# 2-Benzimidazol-6-pyrazol-pyridine Chromium(III) Trichlorides: Synthesis, Characterization, and Application for Ethylene Oligomerization and Polymerization

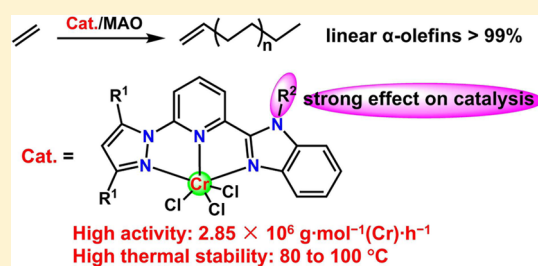Wenlong Luo,[†,‡] Antai Li,[§] Shaofeng Liu,*[,†,‡] Hongqi Ye,[§] and Zhibo Li[†]

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Ⓢ *Supporting Information*

**ABSTRACT:** A series of chromium(III) complexes, LCrCl$_3$ (**Cr1−Cr4**: L = 2-(*N*-R$^2$-benzimidazol-2-yl)-6-(3,5-R$^1$-pyrazol-1-yl)pyridine; **Cr1**: R$^1$ = H, R$^2$ = H; **Cr2**: R$^1$ = Me, R$^2$ = H; **Cr3**: R$^1$ = Me, R$^2$ = Me; **Cr4**: R$^1$ = Me, R$^2$ = Bn), were synthesized and characterized by IR spectroscopy and elemental analysis. The studies of the solid state of **Cr2** and **Cr3** revealed distorted octahedral geometries around the chromium centers by X-ray diffractions. In the presence of MAO, **Cr1−Cr4** exhibited high activities toward ethylene oligomerization (up to $2.17 \times 10^6$ g·mol$^{-1}$(Cr)·h$^{-1}$) and ethylene polymerization (up to $6.78 \times 10^5$ g·mol$^{-1}$(Cr)·h$^{-1}$). The oligomers were produced with high selectivity for *α*-olefins (>99%), confirmed by FT-IR and $^{13}$C NMR, and the distributions followed the Schulz−Flory equation. Various reaction parameters including the amount of cocatalyst, reaction temperature, and time were evaluated in detail, and it was evident that the title complexes had good thermal stability and the substituents on imidazole-N of the ligands dramatically impacted the catalytic activities as well as the distribution of the products.



linear α-olefins > 99%

**R$^2$ strong effect on catalysis**

Cat. =

**High activity: $2.85 \times 10^6$ g·mol$^{-1}$(Cr)·h$^{-1}$**
**High thermal stability: 80 to 100 °C**

## 1. INTRODUCTION

Chromium is the key element in the heterogeneous Phillips catalytic system which is commercially used for the production of more than one-third of the high density polyethylene (HDPE) sold worldwide.[1] Beyond ethylene polymerization catalysis, more than 90% of ethylene oligomerization catalysts are based on the chromium element.[2] In particular, homogeneous chromium complexes have attracted increasing attention in the past 15 years as their selective ethylene trimerization and tetramerization,[3] since 1-hexene and 1-octene produced are wildly used as comonomers for LLDPE production. In contrast to the ill-defined nature of the heterogeneous Phillips catalyst, homogeneous chromium systems provide the opportunity to better understand the catalytic mechanism[4] and, in turn, are of great help on designing new-generation catalysts with intriguing performances. For this purpose, considerable attention has been paid on developing homogeneous chromium complexes including both cyclopentadienyl (Cp)-based[5] and, in particular, non-cyclopentadienyl-based systems,[6] because that attentively tuning surrounding ligands around the chromium center can significantly affect the catalytic performances. Thus, various chromium complexes coordinated by multidentate ligand sets such as N^O,[7] N^N,[8] P^P,[9] P^N^P,[3g] and S^N^S[3f] have been reported. Recentaly, tridentate nitrogen ligands (N^N^N) have drawn considerable attention in the construction of chromium

