# **ORGANOMETALLICS**

# New Half-Sandwich Chromium(III) Complexes Bearing Phenoxy-Phosphine (Oxide) [O,P(=O)] Ligands: Synthesis, Structures, and Catalytic Properties for Ethylene (Co)Polymerization

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**Supporting Information** 

**ABSTRACT:** A series of novel half-sandwich-type chromium complexes bearing phenoxy-phosphine [O,P] ligands (3a-3f) or phenoxyphosphine oxide [O,P=O] ligands (4b-4e) were synthesized in high yields from CpCrCl<sub>2</sub>(thf) with corresponding ligands in THF. X-ray structure analyses for 3b, 3c, 3e, and 4c revealed that these complexes adopt a three-legged piano stool geometry. When activated by modified methylaluminoxane, complexes 3a-3f exhibited moderate to high activities toward ethylene polymerization, giving high molecular weight polymers with unimodal molecular weight distributions. Excitingly, complex 3c could efficiently promote ethylene/NBE copolymerization, therefore, high molecular weight copolymers with high NBE content could easily be obtained under optimized conditions. The [O,P=O]complexes showed higher catalytic activities than [O,P] analogues but



produced much lower molecular weight polymers. The difference in polymerization behavior might be caused by the change of both the steric bulk and the electronic effect around the metal center.

# INTRODUCTION

The design and synthesis of novel transition metal catalysts for olefin polymerization has been one of the most attractive subjects in the field of chemistry.<sup>1</sup> Chromium is the key element in the silica-supported Phillips and Union Carbide catalytic systems commercially used for olefin polymerization.<sup>2,3</sup> The ill-defined nature of these systems led to certain heterogeneities in the produced polymers. Therefore, more recent studies have focused on developing well-defined homogeneous chromium catalysts for improving catalytic activities and polymer properties.<sup>4-6</sup> Research in this area frequently involves the design of new ancillary ligands to support and activate the metal center toward olefin polymerization. Among the homogeneous chromium-based catalysts with various ligands, monocyclopentadienyl chromium(III) complexes have been extensively studied for ethylene (co)-polymerization.  $^{7-23}$  For instance,  $[Cp*CrL_2R]^+A^-$  complexes  $(L = py, 1/2dppe, MeCN, THF; R = Me, Et; A = PF_{6t} BPh_{4};$  $Cp^* = \eta^5$ -pentamethylcyclopentadienyl), discovered by Theopold et al., were first reported to promote ethylene polymerization in the absence of any cocatalyst.<sup>7</sup> Jolly et al. found the  $Cp*Cr(acac)Cl/Et_3Al$  (Al/Cr = 300) system, showing a catalytic activity of  $4.2 \times 10^4$  g/mol<sub>Cr</sub> h under 50 atm of ethylene at room temperature.<sup>8</sup> Mu et al. reported that  $Cp*Cr[2,4-^{t}Bu_{2}-6-(CH=NR)-C_{6}H_{2}O]Cl$  can produce linear high molecular weight polyethylenes ( $M_{\rm n} = 1.0 - 1.5 \times 10^6$  g/

mol) with high catalytic activities (ca. 4.0 × 10<sup>6</sup> g/mol<sub>Cr</sub> h) upon activation with only a small amount of AlR<sub>3</sub> (Al/Cr = 25).<sup>23</sup> Jin et al. found that the half-sandwich chromium(III) complexes bearing  $\beta$ -ketoiminato,  $\beta$ -diketiminato, and hydroxyindanimine ligands exhibited good catalytic activities (ca. 1.5 × 10<sup>5</sup> g/mol<sub>Cr</sub> h) for ethylene polymerization in the presence of a small amount of triethylaluminium.<sup>24</sup>

Recent search on transition metal catalysts indicated that introducing soft second-row donors, such as sulfur or phosphine, in the ligands could offer beneficial stabilization of the highly reactive metal center.<sup>25–30</sup> However, the examples on half-sandwich chromium(III) complexes containing soft donors ligands are limited so far. The phenoxy-phosphine [O,P] ligands were very attractive and widely employed in transition metal polymerization catalysis.<sup>25,29b-d</sup> Moreover, these ligands could be easily transformed to phenoxyphosphine oxide [O,P=O] ligands by adding a spot of  $H_2O_2$ in the solution. Herein, we thus synthesized and characterized some novel half-sandwich chromium complexes containing phenoxy-phosphine (oxide) [O,P(=O)] chelating ligands, and explored the effect of ligand structure toward catalytic activity for ethylene (co)polymerization in the presence of modified methylaluminoxane (MMAO).

