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Highly active half-sandwich chromium(III) catalysts bearing bis(imino)pyrrole ligands for ethylene (co)polymerization

Jing-Yu Liu, Ping Tao, Yong-Xia Wang, Yue-Sheng Li*

† State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun 130022, P. R. China

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* Corresponding Author. E-mail: ysli@ciac.ac.cn

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A series of half-sandwich chromium(III) complexes bearing bis(imino)pyrrole ligands, Cp'[2,5-$C_4H_2N(CH{=}NAr)_2$]CrCl (Cp' = C_5H_5, Ar = C_6H_5 (**2a**), 2,6-$Me_2C_6H_3$ (**2b**), 2,6-$^iPr_2C_6H_3$ (**2c**), C_6F_5 (**2d**); Cp' = C_5Me_5, Ar = C_6H_5 (**3a**), 2,6-$^iPr_2C_6H_3$ (**3c**)) have been synthesized in good yields. These complexes were characterized by FT-IR and mass spectra as well as elemental analyses. X-ray structure analyses for **2a-c** revealed that the chromium complexes have a pseudo-octahedral coordination environment with a three-legged piano stool geometry. One of the imino nitrogen atoms coordinated with chromium metal. Upon activation with methylaluminoxane, Cp-based complexes exhibited high catalytic activities for ethylene polymerization. High molecular weight polymers with unimodal molecular weight distributions were obtained, indicating the polymerization took place in a single-site nature. In addition, the copolymerization of ethylene with norbornene by precatalysts **2a-d** were also explored in the presence of methylaluminoxane. Catalytic activity, comonomer incorporation, and the properties of the resultant polymers can be controlled over a wide range by tuning catalyst structures and reaction parameters.

Introduction

Chromium-based catalysts polymerization hold a quite interesting position among transition metal catalysts for olefin polymerization. Heterogeneous chromium-based systems such as the silica-supported Phillips[1] and Union Carbide[2] catalysts have been among the most important catalysts to product polyethylene materials. However, the ill-defined nature of these paramagnetic chromium catalysts resulted in intense debate about the nature of the active species and the catalytic reaction mechanisms, which prompted considerable efforts to develop well-defined homogeneous Cr-based catalysts.[3] Among the homogeneous chromium catalysts, Cp-based chromium(III) complexes have attracted particular attention since these complexes have close structural models of the active site proposed for the Union Carbide heterogeneous catalyst.[4-11] The $[Cp^*CrL_2R]^+A^-$ complexes (L = py, 1/2dppe, MeCN, THF; R = Me, Et; A = PF_6, BPh_4; Cp* = ç^5-pentamethylcyclopentadienyl) were first reported to catalyze ethylene polymerization in the absence of any cocatalyst. The half-sandwich chromium(III) complexes ligated with bidentate ancillary ligands also showed great potential in catalyzing ethylene polymerization. For example, half-sandwich salicylaldiminato chromium(III) catalysts, $Cp^*Cr[2,4\text{-}^tBu_2\text{-}6\text{-}(CH{=}NR)\text{-}C_6H_2O]Cl$ (R = ^{t}Bu, Ph, 2,6-^{i}PrC_6H_3), showed high catalytic activity for ethylene polymerization and produced linear high molecular weight polyethylene upon activation with only a small amount of AlR_3 (Al/Cr = 25).[12] The half-sandwich chromium(III) complexes bearing β-ketoiminato, β-diketiminato and hydroxyindanimine ligands exhibited good catalytic activity for ethylene polymerization in the presence of triethylaluminium.[13]