catalysts toward ethylene oligomerization or polymerization,[10] including triazacyclohexane,[11] bis(imino)pyridines,[12] bis(2-pyridylmethyl)amines,[13] bis(oxazolinyl)pyridine,[14] and bis-(benzimidazolyl)pyridines.[15] It is explicit that attentively tuning of the coordination environment, namely, introduction of various substituents or heteroatoms into the coordinated ligands, can dramatically impact the catalytic performances, in terms of activity, selectivity, as well as the products. From this point of view, the pyridyl-based imidazolyl-pyrazolyl ligand, which mixed three *N*-heterocycles (imidazole, pyrazole, and pyridine) in one molecule and constructed a hemilable unsymmetric NNN ligand, is a promising candidate for synthesis of metal catalysts.[16] Recently, Yu[17] reported the corresponding ruthenium complexes, which showed extremely high activities toward transfer hydrogenation reactions of ketones with TOFs up to $7.2 \times 10^5$ h$^{-1}$. Inspired by these studies, the chromium complexes bearing 2-benzimidazol-6-pyrazol-pyridine with different substituents were reported herein as precatalysts toward ethylene oligomerization and polymerization. Upon activation with MAO, these Cr complexes exhibited high thermal stability (up to 100 °C), high activities (up to $2.85 \times 10^6$ g·mol$^{-1}$(Cr)·h$^{-1}$) with high

selectivity for $\alpha$-olefins (>99%), and the reaction parameters were also investigated in detail.

## 2. RESULTS AND DISCUSSION

### 2.1. Synthesis and Characterization of the Tridentate Nitrogen Ligands and Chromium Complexes.

2-Benzimidazol-6-pyrazol-pyridine derivatives (**L1−L4**) were prepared following previously reported procedures. The green powders of **Cr1−Cr4** (Scheme 1) were synthesized by the stoichio-

**Scheme 1. Synthesis of Chromium Complexes (Cr1−Cr4)**



| | Cr1 | Cr2 | Cr3 | Cr4 |
|---|---|---|---|---|
| R$^1$ | H | Me | Me | Me |
| R$^2$ | H | H | Me | Bn |
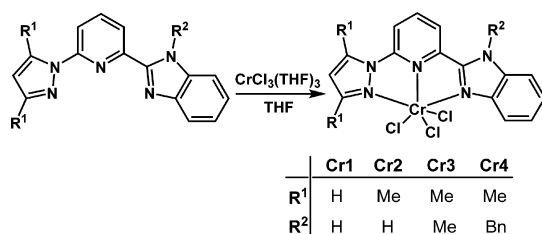
metric reactions of $CrCl_3(THF)_3$ and the corresponding ligands with high yields (87−95%) using THF as solvent. These Cr(III) complexes were air-stable, and their composition was **LCrCl$_3$**, confirmed by elemental analysis.

Diffusion of $Et_2O$ into the DMF solutions gave single crystals of **Cr2** and **Cr3**, respectively, suitable for X-ray diffractions. The solid-state structures are illustrated in Figures 1 and 2, which
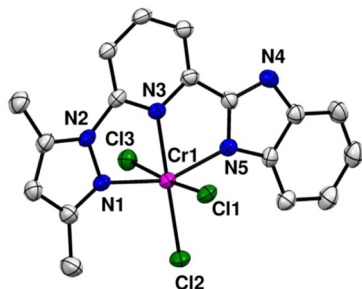


**Figure 1.** ORTEP of the molecular structure of **Cr2**. Ellipsoids at 50% probability level. Hydrogen atoms and two DMF moleculars uncoordinated were omitted for clarity. Selected distances (Å) and angles (deg): Cr1−Cl1 2.3407(11), Cr1−Cl2 2.3404(10), Cr1−Cl3 2.3182(11), Cr1−N1 2.091(3), Cr1−N3 2.026(3), Cr1−N5 2.061(3); N1−Cr1−N3 76.19(10), N5−Cr1−N3 78.64(10), N1−Cr1−Cl2 104.61(8), N5−Cr1−Cl2 100.56(8), N3−Cr1−Cl2 178.86(8), Cl1−Cr1−Cl3 174.84(4).