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Synthesis and Structural Analysis of Half-Sandwich Chromium(III) Complexes. A series of new chromium complexes, adopted in this study, bearing phenoxy-phosphine [O,P] ligands and phenoxy-phosphine oxide [O, P==O]ligands,  $Cp[O-2R^1-4R^2-6(Ph_2P)C_6H_2]CrCl$  (**3a**:  $R^1 = R^2 = H$ ; **3b**:  $R^1 = Ph$ ,  $R^2 = H$ ; **3c**:  $R^1 = tBu$ ,  $R^2 = H$ ; **3d**:  $R^1 = R^2 = tBu$ ; **3e**:  $R^1 = F$ ,  $R^2 = H$ ; **3f**:  $R^1 = C_6F_5$ ,  $R^2 = H$ ) and  $Cp[O-2R^1-4R^2-6(Ph_2P=O)C_6H_2]CrCl$ ; **4b**:  $R^1 = Ph$ ,  $R^2 = H$ ; **4c**:  $R^1 = tBu$ ,  $R^2 = H$ ; **4d**:  $R^1 = R^2 = tBu$ ; and **4e**:  $R^1 = F$ ,  $R^2 = H$ ), were synthesized in high yields (66–79%) via the reaction of in situ produced CpCrCl<sub>2</sub>(thf) with 1.0 equiv of lithium salts of  $2R^1-4R^2-6(Ph_2P=O)-C_6H_2OH$  (**1a**-**1f**) or  $2R^1-4R^2-6(Ph_2P=O)-C_6H_2OH$  (**1a**-**1f**) or  $2R^1-4R^2-6(Ph_2P=O)-C_6H_2OH$  (**1a**-**1e**) in THF, as shown in Scheme 1. Pure

Scheme 1. Synthesis of New Half-Sandwich Chromium(III) Complexes



samples were collected from the chilled concentrated mixture of dichloromethane and hexane solution placed in the freezer

 $(-30 \ ^{\circ}C)$ . These complexes were identified by IR and UV-vis spectroscopy, mass spectra, and elemental analyses. Moreover, complexes **3e**, **3f**, and **4e** were further characterized by  $^{19}F$  NMR spectra. <sup>1</sup>H NMR spectra indicated the paramagnetic character of these chromium complexes.

The IR spectra of the precatalysts were obviously different from those of the corresponding ligands. The disappearance of the band related to the O-H stretching at about 3350 cm<sup>-1</sup> indicated the formation of the  $\sigma$  bond between the oxygen atom in the phenoxy group and the chromium atom. For complexes 3a-3f, the strong band of  $\nu$ (P-Ph) at around 1182 cm<sup>-1</sup> shifted to low frequency around 1100 cm<sup>-1</sup> due to the phosphorus atom coordinating with chromium metal. The spin state of the complexes was confirmed by magnetic susceptibility measurements. The results indicated the presence of three unpaired electrons on the chromium center. In addition, the proposed structures were in line with the elemental analyses. Crystals of 3b, 3c, 3e, and 4c suitable for crystallographic analysis were grown from the chilled CH<sub>2</sub>Cl<sub>2</sub>-hexane mixture solution. 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 3b, 3c, 3e, and 4c are listed in Table 1.