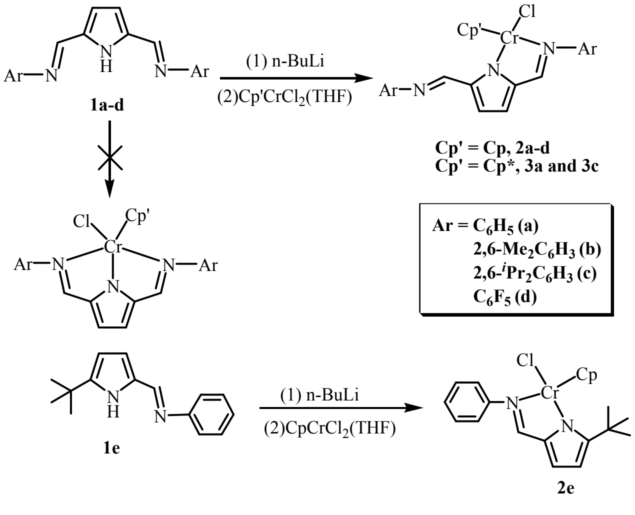
Nitrogen-based polydentate ligands have been widely used in olefin polymerization catalysis over the past decades. A key attraction of these ligands is their availability and amenability to modification *via* straightforward Schiff-base condensation procedures.[14-23] Recently, our group reported synthesis of vanadium(III) complexes bearing bis(imino)pyrrolyl ligands and their use as the catalyst precursors for olefin polymerization.[24] Although the bis(imino)pyrrole ligands actually acted as a bidentate ligand rather than tridentate one, these complexes exhibited much higher thermal stability than mono(imino)pyrrole-based analogues under the similar conditions due to increasing the steric hindrance effect and electron withdrawing effect in N-aryl moiety of the ligands. We were attracted by the potential of bis(imino)pyrrole ligands in homogeneous polymerization catalysis.

Considering that the atomic radii of chromium is similar to that of vanadium, we thus prepared a new family of half-sandwich chromium complexes containing bis(imino)pyrrole ligands. Herein, we described the synthesis and characterization of a number of novel chromium complexes with bis(imino)pyrrole chelating ligands and cyclopentadienyl or pentamethylcyclopentadienyl (Scheme 1), and explored their application to catalyze ethylene polymerization and ethylene/NBE copolymerization.

Results and discussion

Synthesis and characterization of half-sandwich chromium(III) complexes

A general synthetic route of new half-sandwich chromium(III) complexes bearing bis(imino)pyrrole ligands used in this study is shown in **Scheme 1**. The bis(imino)pyrrole ligands **1a-d** were deprotonated by 1.0 equiv. of *n*-BuLi, followed by treating with Cp'CrCl$_2$(THF) in THF at -78 ºC. In addition, the bidentate chromium complex containing iminopyrrolide chelate ligand **2f** was also prepared for comparison. Then the pure complexes were isolated by recrystallization from a mixture of dichloromethane and hexane at room temperature. The severe line broadening in the ^{1}H NMR spectra indicates that these complexes are certain of paramagnetic species.



Scheme 1. General synthetic route of the chromium complexes used in this study.

These complexes were identified by FT-IR and mass spectra as well as elemental analyses. The N-H stretching at about 3452 cm^{-1} disappeared in IR spectra. The decrease of the signal intensity of ν(C=N) at around 1622 cm^{-1} and the appearance of a low frequency signal around 1559 cm^{-1} indicate that one of the imino nitrogen atoms coordinated with chromium metal. To further confirm the structures of these new complexes, crystals of **2a-c** suitable for X-ray diffraction were grown from the chilled concentrated toluene/hexane mixture solution. The ratio of toluene/hexane was adjusted in the range of 1:3 to 1:6, according to the solubility of the complexes. The crystallographic data together with the collection and refinement parameters are summarized in Table S1 of the Supporting Information. Selected bond distances and angles for complexes **2a-c** are listed in Table 1.

Table 1. Selected bond distances (Å) and angles (deg) for complexes **2a-c**.

	2a	**2b**	**2c**
		Bond Distances in Å	
Cr(1)-N(1)	2.0304(16)	2.036(3)	2.017(4)
Cr(1)-N(2)	2.0766(17)	2.070(3)	2.080(4)
Cr(1)-Cl(1)	2.206(2)	2.2883(11)	2.2885(11)
Cr(1)-Cp(centroid)	1.876	1.889	1.889
N(2)-C(11)	1.435(2)	1.445(4)	1.439(5)
N(3)-C(17)	1.280(3)	1.256(5)	1.274(5)
		Bond Angles in °	
N(1)-Cr(1)-Cl(1)	97.74(5)	92.81(9)	92.77(9)
N(1)-Cr(1)-N(2)	80.95(6)	80.59(11)	80.60(11)
N(2)-Cr(1)-Cl(1)	96.97(5)	99.20(8)	99.19(8)
Cp(centroid)-Cr(1)-Cl(1)	122.91	122.01	122.02
Cp(centroid)-Cr(1)-N(2)	121.94	121.81	121.85
Cp(centroid)-Cr(1)-N(1)	126.04	129.96	129.94
N(1)-C(6)-C(17)	127.20(18)	124.0(3)	122.0(4)
N(3)-C(17)-C(6)	126.47(18)	124.5(4)	121.8(4)