also showed the selected bond lengths and angles. In the structure of **Cr2**, the coordination geometry of the Cr center was a distorted octahedron and the 2-benzimidazol-6-pyrazol-pyridine ligand coordinated to the Cr center by N^N^N (meridional manner), which was similar as the Ru analogue.[17c] The two chelating rings (Cr1-N1-N2-C6-N3, Cr1-N5-C11-C10-N3) were almost coplanar, and the dihedral angle was 0.27°. The metal center Cr1 and two *trans*-disposed chlorines Cl1 and Cl3 were essentially in one line [Cl1−Cr1−Cl3 = 174.84(4)°], while the atoms of N1, N3, N5, and Cl2 located in the equatorial plane, in which plane the sum of the bond angles around Cr atom (N1−Cr1−N3 = 76.19(10)°, N5−Cr1−N3 = 78.64(10)°, N1−Cr1−Cl2 = 104.61(8)°, N5−Cr1−Cl2 = 100.56(8)°) was 360.0°, indicating that atoms N1, N3, N5, Cl2, and Cr1 were essentially coplanar. In the coordination
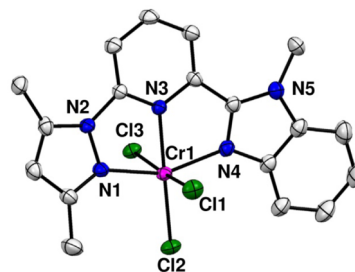


**Figure 2.** ORTEP of the molecular structure of **Cr3**. Ellipsoids at 50% probability level. Hydrogen atoms and one free DMF molecular uncoordinated were omitted for clarity. Selected distances (Å) and angles (deg): Cr1−Cl1 2.2954(10), Cr1−Cl2 2.2976(10), Cr1−Cl3 2.3593(10), Cr1−N1 2.070(3), Cr1−N3 2.023(3), Cr1−N4 2.061(3); N1−Cr1−N3 76.67(10), N4−Cr1−N3 77.88(10), N1−Cr1−Cl2 105.42(8), N4−Cr1−Cl2 100.14(8), N3−Cr1−Cl2 176.06(8), Cl1−Cr1−Cl3 174.55(4).

sphere, the same type of bonds (Cr−Cl and Cr−N) possessed similar bond lengths (Cr1−Cl1 = 2.3407(11) Å, Cr1−Cl2 = 2.3404(10) Å, Cr1−Cl3 = 2.3182(11) Å; Cr1−N1 = 2.091(3) Å, Cr1−N3 = 2.026(3) Å, Cr1−N5 = 2.061(3) Å). The molecular structure of **Cr3** is shown in Figure 2, which displayed similar coordination features to **Cr2**. Thus, it was believed that the coordinated characteristics of **Cr1** and **Cr4** would be similar as those of **Cr2** and **Cr3**.
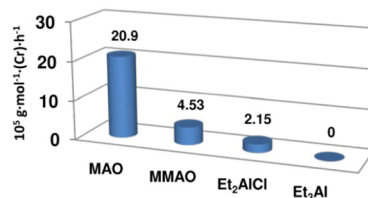
### 2.2. Ethylene Oligomerization and Polymerization.

Various aluminum compounds (MAO, MMAO, $Et_2AlCl$, and $Et_3Al$) were evaluated as cocatalysts with **Cr2**. The results are summarized in Table 1 and indicated that the activity and

**Table 1. Effect of Cocatalysts on Ethylene Reactivity with Cr2$^a$**

| entry | cocatalyst | Al/Cr | oligomers$^c$ | | K | waxes$^b$ |
|---|---|---|---|---|---|---|
| | | | activity$^b$ | distribution | | |
| 1 | MAO | 1000 | 14.3 | $C_4$−$C_{28}$ | 0.76 | 6.60 |
| 2 | MMAO | 1000 | 2.88 | $C_4$−$C_{28}$ | 0.65 | 1.65 |
| 3 | $Et_2AlCl$ | 200 | | | | 2.15 |
| 4 | $Et_3Al$ | 200 | | | | |

$^a$Conditions: 2 $\mu$mol of Cr; 10 atm of ethylene; 80 °C, 30 min, toluene (total volume: 100 mL). $^b$In units of $10^5$ g·mol$^{-1}$(Cr)·h$^{-1}$. $^c$Determined by GC.

products were dramatically influenced by the nature of the cocatalysts (Figure 3). The catalytic system with $Et_2AlCl$ (entry 3, Table 1) produced only polymer, but low activity. It was inactive when $Et_3Al$ was employed as the cocatalyst (entry 4, Table 1). In contrast, high activity was observed by the **Cr2**/MAO system (entry 1, Table 1) and the oligomer distributions resembled the Schulz−Flory equation, which had a constant $K$



**Figure 3.** Effect of cocatalysts on ethylene reactivity (the sum of polymerization and oligomerization) with **Cr2** (Table 1).