Structures for 3b, 3c, and 3e are shown in Figures 1–3. These complexes have a pseudo-octahedral coordination



**Figure 1.** Molecular structure of complex **3b** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

# Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes 3b, 3c, 3e, and 4c

	3b (A)	<b>3b</b> (B)	3c	3e	4c		
bond distances (Å)							
Cr(1) - O(1)	1.929(4)	1.939(4)	1.910(2)	1.9388(15)	1.920(3)		
Cr(1)-P(1)	2.4127(18)	2.4295(17)	2.4720(12)	2.4274(7)			
Cr(1) - O(2)					1.968(3)		
Cr(1)-Cl(1)	2.2908(17)	2.2965(18)	2.2771(12)	2.2862(7)	2.2879(14)		
Cr(1)–Cp(centroid)	1.881	1.881	1.882	1.874	1.884		
Cr(1)–Cav	2.225	2.231	2.229	2.217	2.225		
		bond angles (de	g)				
O(1)-Cr(1)-Cl(1)	97.68(3)	97.61(13)	98.20(9)	94.95(6)	98.37(9)		
P(1)-Cr(1)-Cl(1)	95.51(6)	96.92(6)	96.09(4)	96.89(2)			
O(1)-Cr(1)-P(1)	79.85(12)	80.45(12)	77.95(8)	80.94(5)			
O(2) - Cr(1) - Cl(1)					93.80(9)		
O(1) - Cr(1) - O(2)					92.23(12)		
Cp(centroid) - Cr(1) - Cl(1)	123.85	123.85	124.82	123.80	122.95		
Cp(centroid) - Cr(1) - P(1)	123.65	123.65	126.57	128.01			
Cp(centroid) - Cr(1) - O(1)	123.76	123.76	121.38	126.34	119.57		
Cp(centroid) - Cr(1) - O(2)					122.74		
Cp-phenyl ring	70.27	67.44	74.36	72.10			
Cp-[O-Cr-P]	45.63	45.84	45.48	48.05			



**Figure 2.** Molecular structure of complex **3c** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity.



**Figure 3.** Molecular structure of complex **3e** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

environment in the solid state and adopt a three-legged piano stool geometry with the O, P, Cl atoms being the three legs and the Cp ring being the seat. Crystals of 3b consist of two crystallographically independent molecules in the unit cell, with only minor differences from each other [e.g., bond angles Cl(1)-Cr(1)-P(1) and Cl(2)-Cr(2)-P(2) are 95.51(6)° and 96.92(6)°, respectively]. The Cr-P(1) bond distances in these complexes are in the range of 2.4127(18) - 2.4720(12), indicating the significant coordination of the phosphorus atom to the metal center. It should be noted that the complex **3e** with a F atom in the  $R^1$  position of the phenoxy-phosphine ligand has shorter Cr(1)-Cp(centroid) and Cr(1)-C(average)distances than do 3b or 3c, which might be caused by the strong electron withdrawing effect of the F atom. In addition, the Cr-Cl(1) bond lengths in 3b, 3c, and 3e change slightly with the variation of the  $R^1$  group in the ligands [3b: 2.2908(17) and 2.2965(18) Å, 3c: 2.2771(12) Å, and 3e: 2.2862(7) Å]. However, the Cr-O(1) [3b: 1.929(4) and 1.939(4) Å, 3c: 1.910(2) Å, and 3e: 1.9388(15) Å] and Cr-P(1) [3b: 2.4127(18) and 2.4295(17) Å, 3c: 2.4720(12) Å, and **3e**: 2.4274(7) Å] bond lengths are obviously affected by the  $R^1$ group. The O-Cr-P, O-Cr-Cl, and P-Cr-Cl bond angles in these complexes occur in the ranges of 77.95-80.94°, 94.95-98.20°, and 95.51-96.89°, respectively. A bulkier substituent in the  $R^1$  position would lead to a larger  $O{-}Cr{-}$ Cl bond angle and a smaller O-Cr-P bond angle. Moreover, these complexes have similar dihedral angles between the Cp ring and the plane through Cr, O, and P atoms in the range of  $45.48-48.05^{\circ}$ . The impact of the R<sup>1</sup> group on the dihedral angle between the Cp ring and the phenyl ring in the aryloxy moiety of the ligand is also slight, which makes the Cp-phenyl ring dihedral angle change in a small range from 67.44 to 74.36°.

