, 2.43. Found: C, 66.51; H, 6.94; N, 2.47. IR (cm^{-1}): 3054 (w), 2966 (m), 2926 (m), 2872 (w), 1630 (m), 1586 (m), 1471 (s), 1385 (m), 1327 (m), 1292 (m), 1265 (m), 1175 (m), 1158 (m), 1106 (w), 1054 (w), 958 (w), 876 (w), 832 (m), 800 (m), 746 (w), 665 (w), 537 (w).

Synthesis of Complex 2e. Complex **2e** was synthesized the same way as for the synthesis of complex **2a**. Cooling to −30 °C gave green solid **2e** (0.101 g, 56%). Anal. Calcd for $C_{31}H_{39}NOCrCl$ (529.1): C, 70.37; H, 7.43; N, 2.65. Found: C, 70.34; H, 7.39; N, 2.67. IR (cm^{-1}): 3052 (w), 2957 (m), 2929 (m), 2867 (w), 1621 (m), 1595 (s), 1548 (m), 1491 (m), 1445 (s), 1392 (m), 1259 (m), 1206 (m), 1092 (w), 1026 (w), 870 (w), 799 (m), 758 (w), 701 (w), 529 (w).

Synthesis of Complex 2f. NaH (0.02 g, 0.86 mmol) was added to a stirred solution of ligand **1e** (0.106 g, 0.34 mmol) in THF (10 mL) at 0 °C. The mixture was slowly warmed to room temperature and stirred for 12 h; then the filtrate of the sodium salt was channeled at −78 °C to a solution of CpCr(THF)Cl_2, which was prepared by the reaction of $CrCl_3(THF)_3$ (0.13 g, 0.34 mmol) and $CpNa(THF)_{0.38}$ (0.040 g, 0.35 mmol) in THF (15 mL). The mixture was slowly warmed to room temperature and continuously stirred overnight. A green solution was obtained, and the solvent was removed under vacuum. After the residual solid was solved in CH_2Cl_2 and filtered to remove inorganic salts, the filtrate was concentrated to about 2 mL and mixed with hexane (20 mL). Cooling to −30 °C gave green solid **2f** (0.09 g, 58%). Anal. Calcd for $C_{26}H_{29}NOCrCl$ (458.96): C, 68.04; H, 6.37; N, 3.05. Found: C, 68.01; H, 6.39; N, 3.09. IR (cm^{-1}): 3054 (w), 2962 (m), 2908 (m), 2868 (w), 1627 (m), 1608 (s), 1559 (m), 1463 (s), 1385 (m), 1335 (m), 1260 (m), 1093 (w), 1027 (w), 873 (w), 801 (m), 699 (m), 505 (m).

Ethylene Polymerization. A flame-dried 100 mL Schlenk flask with a magnetic stirrer was charged with 50 mL of toluene and saturated with ethylene (1.0 bar). The precatalyst and $AlEt_3$ were mixed in toluene at −78 °C, and the color of the mixtures quickly changed from green to light yellow. The polymerization reaction was started immediately by injection of a mixture of $AlEt_3$ and a precatalyst in toluene (10 mL). The contents were magnetically stirred and maintained under ethylene (1 bar) for designated time. The polymerization was quenched by injecting 10% acidified ethanol, and the polymer was collected by filtration, washed with water and ethanol, and dried at 70 °C in vacuo to a constant weight.

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Supporting Information Available: Crystallographic data for **2c** and selected experimental information are available free of charge via the Internet at http://pubs.acs.org.

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