**Table 2. Oligomerization and Polymerization of Ethylene with Cr2/MAO**[a]

| entry | T (°C) | Al/Cr | t (min) | activity[c] | oligomers[b] (wt %) | K | waxes (wt %) |
|---|---|---|---|---|---|---|---|
| 1 | 20 | 1500 | 30 | 2.45 | 68.2 | 0.79 | 31.8 |
| 2 | 40 | 1500 | 30 | 8.76 | 68.4 | 0.76 | 31.6 |
| 3 | 60 | 1500 | 30 | 16.7 | 72.0 | 0.74 | 28.0 |
| 4 | 80 | 1500 | 30 | 28.5 | 76.2 | 0.76 | 23.8 |
| 5 | 100 | 1500 | 30 | 25.0 | 78.5 | 0.76 | 21.5 |
| 6 | 80 | 500 | 30 | 10.8 | 68.0 | 0.77 | 32.0 |
| 7 | 80 | 1000 | 30 | 20.9 | 68.4 | 0.74 | 31.6 |
| 8 | 80 | 2000 | 30 | 24.5 | 77.5 | 0.73 | 22.5 |
| 9 | 80 | 1500 | 15 | 29.2 | 76.0 | 0.76 | 24.0 |
| 10 | 80 | 1500 | 60 | 26.8 | 76.2 | 0.75 | 23.8 |

[a]Conditions: 2 μmol of Cr; 10 atm of ethylene; toluene (total volume: 100 mL). [b]Determined by GC. [c]In units of $10^5$ g·mol$^{-1}$(Cr)·h$^{-1}$.

representing the probability of chain propagation ($K = r_p/(r_p + r_t)$). The constant $K$ was determined by the molar ratio of $C_{14}$ and $C_{12}$ in this context.[18]

*2.2.1. Effects of Reaction Parameters on Catalytic Behavior.* The influence of the reaction parameters on the catalytic activities, including reaction temperature (20, 40, 60, 80, and 100 °C), molar ratio of MAO to Cr complex (500, 1000, 1500, and 2000), and reaction time (15, 30, and 60 min), was studied with the system of **Cr2**/MAO. The data are collected in Table 2. Both the reaction temperature and the ratio of cocatalyst to Cr complex significantly influenced the activity and product properties. The catalytic activities of oligomerization and polymerization increased with elevating the reaction temperature from 20 to 80 °C (entries 1−4, Table 2). Note that further elevating to 100 °C would only lead to a slight decrease of activity (entry 5, Table 2). Considering the fact of lower solubility of ethylene at elevating temperature, the current Cr system displayed higher thermal stability as comparing to the 2,6-bis(2-benzimidazolyl)pyridyl-Cr system, having the highest activity around 60 °C.[15a] Although the temperature dramatically impacted the activities, it had an insignificant influence on the oligomer distributions with the $K$ in the range of 0.74−0.79 (entries 1−5, Table 2). Note that elevating the reaction temperature would not result in the loss of high selectivity for α-olefins. However, elevating the temperature would lead to less production of polyethylene waxes (entries 1−5, Table 2). According to previous reports, β-hydrogen elimination would be much faster than chain propagation at high temperature.[6e,15a,19]

In addition, the catalytic performances were also affected by the amount of MAO. The best activity of 2.85 × 10$^6$ g·mol$^{-1}$(Cr)·h$^{-1}$ was obtained at the ratio of 1500 (entry 4, Table 2). With the Al/Cr molar ratio increasing from 500 to 1500, a gradual higher activity was observed (entries 4, 6−8, Table 2), although a slight decrease was obtained with increasing of the Al/Cr molar ratio to 2000. The commercial MAO usually contains an impurity like AlMe$_3$, which could react with the catalystic species and lead to the deactivation.[20]

The catalysis of the **Cr2**/MAO system was carried out for 15, 30, and 60 min to investigate the lifetime of the catalyst (entries 4, 9, and 10, Table 2; Figure 4), and the results showed that the activities were almost maintained over 60 min, indicating that the ligand 2-benzimidazol-6-pyrazol-pyridine could stabilize the active species and is a good candidate to support chromium.