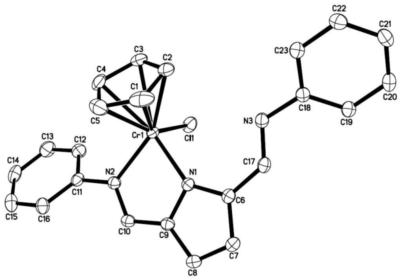


Fig. 1 Molecular structure of **2a** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity.

The structure for **2a** is shown in Figure 1. Complex **2a** adopted a three-legged piano stool geometry with the N, N, Cl atoms being the three legs and the Cp ring being the seat, which is similar to half-sandwich salicylaldiminato[12] and β-ketoiminato[13] chromium complexes. The Cr-N(1) bond length is 2.0304(16) Å, suggesting N atom in pyrrole formed a σ-bond with Cr. The Cr-N(2) bond distances in **2a** is 2.0766(17) Å, indicative of significant coordination of this imino nitrogen atom to the metal center in the solid state. The distance from N(3) to Cr is 3.686 Å, therefore, the interaction between N(3) atom and Cr in **2a** is rather weak.

The structures of **2b** and **2c** are shown in Figures S1 and S2, with selected bond distances and angles summarized in Table 1. These complexes also adopt a pseudo octahedral coordination environment with a three-legged piano stool geometry. The Cr-Cl bond distance in **2b** or **2c** is longer than that in **2a** (**2a**, 2.206(2) Å; **2b**, 2.2883(11) Å; **2c**, 2.2885(11) Å), in line with the Cr-Cp (centroid) distances in **2a-c** (**2a**, 1.876 Å; **2b**, 1.889 Å; **2c**, 1.889 Å). These bond distances might be related to the catalytic activity of these complexes towards ethylene polymerization. The N(1)-Cr(1)-N(2), N(1)-Cr(1)-Cl(1) and N(2)-Cr(1)-Cl(1) bond angles in these complexes occur in the ranges of 80.59-80.95, 92.77-97.74 and 96.97-99.20º, respectively, with the variation in imino groups. These complexes have similar dihedral angles between the Cp ring and the plane through Cr, N(1) and N(2) atoms in the range of 46.30-49.73º. In comparison, the impact of the imino groups on the dihedral angle between the Cp ring and the pyrrole ring in the bis(imino)pyrrole ligand is much more remarkable for these complexes, which makes the Cp-pyrrolyl ring dihedral angle changes in a large range from 44.76 to 60.92º. In addition to the steric effect of the substituents, the packing force in some cases may also be an important factor to affect the bond parameters.

Ethylene polymerization

All the complexes are inactive for ethylene polymerization in the presence of alkylaluminium compounds or halogen contained alkylaluminium compounds. Interestingly, upon activation with a small amount of methylaluminoxane (MAO), these complexes showed notable activity twoards ethylene polymerization, and the results are summarized in Table 2.

Complex **2a** showed high catalytic activity (1170 kg/mol$_{Cr}$·h·bar) for ethylene polymerization. Analogue **2b** containing a dimethylphenyl substituted bis(imino)pyrryl ligand exhibited a little higher catalytic activity (1320 kg/mol$_{Cr}$·h·bar) than **2a** under the same conditions. Further improvement was observed when complex **2c** with a di(isopropyl)phenyl substituted bis(imino)pyrryl ligand was used (1770 kg/mol$_{Cr}$·h·bar). The resultant polymers prepared by **2a-c** possessed high molecular weights and unimodal molecular weight distributions. The molecular weight of the polymers also increased in the order: **2c**, 42.7 kg/mol > **2b**, 32.4 kg/mol > **2a**, 23.6 kg/mol. These results suggested that the bulky substituents at the *ortho*-positions in N-aryl moiety (^{i}Pr > Me > H) seem to be important for these complexes to show high catalytic activity and produce high molecular weight polyethylenes. This is because that a bulky substituent could not only provide efficient protect to the metal center from inactivation, but also restrain the chain transfer reaction. The catalytic activity of complexes **2d** was found between **2a** and **2b** (entries 1-2 *vs* entry 4). These data suggested that the electron-donating effect of aliphatic group was not important, but the steric bulk effect played a key role to the enhanced catalytic activity.