Complex **4c** also has a pseudo-octahedral coordination environment and adopts a three-legged piano stool geometry with the O, O, Cl atoms being the three legs and the Cp ring being the seat. As shown in Figure 4, the phenoxy-phosphine



**Figure 4.** Molecular structure of complex **4c** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

oxide ligand coordinating with the chromium atom formed a six-membered ring structure (O1-Cr-O2-P1-C2-C1). Therefore, the Cr(1)-O(1) and Cr(1)-Cl(1) bond distances in 4c [1.920(3) and 2.2879(14) Å] are longer than those of 3c. Moreover, the C(1)-C(2)-P bond angle in 4c (115.9°) is larger than that in 3c (112.8°). The observed difference in the molecular structures between 3c and 4c may have a great influence on the behaviors for polymerization catalysis.

Ethylene Polymerization by the New Half-Sandwich Chromium Complexes. Ethylene polymerization by novel half-sandwich chromium complexes 3a-3f and 4b-4e in the presence of MMAO were explored (3  $\mu$ mol catalyst, 25 °C, in toluene,  $V_{total} = 70$  mL), and typical results are summarized in Table 2. Complex 3a, without any substituent in the aryloxy moiety of the ligand, showed only low catalytic activity for ethylene polymerization (entry 1). Introducing a conjugated phenyl group in the R<sup>1</sup> position (3b) clearly increased the catalytic activity (3a, 40 kg/mol<sub>Cr</sub> h; 3b, 340 kg/mol<sub>Cr</sub> h). Note

Table 2. Ethylene Polymerization by Half-Sandwich Chromium(III) Complexes 3a-3f and  $4b-4e^{a}$ 

entry	catalyst	pressure (atm)	time (min)	yield (g)	activity (kg/mol <sub>Cr</sub> h)	$M_{w_{4}}^{b}$ (10 <sup>-4</sup> )	$M_{ m w}^{\prime}_{b}$ $M_{ m n}^{\prime}$
1	3a	5	10	0.02	40	17	2.1
2	3b	5	10	0.17	340	24	2.3
3	3c	5	10	1.71	3420	53	1.8
4	3d	5	10	0.59	1180	31	2.9
5	3e	5	10	0.23	460	27	2.4
6	3f	5	10	0.39	780	25	2.6
7	4b	5	10	0.43	860	0.6	2.5
8	4c	5	10	1.85	3700	1.2	2.9
9	4d	5	10	1.98	3960	0.7	2.5
10	4e	5	10	0.61	1220	0.4	2.6
11	3c	2	10	0.66	1320	21	2.9
12	3c	5	5	0.95	3800	35	2.4
13	3c	5	30	2.04	1360	60	2.8
14	4c	5	5	1.01	2020	0.5	2.9
15	46	5	30	2.11	4220	17	28

"Reaction conditions: 3  $\mu$ mol catalyst, Al/Cr = 1000, MMAO as cocatalyst, 25 °C, in toluene,  $V_{total} = 70$  mL. <sup>b</sup>Weight-average molecular weights and polydispersity indexes determined by high temperature GPC at 150 °C in 1,2,4-C<sub>6</sub>Cl<sub>3</sub>H<sub>3</sub> versus narrow polystyrene standards.

that replacement of H at the  $R^1$  position in complex 3a with a tert-butyl group (3c and 3d) brought about dramatic improvement in the catalytic performance. Complex 3c showed the highest catalytic activity (3420 kg/mol<sub>Cr</sub> h) among these complexes. It was assumed that a bulky R<sup>1</sup> in the ortho-position of the oxygen atom in the phenoxy-phosphine ligands could prevent the coordinated oxygen atom from further coordinating to AlR<sub>3</sub> or another chromium complex and, therefore, keep the active catalyst molecule from inactivation by forming inactive binuclear species.<sup>23c</sup> Moreover, the R<sup>2</sup> group also had a significant effect on the polymerization behaviors. Complex 3d, bearing tert-butyl groups in both the  $R^1$  and  $R^2$  positions, exhibited lower activity than 3c under similar conditions (3c, 3420 kg/mol<sub>Cr</sub> h; 3d, 1180 kg/mol<sub>Cr</sub> h) and produced relatively lower molecular weight polymers. Complexes  $3e(R^1 = F)$  and 3f  $(R^1 = C_6F_5)$  were also synthesized in order to clarify the electronic effect of the R<sup>1</sup> group on the catalytic performance. It was found that 3e displayed higher activity than 3a (3e, 460 kg/ mol<sub>Cr</sub> h), while the activity could be further increased if complex 3f was used (3f, 780 kg/mol<sub>Cr</sub> h) under similar conditions. Taking these results into account, it is therefore clear that the steric bulk effect in the R<sup>1</sup> position played a key role in the enhanced catalytic activity for complexes 3a-3f.