*2.2.2. Effect of the Nature of Cr Complexes on Their Catalytic Performances.* The coordinated ligands determined the nature of Cr complexes and affected their catalytic performances. Using the reaction conditions selected by the
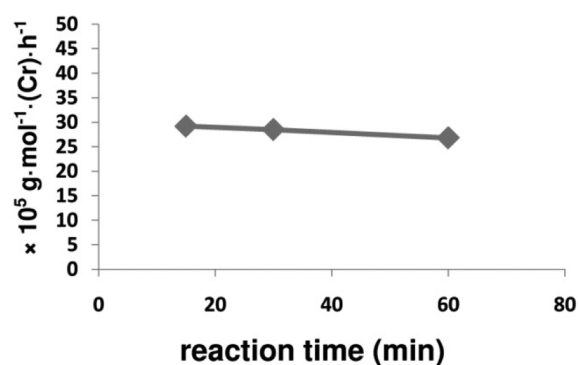


**Figure 4.** Relationship of the catalytic reactivity and reaction time with **Cr2**/MAO (entries 4, 9, and 10, Table 2).

**Cr2**/MAO system (molar ratio of MAO/Cr = 1500, temperature = 80 °C, 30 min and 10 atm of ethylene), **Cr1−Cr4** exhibited high catalytic activities (Table 3). The substituents,

**Table 3. Oligomerization and Polymerization of Ethylene with Cr1−Cr4/MAO**[a]

| entry | complex | activity[b] | oligomers[c] (wt %) | K | waxes (wt %) |
|---|---|---|---|---|---|
| 1 | **Cr1** | 28.2 | 79.8 | 0.77 | 20.2 |
| 2 | **Cr2** | 28.5 | 76.2 | 0.76 | 23.8 |
| 3 | **Cr3** | 15.6 | 68.2 | 0.72 | 31.8 |
| 4 | **Cr4** | 10.1 | 60.8 | 0.71 | 39.2 |

[a]Conditions: 2 μmol of Cr; 10 atm of ethylene; 80 °C, 30 min, Al/Cr = 1500, toluene (total volume: 100 mL). [b]In units of $10^5$ g·mol$^{-1}$(Cr)·h$^{-1}$. [c]Determined by GC.

especially, on imidazole-N, have a tremendous effect on both the activity and the product distributions. It was clear that the electron-donating group negatively influenced the catalytic activities. Complexes **Cr3** and **Cr4** with electron-donating substituents on the imidazole, namely, Me and benzyl, exhibited much lower activity comparing to complex **Cr2** bearing H group, which phenomenon was also observed for the bis(benzimidazolyl)pyridines chromium system.[15a] This could be illuminated by the reaction rate depending on the coordination/insertion of monomer at the metal center.[21] The ligand with electron-donating groups would increase the electronic density and decrease the net charge of the Cr metal center, which could result in a slower coordination/insertion reaction and thus lower activity. On the other hand, according to the study of Cr-PNP and Cr-SNS systems by McGuinness and Wasserscheid, the N-H functionality is vital for high activity

and selectivity with these two systems, and substitution of an alkyl group for the proton results in greatly attenuated activity and selectivity, because only the ligand with the N-H functionality could be deprotonated by direct action of MAO (or residual AlMe$_3$) during activation, yielding a monoanionic tridentate species.[22] The similar scenario could also be employed here. The oligomer distributions obtained by the **Cr1−Cr4**/MAO systems (Table 3) are shown in Figure 5 and
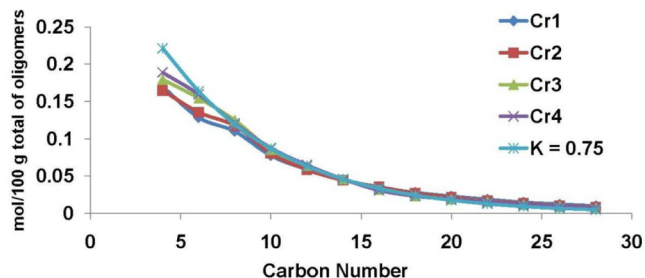


**Figure 5.** Plot of the molar amount of oligomers formed by **Cr1−Cr4**/MAO (Table 3) versus carbon number (C$_6$−C$_{28}$) and the calculated distribution for a $K$ value of 0.75.