Table 2. Ethylene polymerisation by chromium complexes/MAO catalytic systems.[a]

Entry	Cat	Al/Cr (molar ratio)	Ethylene (atm)	Time (min)	Yield (g)	Activity (kg/mol$_{Cr}$·h·bar)	M_w [b] (10^4)	M_w/M_n [b]
1	**2a**	250	5	10	2.93	1170	23.6	2.2
2	**2b**	250	5	10	3.31	1320	32.4	2.5
3	**2c**	250	5	10	4.43	1770	42.7	2.6
4	**2d**	250	5	10	3.23	1290	24.6	2.6
5	**2e**	250	5	10	0.58	230	6.7	3.8
6	**3a**	250	5	10	0.77	310	- [c]	-
7	**3c**	250	5	10	trace	-	- [c]	-
8	**2c**	60	5	10	2.38	950	58.6	2.7
9	**2c**	125	5	10	3.96	1580	52.5	3.0
10	**2c**	500	5	10	2.66	1060	22.9	2.9
11	**2c**	1000	5	10	1.56	620	10.3	2.7
12	**2c**	250	5	5	2.81	2250	25.8	2.3
13	**2c**	250	5	30	9.14	1220	60.1	2.9
14	**2c**	250	2	10	1.12	1120	30.8	2.5

[a] Reaction conditions: 3 μmol catalyst, MAO as the cocatalyst, 25°C, V_{total} = 80 mL. [b] Weight-average molecular weights and polydispersity indexes of the polymer samples determined by high temperature GPC at 150°C in 1,2,4-$C_6Cl_3H_3$ *vs* narrow polystyrene standards. [c] Insoluble in 1,2,4-$C_6Cl_3H_3$ at 150°C.

Compared with **2a**, complex **2e** containing mono(iminopyrrolyl) chelate ligand exhibited a low catalytic activity for ethylene polymerisation (**2e**: 230 kg/mol$_{\text{Cr}}$·h·bar). In addition, **2e** produced low molecular weight polymers with broad molecular weight distributions under the same conditions (entry 5 in Table 2). These results provided the further evidence of the advantage of using these novel half-sandwich chromium(III) complexes bearing bis(imino)pyrrole ligands for ethylene polymerisation.

The Cp*-based complexes displayed much lower activities and produced much higher molecular weight polymers than the Cp analogues. The resultant polymers by **3a** and **3c** were insoluble in 1,2,4-$C_6Cl_3H_3$ at 150°C. Moreover, complex **3a** showed higher activity compared with **3c**. The observed result was an interesting contrast to that found by **2a** and **2c**, in which **2c** showed higher activity than **2a**. It may be assumed that the bulky steric hindrance around the metal center prevented ethylene insertion in this case. These results suggested that both cyclopentadienyl ligand and anionic donor ligand could affect the polymerization behaviors.

Due to better performance observed by the catalysts containing 2,6-^{i}Pr substituents at imine group, precatalyst **2c** was investigated in detail by changing the reaction parameters such as cocatalyst concentration and ethylene pressure. It was found that Al/Cr molar ratio strongly influenced the catalytic activity. Note that even at an extremely low amount of MAO (Al/Cr molar ratio = 60), complex **2c** still showed very high activity towards etnylene polymerization (entry 8). The molecular weights of the resultant polymers decreased with Al/Cr molar ratio, suggesting the chain transfer to aluminum occurred during the polymerisation (Figure 2).