The [O,P=O] half-sandwich chromium(III) complexes exhibited higher catalytic activities than the [O,P] analogues. For instance, complex 4e with an electron withdrawing -F group at the  $R^1$  position was found to display a relatively high catalytic activity of 1220 kg/mol<sub>Cr</sub> h at 25 °C, which was ca. 3 times larger than 3e (460 kg/mol<sub>Cr</sub> h). In addition, complex 4d showed higher activity than 4c. The observed result was an interesting contrast to that found by 3c and 3d, in which 3c showed higher activity than 3d. However, the molecular weights of the resultant polymers produced by complexes 4b-4e were much lower than those by 3b-3e under similar conditions, suggesting that a reduced congestion degree around the metal center might be not only favored for chain propagation but also for chain transfer. The difference in polymerization behaviors might be caused by the change of both the steric bulk and electronic effect around the metal center.

The effect of reaction condition on ethylene polymerization was also investigated by using precatalysts 3c and 4c. For these two systems, the catalytic activities were somewhat dependent upon the Al/Cr molar ratio, as shown in Figure 5. The



Figure 5. Plot of catalytic activities and molecular weights of the resultant polyethylenes vs Al/Cr (molar ratio). Reaction conditions: 3  $\mu$ mol of catalyst, ethylene at 5 atm, 10 min, 25 °C.

molecular weights of the resultant polymers obtained by 3c/ MMAO system changed slightly with the Al/Cr molar ratio, suggesting that the dominant chain-transfer pathway is not chain transfer to aluminum alkyls but seems to be  $\beta$ -hydrogen transfer under these conditions. Moreover, the molecular weight values sharply decreased when the polymerization was conducted at a low ethylene pressure (entry 11 in Table 2). This result also supported the above suggestion that the dominant chain transfer would be the  $\beta$ -hydrogen transfer from propagating metal alkyl species. In contrast, the molecular weights of the resultant polyethylenes obtained by complex 4c decreased with increasing cocatalyst dosage, suggesting that the dominant chain-transfer pathway is chain transfer to aluminum in this case. The typical sample obtained by 4c (entry 8 in Table 2) was further characterized by high temperature <sup>13</sup>C NMR spectra (Figure 6). Two kinds of terminal groups, methyl



Figure 6. <sup>13</sup>C NMR (100 MHz, o-C<sub>6</sub>D<sub>6</sub>Cl<sub>2</sub>, 135 °C) spectra of the polymer sample obtained by catalyst 4c/MMAO (entry 8 in Table 2).

and isopropyl, were detected for the polyethylenes, which further conformed the occurrence of chain transfer to aluminum. However, it is very difficult to observe the unsaturated chain ends of the polymers which are produced with precatalyst **3c** by <sup>13</sup>C NMR due to a high molecular weight. IR spectra were also employed to assess the chain end groups. The IR spectrum of the sample obtained by **3c** showed resonances at 1643 (C=C) cm<sup>-1</sup> and 922 and 910 (=CH<sub>2</sub>) cm<sup>-1</sup>. The signals for  $\nu$ (C=C) and  $\nu$ (=CH<sub>2</sub>) were seldom detected in IR spectrum of the sample obtained by **4c**.