Table S1, indicating a Schulz−Flory distribution. In addition to the production of high selectivity for $\alpha$-olefins, polyethylene waxes were also produced. Similar as the cases of Cr-PNP and Cr-SNS, incorporation of a methyl group on N led to a significant increase of polymer product (entry 3, Table 3). In the current case, 31.8% of the product was polyethylene waxes. Introducing a benzyl group (entry 4, Table 3) resulted in a further decrease in activity but a higher polymer content of 39.2%. The polyethylene waxes produced were confirmed as linear $\alpha$-olefins by IR spectra (KBr disks), which clearly showed the vibration absorption bands for C−H and C=C bonds. Moreover, the high-temperature $^{13}$C NMR spectrum (Figure S1) of the polyethylene waxes (entry 2, Table 3) also indicated

linear $\alpha$-olefins of the waxes predominating in the polymers. The resonances of 139.12 ppm (CH=) and 114.21 ppm (CH$_2$=) ppm were representative for the vinyl end group (CH$_2$=CH−).

## 3. CONCLUSIONS

The chromium(III) complexes (**LCrCl$_3$**, **Cr1−Cr4**) have been successfully synthesized and fully characterized, including the solid-state structures of **Cr2** and **Cr3** by X-ray diffractions. All Cr complexes showed high thermal stability (up to 100 °C), high activities (up to 2.85 × 10$^6$ g·mol$^{-1}$(Cr)·h$^{-1}$) toward ethylene oligomerization and polymerization in the presence of MAO. $\alpha$-Olefins were obtained with high selectivity (>99%), and the distributions followed the Schulz−Flory equation, while the produced polyethylene waxes were confirmed by IR and $^{13}$C NMR spectra as long linear olefins with vinyl end groups. The N-H functionality was found to be crucial for high activity and also was favorable for oligomerization instead of polymerization. Thus, the Cr complexes (**Cr1** and **Cr2**) bearing ligands with a H on imidazole-N exhibited higher activity and higher percentage of oligomers ($\alpha$-olefins) in the productions.

## 4. EXPERIMENTAL SECTION

**4.1. General Considerations.** Standard Schlenk techniques were used for the manipulations of compounds sensitive to air and/or moisture. Toluene was dried over sodium and benzophenone and distilled under N$_2$ prior to use. The 1.46 M MAO solution in toluene and 1.93 M MMAO solution in heptane were purchased from Akzo Nobel Corp. The 1.7 M Et$_2$AlCl solution in toluene was purchased from Acros Chemicals. Other reagents were purchased from Aladdin, Aldrich, and Acros Chemicals and used as received. FT-IR, elemental analyses, and NMR ($^1$H and $^{13}$C) for the characterization of ligands and Cr complexes were performed on the PerkinElmer 2000 spectrometer, Flash EA 1112 microanalyzer, and Bruker DMX 500 instrument, respectively. High-temperature NMR of polyethylene waxes was carried out on the Bruker DMX 300 instrument at 110 °C in o-C$_6$D$_4$Cl$_2$-d$_4$. GC analyses for oligomers were recorded with the Varian CP-3800 with the CP-Sil 5 CB columns (30 m, 0.2 mm i.d.,