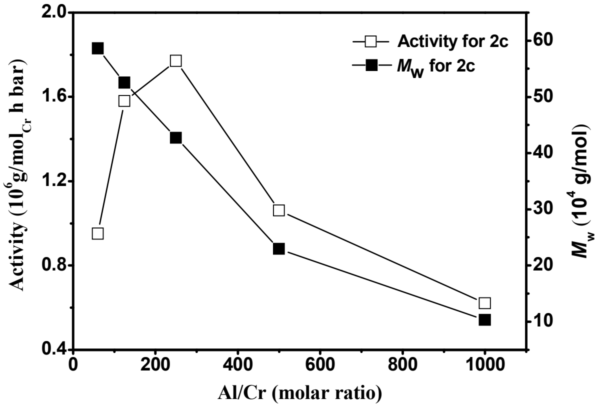


Fig. 2 Plots of the catalytic activity of catalyst **2c** and the molecular weight of the resultant polyethylenes *vs* Al/Cr molar ratio (3 μmol, 10 min, 25°C, 5 atm ethylene)

Elevating ethylene pressure resulted in the increase both in the polymer yields and the molecular weight of the resultant polymers, which also supported above suggestion that the dominant chain transfer would be the aluminum transfer from propagating metal alkyl species. Note that these catalysts showed a long life for ethylene polymerization. The polymer yields kept increasing within 30 min, although the activity decreased with the time. The decrease in activity might be caused by the occurrence of mass transport limitations since large amounts of polymers were produced during the polymerization (Figure 3). The obtained polyethylene samples were all analyzed by differential scanning calorimetry (DSC), and the melting temperature (T_m) in the of range between 134 and 139 °C, which were the classical T_m for HDPE (high-density polyethylene). This was in full accordance with the ^{13}C NMR studies of the polyethylenes, which showed no branches on the polymer backbone.

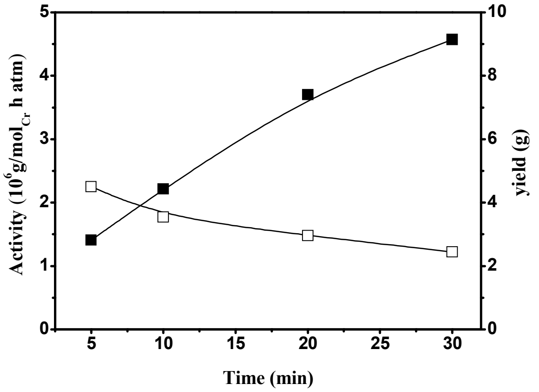


Fig. 3 Kinetic profiles of ethylene polymerization using catalysts **2a** (3 μmol, Al/Cr = 250, 25°C, 5 atm ethylene)

Half-sandwich type *β*-ketoiminato and *β*-diketiminate chromium(III) catalyst systems are inactive for ethylene polymerization in the presence of MAO, but they displayed high catalytic activities upon activation with a small amount of $AlEt_3$.[12,13] The formation of a heterobimetallic chromium-aluminium intermediate was thus assumed. In contrast, complexes used in this study displayed rather low activities upon activation with $AlEt_3$. Attempt to isolate an intermediate by treatment of **2c** with 10 equiv of MAO in toluene for 2 h was unsuccessful, no exact information was observed from IR spectrum. Taking into account these results, it is thus demonstrated that, the catalyst structures strongly affected the formation of the active species, although the true active species remains unknown at this moment.

Ethylene/NBE copolymerization

One of the greatest advantages of these novel precatalysts for olefin polymerization is that they could promote copolymerization of ethylene with norbornene (NBE). The typical results of the copolymerization were summarized in Table 3. It was very interesting that the trend of catalytic activity for the copolymerization was similar to that for ethylene homopolymerization. Except **2d**, catalysts **2a-e** showed high activities towards ethylene/NBE copolymerization. The resultant polymers were poly(ethylene-*co*-NBE)s with high molecular weights as well as with unimodal molecular weight distributions. However, NBE incorporation would be dependent upon the imino substituent employed (**2a** > **2b** > **2c**). The steric bulk of aryl moiety in the bis(imino)pyrrole ligands might be responsible for this issue.