**Table 4. Crystal Data and Structure Refinement for Cr2 and Cr3**

| complex | **Cr2·2DMF** | **Cr3·DMF** |
|---|---|---|
| empirical formula | C$_{17}$H$_{15}$Cl$_3$CrN$_5$·2C$_3$H$_7$NO | C$_{18}$H$_{17}$Cl$_3$CrN$_5$·C$_3$H$_7$NO |
| formula weight | 593.88 | 534.81 |
| temperature/K | 173.15 | 173.15 |
| crystal system | monoclinic | monoclinic |
| space group | P2$_1$/c | P121/n1 |
| a/Å, b/Å, c/Å | 8.127(3), 19.795(6), 17.268(5) | 7.8822(19), 26.447(6), 11.389(3) |
| $\alpha$/deg, $\beta$/deg, $\gamma$/deg | 90, 101.636(5), 90 | 90, 93.064(4), 90 |
| volume/Å$^3$ | 2721.0(14) | 2370.8(10) |
| Z | 4 | 4 |
| $\rho_{calc}$/mg mm$^{-3}$ | 1.450 | 1.498 |
| $\mu$/mm$^{-1}$ | 0.750 | 0.847 |
| F(000) | 1228.0 | 1100 |
| crystal size/mm$^3$ | 0.274 × 0.081 × 0.065 | 0.26 × 0.05 × 0.04 |
| 2Θ range for data collection (deg) | 3.168−54.996 | 1.540−27.475 |
| index ranges | −10 ≤ h ≤ 10, −25 ≤ k ≤ 25, −14 ≤ l ≤ 22 | −10 ≤ h ≤ 10, −34 ≤ k ≤ 33, −14 ≤ l ≤ 14 |
| reflections collected | 20 363 | 19 379 |
| independent reflections | 6255 [R(int) = 0.0794] | 5418 [R(int) = 0.0559] |
| data/restraints/parameters | 6255/0/331 | 5418/0/294 |
| goodness-of-fit on F$^2$ | 1.131 | 1.121 |
| final R indexes [I > 2$\sigma$(I)] | R$_1$ = 0.0639, wR$_2$ = 0.1430 | R$_1$ = 0.0616, wR$_2$ = 0.1138 |
| final R indexes [all data] | R$_1$ = 0.0759, wR$_2$ = 0.1500 | R$_1$ = 0.0702, wR$_2$ = 0.1388 |
| largest diff. peak/hole/e Å$^{-3}$ | 0.40/−0.64 | 0.849/−0.406 |

0.25 $\mu$m film thickness). Selectivity of $\alpha$-olefin in oligomers was calculated as (amount of $\alpha$-olefin)/(total amounts of olefin) in percent. The ligands 2-(benzimidazol-2-yl)-6-(pyrazol-1-yl)pyridine (**L1**),[17c] 2-(benzimidazol-2-yl)-6-(3,5-dimethylpyrazol-1-yl)pyridine (**L2**),[17d] and 2-(N-methylbenzimidazol-2-yl)-6-(3,5-dimethylpyrazol-1-yl)pyridine (**L3**)[17d] were prepared according to literature procedures.

**4.2. Synthesis of 2-(N-Benzylbenzimidazol-2-yl)-6-(3,5-dimethylpyrazol-1-yl)pyridine (L4).** A mixture of 2-(benzimidazol-2-yl)-6-(3,5-dimethylpyrazol-1-yl)pyridine **L2** (0.289 g, 1.00 mmol) and Cs$_2$CO$_3$ (0.65 g, 2.00 mmol) in DMSO (50 mL) was stirred at 80 °C for 30 min and cooled to room temperature. Benzyl bromide (0.256 g, 1.50 mmol) was added with syringe, and the mixture was stirred at room temperature. After 3 h, 50 mL of water was added and the solution was extracted by 20 mL of CH$_2$Cl$_2$ for three times. The solvent was removed and the residue was purified by column chromatography (petroleum ether/ethyl acetate, v/v = 1:2) to give **L4** as a white solid (0.368 g, 97.1%). $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) $\delta$: 8.63 (dd, J = 4.5, 1.4 Hz, 1 H, py), 7.98 (dd, J = 7.6, 1.7 Hz, 1 H, py), 7.57 (d, J = 7.7 Hz, 1 H, py), 7.46 (dd, J = 7.7, 4.8 Hz, 1 H, Ph), 7.24−7.19 (m, 4 H, Ph), 7.24−7.19 (m, 4 H, Ph), 5.88 (s, 1 H, pz), 5.17 (s, 2 H, CH$_2$), 2.44 (s, 3 H, CH$_3$), 1.78 (s, 3 H, CH$_3$). $^{13}$C NMR (125 MHz, (CD$_3$)$_2$CO) $\delta$: 151.24, 149.70, 149.50, 143.30, 141.94, 141.50, 136.60, 135.38, 128.71, 127.71, 127.01, 122.84, 122.07, 119.73, 110.81, 107.94, 48.13, 13.10, 12.62. Anal. Calcd for C$_{24}$H$_{21}$N$_5$: C, 75.97; H, 5.58; N, 18.46. Found: C, 75.75; H, 5.46; N, 18.21.