Table 3. Copolymerisation of ethylene with NBE using complexes **2a-e** with MAO [a]

Entry	Cat. (μmol)	Al/Cr	NBE (mol/L)	Yield (g)	Activity (kg/mol$_{Cr}$·h·bar)	NBE Incorp. (mol %)	M_w [b] (10^4)	M_w/M_n
1	**2a**	1000	0.5	0.23	180	32.8	13.4	2.4
2	**2b**	1000	0.5	0.31	250	26.7	19.8	2.1
3	**2c**	1000	0.5	0.56	450	18.1	25.8	2.3
4	**2d**	1000	0.5	0.26	210	22.5	22.1	2.6
5	**2c**	1000	1.0	0.34	2700	31.5	19.9	2.1
6	**2c**	1000	1.5	0.11	90	38.8	9.8	2.3
7	**2c**	500	0.5	trace	-	-	-	-
8	**2c**	2000	0.5	1.21	970	18.8	16.7	2.7

[a] Reaction conditions: 1.5 μmol catalyst, MAO as the cocatalyst, ethylene 5 atm, 25°C, V_{total} = 50 mL, copolymerization for 10 min. [b] Weight-average molecular weights and polydispersity indexes of the copolymer samples determined by high temperature GPC at 150°C in 1,2,4-$C_6Cl_3H_3$ *vs* narrow polystyrene standards.

The effect of reaction conditions on ethylene/NBE copolymerization were also investigated using catalyst **2c**. Both the observed catalytic activities and the molecular weights for the resultant copolymers decreased upon increasing the initial NBE concentration (entries 3, 5 and 6 in Table 3). The NBE incorporation increased at higher NBE concentrations, the level of NBE incorporation approached 40 mol% in the resultant copolymer. A certain excessive amount of MAO was required for exhibiting high catalytic activity (entries 3, 7 and 8) in this catalyst system. In addition, the increase in Al/Cr molar ratio led to the decrease in the molecular weight of the copolymer, indicating that chain-transfer to aluminum alkyls is also the dominant chain-transfer pathway in the E/NBE copolymerization under these conditions. The NBE contents for the resultant poly(ethylene-*co*-NBE)s were independent of the Al/Cr molar ratio.

The microstructures of ethylene/NBE copolymers were established by ^{13}C NMR in *o*-$C_6D_4Cl_2$ at 125 °C with the assignment of the microstructure following previous work.[21] As shown in Figure S3, the resultant copolymer predominantly possessed isolated NBE inserted unit ([ENE] assigned as 47.7 ppm) among the repeated ethylene insertions when NBE incorporation of the copolymer was not high (entry 3). However, when NBE incorporation reached 38.8 mol% (entry 6), the resultant copolymer possessed isolated NBE inserted unit ([ENE] assigned as 47.7 ppm) among the repeated ethylene insertions, and the alternating sequence ([NEN] assigned as 48.4 and 47.9 ppm) was also present. No resonances ascribed to repeated NBE insertion was observed.

Conclusions

A series of half-sandwich chromium(III) complexes bearing bis(imino)pyrrole ligands, Cp'[2,5-$C_4H_2N(CH{=}NAr)_2$]CrCl (Cp' = C_5H_5, Ar = C_6H_5 (**2a**), 2,6-$Me_2C_6H_3$ (**2b**), 2,6-^{i}$Pr_2C_6H_3$ (**2c**), C_6F_5 (**2d**); Cp' = C_5Me_5, Ar = C_6H_5 (**3a**), 2,6-^{i}$Pr_2C_6H_3$ (**3c**)) have been synthesized, characterized and investigated as the efficient catalysts for olefin polymerization. These complexes adopt a pseudo octahedral coordination environment with a three-legged piano stool geometry in the solid state. The bis(imino)pyrrole ligands acted as a bidentate ligand, one of the imino nitrogen atoms coordinated with chromium metal. Both cyclopentadienyl group and anionic donor ligand could affect the polymerization behaviors. The high molecular weight polymers with unimodal molecular weight distributions were obtained, indicating the polymerization took place in a single-site nature. In addition, complexes **2a-d** exhibited high catalytic activities for ethylene/NBE copolymerization. The level of NBE incorporation reached 38.8 mol% in the resultant copolymers by catalyst **2c**. We believe that these results through this study would introduce important information for designing efficient transition metal catalysts for olefin polymerization.

Experimental

General procedures and materials.

All work involving air and/or moisture-sensitive compounds was carried out under a dry nitrogen atmosphere by using standard Schlenk techniques or under a dry argon atmosphere in an MBraun glovebox, unless otherwise noted. All solvents used were purified from an MBraun SPS system. The NMR data of ligands were obtained on a Bruker 400 MHz spectrometer at ambient temperature with $CDCl_3$ as the solvent. The NMR analyses of polymer samples were performed on a Bruker 400 MHz spectrometer at 135 ºC, using *o*-$C_6D_4Cl_2$ as the solvent. The IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. Elemental analyses were recorded on an elemental Vario EL spectrometer. Mass spectra were obtained using electron impact (EI-MS) and LDI-1700 (Linear Scientific Inc). The differential scanning calorimetric (DSC) measurements were performed with a Perkin-Elmer Pyris 1 DSC differential scanning calorimeter at a rate of 10 ºC/min. The molecular weight and the polydispersity indices of the polymer samples were determined at 150 ºC by a PL-GPC 220 type high-temperature chromatograph equipped with three PLgel 10 μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by the polystyrene standard EasiCal PS-1 (PL Ltd.). The 2.20 M *n*-butyllithium solution in hexane was purchased from Acros. $CrCl_3(THF)_3$ was purchased from Aldrich. Methylaluminoxane was purchased from Akzo Nobel Chemical Inc. Commercial ethylene was used without further purification. The ligands used were synthesized according to the literature methods.[23]

Synthesis of half-sandwich chromium(III) complexes.

A suspension of CpLi (0.15 g, 2.00 mmol) in THF (10 mL) was slowly added to a purple suspension of $CrCl_3(THF)_3$ (0.75 g, 2.00 mmol) in THF (20 mL) at -20 ºC. The mixture was warmed to room temperature and stirred overnight to get a blue solution. In another flask, a solution of *n*-BuLi (2.20 M, 2.00 mmol) in hexane was slowly added to a solution of compound **1a** (0.55 g, 2.00 mmol) in dried THF (15 mL). The reaction mixture was allowed to warm to room temperature and stirred for 2.5 h, then added slowly to the above reaction mixture at -78 ºC. The obtained reaction mixture was allowed to warm to room temperature and stirred overnight. During the reaction, the color of the reaction mixture changes from blue to green. The evaporation of the solvent in reduced pressure yielded a crude product, followed by extraction with toluene (20 mL) to remove the insoluble impurities. The filtrate was concentrated and recrystallized in toluene-hexane and yielded 601 mg of the pure complex as dark green block solid of **2a**. Complexes **2b-e**, **3a** and **3c** were synthesized in the same manner as complex **2a** with different starting materials.

Cp[2,5-(CH=NC_6H_5)$_2C_4H_2$N]CrCl (2a). Yield: (71%). FT-IR (KBr, cm^{-1}): $\nu_{C=N}$ 1558, 1621. EI-MS (70 eV): *m*/*z* = 423 [M^+]. Anal. Calcd for: $C_{23}H_{19}ClCrN_3$: C, 65.02; H, 4.51; N, 9.89. Found: C, 64.84; H, 4.46; N, 9.83.

Cp[2,5-(CH=N-2,6-MeC_6H_3)$_2C_4H_2$N]CrCl (2b). Yield: (75%). FT-IR (KBr, cm^{-1}): $\nu_{C=N}$ 1561, 1629. EI-MS (70 eV): *m*/*z* = 479 [M^+]. Anal. Calcd for: $C_{27}H_{27}ClCrN_3$: C, 67.42; H, 5.66; N, 8.74. Found: C, 67.27; H, 5.61; N, 8.68.

Cp[2,5-(CH=N-2,6-^{i}PrC_6H_3)$_2C_4H_2$N]CrCl (2c). Yield: (64%). FT-IR (KBr, cm^{-1}): $\nu_{C=N}$ 1559, 1620. EI-MS (70 eV): *m*/*z* = 592 [M^+]. Anal. Calcd for: $C_{35}H_{43}ClCrN_3$: C, 70.87; H, 7.31; N, 7.08. Found: C, 71.03; H, 7.39; N, 7.01.