**4.3. Synthesis of Chromium Complexes.** General Procedure: Solid [CrCl$_3$(THF)$_3$] was added to a 20 mL THF solution of ligand. The mixture was stirred overnight at room temperature, and a green suspension was obtained. The solvent was removed under reduce pressure. The green powder was collected after being washed with 20 mL of Et$_2$O for twice and dried under vacuum.

**Cr1**: green powder in 87%. FT-IR (KBr disk, cm$^{-1}$): 3227, 3120, 1610, 1484, 1442, 1392, 1171, 1047, 963, 791, 751. Anal. Calcd for C$_{15}$H$_{11}$Cl$_3$CrN$_5$: C, 42.93; H, 2.64; N, 16.69. Found: C, 42.70; H, 2.58; N, 16.33.

**Cr2**: green powder in 95%. FT-IR (KBr, cm$^{-1}$): 3243, 3073, 1611, 1567, 1493, 1367, 1318, 1127, 990, 807, 759. Anal. Calcd for C$_{17}$H$_{15}$Cl$_3$CrN$_5$: C, 45.61; H, 3.38; N, 15.64. Found: C, 45.43; H, 3.20; N, 15.61.

**Cr3**: green powder in 91%. FT-IR (KBr disk, cm$^{-1}$): 3114, 1608, 1565, 1493, 1130, 1052, 992, 757. Anal. Calcd for C$_{18}$H$_{17}$Cl$_3$CrN$_5$: C, 46.82; H, 3.71; N, 15.17. Found: C, 46.69; H, 3.66; N, 15.55.

**Cr4**: green powder in 88%. FT-IR (KBr disk, cm$^{-1}$): 3074, 1610, 1570, 1444, 1364, 1145, 1040, 990, 749. Anal. Calcd for C$_{24}$H$_{21}$Cl$_3$CrN$_5$: C, 53.60; H, 3.94; N, 13.02. Found: C, 53.49; H, 3.79; N, 12.99.

**4.4. X-ray Crystallographic Studies.** Single crystals of **Cr2** and **Cr3** were grown by slowly diffusing Et$_2$O into their DMF solutions. X-ray diffraction studies for **Cr2** and **Cr3** were recorded on a Rigaku RAXIS Rapid IP diffractometer (graphite-monochromated Mo KR radiation). Using Olex2,[23] the structure was solved with the XS[24] and refined with the SHELXL.[25] All the hydrogens were introduced by the SHELXS-97 procedure and placed in the calculated position. Crystal data and processing parameters for **Cr2** and **Cr3** are tabulated in Table 4. 1494120 and 1494121 were assigned to **Cr2** and **Cr3** as CCDC reference numbers, respectively.

**4.5. General Procedures for Ethylene Oligomerization/Polymerization.** Ethylene oligomerization/polymerization under 10 atm of ethylene pressure was carried out in a 500 mL autoclave steel reactor. The Cr complex was loaded in a Schlenk tube under N$_2$. Toluene and cocatalyst (total volume: 100 mL) were introduced by syringe. The mixture was transferred into the reactor under an ethylene atmosphere by syringe. When the desired reaction temperature was reached, ethylene at 10 atm pressure was introduced and maintained during the experiments by a continuous feeding. After a measured time, a small amount of the catalytic mixture was collected and immediately quenched by addition of 5% aqueous hydrogen chloride at 0 °C. The supernatant was analyzed by GC. The remaining solution was poured into ethanol (containing 5% of HCl), and the

polyethylene waxes were collected by filtration, washed with ethanol, and dried in vacuo at 60 °C to constant weight.

## ■ ASSOCIATED CONTENT

**⑤ Supporting Information**

The Supporting Information is available free of charge on the [ACS Publications website](#) at DOI: [10.1021/acs.organomet.6b00573](#).

Distribution of oligomers and characterization of polyethylene waxes (PDF)
Crystallographic details for **Cr2** and **Cr3** (CIF)

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**Notes**
The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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