Cp[2,5-(CH=NC_6F_5)$_2C_4H_2$N]CrCl (2d). Yield: (66%). FT-IR (KBr, cm^{-1}): $\nu_{C=N}$ 1561, 1617. EI-MS (70 eV): *m*/*z* = 603 [M^+]. Anal. Calcd for: $C_{23}H_9ClCrF_{10}N_3$: C, 45.68; H, 1.50; N, 6.95. Found: C, 45.83; H, 1.55; N, 6.89.

Cp[2-^{t}Bu-5-(CH=NC_6H_5)C_4H_2N]CrCl (2e). Yield: (70%). FT-IR (KBr, cm^{-1}): $\nu_{C=N}$ 1620. EI-MS (70 eV): *m*/*z* = 376 [M^+]. Anal. Calcd for: $C_{20}H_{22}ClCrN_2$: C, 63.57; H, 5.87; N, 7.41. Found: C, 63.32; H, 5.93; N, 7.53.

Cp*[2,5-(CH=NC_6H_5)$_2C_4H_2$N]CrCl (3a). Yield: (77%). FT-IR (KBr, cm^{-1}): $\nu_{C=N}$ 1545, 1618. EI-MS (70 eV): *m*/*z* = 493 [M^+]. Anal. Calcd for: $C_{28}H_{29}ClCrN_3$: C, 67.94; H, 5.91; N, 8.49. Found: C, 67.74; H, 5.96; N, 8.60.

Cp*[2,5-(CH=N-2,6-^{i}PrC_6H_3)$_2C_4H_2$N]CrCl (3c). Yield: (74%). FT-IR (KBr, cm^{-1}): $\nu_{C=N}$ 1560, 1621. EI-MS (70 eV): *m*/*z* = 661 [M^+]. Anal. Calcd for: $C_{40}H_{53}ClCrN_3$: C, 72.43; H, 8.05; N, 6.33. Found: C, 72.61; H, 8.15; N, 6.54.

General procedures for ethylene polymerization

High-pressure polymerization experiments were performed in a mechanically stirred 200 mL stainless steel reactor, equipped with an electric heating mantle controlled by a thermocouple dipping into the reaction mixture. The reactor was baked under nitrogen flow for 12 h at 150 ºC and subsequently cooled to the temperature of polymerization. The reagents were transferred *via* a gastight syringe to the evacuated reactor. Ethylene was introduced into the reactor, and the reactor pressure was maintained at prescribed ethylene pressure throughout the polymerization run by continuously feeding ethylene gas. After proceeding for 10 min, the polymerization was stopped by turning the ethylene off and relieving the pressure. The reaction mixture was poured into a solution of hydrochloric acid/ethanol to precipitate resultant polymer. The polymer was isolated by filtration, washed with ethanol, and dried under vacuum at 60 ºC for 10 h in a vacuum oven.

Copolymerization of ethylene with norbornene

A typical procedure was performed as follows: the prescribed amounts of toluene, norbornene and MAO were added into the autoclave (200 mL, stainless steel) in the autoclave, and the apparatus was then purged with ethylene. The reaction mixture was then pressurized to the prescribed ethylene pressure soon after the addition of a toluene solution containing chromium complex. The reaction mixture was poured into a solution of hydrochloric acid/ethanol (10 vol%) to precipitate the polymer. The polymer was isolated by filtration, washed with ethanol, and dried under vacuum at 60 ºC for 10 h in a vacuum oven.

X-ray crystallography

Single crystals of complexes **2a-c** suitable for X-ray structure determination were grown from hexane solution at -20 °C in a glove box, thus maintaining a dry, O_2-free environment. The intensity data were collected with the ω scan mode (186K) on a Bruker Smart APEX diffractometer with CCD detector using Mo Kα radiation (λ = 0.71073Å). Lorentz, polarization factors were made for the intensity data and absorption corrections were performed using SADABS program. The crystal structures were solved using the SHELXTL program and refined using full matrix least squares. The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons.

Supporting information. Crystal data and structure refinements of complexes **2a-c**; the structures for **2b-c** and X-ray diffraction data for **2a-c** as cif; ^{13}C NMR spectra of E/NBE copolymer with different NBE incorporations produced by **2c**.

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