In order to further evaluate the catalytic performance of these new half-sandwich chromium complexes, the relationship between the catalytic activity and the time represented by **3c** and **4c** was also studied. Note that the catalytic activities by **3c** and **4c** did not significantly decrease, at least for 30 min (entries 12–15, Table 2). These results indicated that either phenoxyphosphine ligands or phenoxy-phosphine oxide ligands can efficiently stabilize active species and maintain single-site catalytic behaviors of the chromium catalyst for ethylene polymerization. All the polymers prepared by the different complexes were linear polyethylenes confirmed by <sup>13</sup>C NMR spectra, which are similar to those by  $\beta$ -enaminoketonato or salicylaldiminato chromium catalysts.<sup>23,24</sup>

**Ethylene/Norbornene (NBE) Copolymerization.** The copolymerization of ethylene/NBE by some complexes bearing phenoxy-phosphine ligands (3c, 3d, and 3f) was also studied, and the representative results were summarized in Table 3. In the presence of MMAO, these complexes showed low to high activities toward ethylene/NBE copolymerization and pro-

Table 3. Copolymerization of Ethylene with NBE Using Chromium Complexes<sup>a</sup>

entry	catalyst	Al/Cr (molar ratio)	NBE (mol/L)	yield (mg)	activity (kg/mol <sub><math>Cr</math></sub> h)	$M_{\rm w}^{\ \ b}~(10^{-4})$	$M_{\rm w}/M_{\rm n}^{\ b}$	incorporation (mol %) $^{c}$
1	3c	1000	0.50	260	1560	75	2.1	33.8
2	3d	1000	0.50	85	510	43	2.7	27.9
3	3f	1000	0.50	40	240	33	2.6	35.4
4	3c	1000	0.25	385	2310	54	2.1	19.7
5	3c	1000	0.75	185	1110	45	2.1	36.7
6	3c	1000	1.00	60	360	36	1.7	40.1
7	3c	500	0.50	140	840	88	1.9	32.1
8	3c	2000	0.50	575	3450	61	2.8	34.1
9	4c	1000	0.50	490	2940	1.1	2.0	36.9
10	4d	1000	0.50	505	3030	0.8	2.3	35.4

<sup>*a*</sup>Reaction conditions: 2  $\mu$ mol catalysts, 5 atm of ethylene, MMAO as cocatalyst, 5 min, 25 °C, in toluene,  $V_{\text{total}} = 50$  mL. <sup>*b*</sup>Weight-average molecular weights and polydispersity indexes determined by high temperature GPC at 150 °C in 1,2,4-C<sub>6</sub>Cl<sub>3</sub>H<sub>3</sub> versus narrow polystyrene standards. <sup>*c*</sup>NBE content (mol %) estimated by <sup>13</sup>C NMR spectra.

duced copolymers with high molecular weights and unimodal molecular weight distributions.

It was revealed that 3c exhibited both high catalytic activity and efficient NBE incorporation. The catalytic activity decreased upon increasing the NBE concentration (entries 1 and 4-6). However, the molecular weights of the resultant copolymers remarkably increased upon increasing the NBE feed from 0.25 to 0.50 mol/L (entry 12 in Table 2 and entries 1 and 4 in Table 3). The maximum molecular weight value of the resultant copolymer could reach 750000. The efficient synthesis of high molecular weight copolymer with high NBE content could thus be accomplished under the optimized conditions. Interestingly, the molecular weights for the resultant copolymers by 3c were highly dependent on the Al/Cr molar ratio. The observed results were an interesting contrast to those found in ethylene homopolymerization, in which the molecular weight values changed slightly with the Al/Cr molar ratio. Complexes 3d and 3f showed somewhat low catalytic activities for ethylene and norbornene copolymerization under similar conditions. The resultant copolymers possessed unimodal molecular weight distributions, suggesting that the copolymerization took place with single catalytically active species. Complexes 4c and 4d were chosen for comparison. The results in the presence of MMAO were also summarized in Table 3. Compared with [O,P] analogues 3c and 3d, complexes 4c and 4d showed high catalytic activities and relatively efficient NBE incorporations, affording low molecular weight copolymers with unimodal molecular weight distributions (entries 1-2 vs 10–11 in Table 3).

<sup>13</sup>C NMR spectra for poly(ethylene-*co*-NBE)s showed that the microstructures formed by **3c** possessed isolated NBE units. The peaks at 47.7, 42.2, and 33.5 ppm are assigned to C2/C3, C1/C4, and C7, respectively. The signals stemming from C5/ C6 and short polyethylene sequences appeared at 30.1–30.7 ppm. E/NBE alternating sequence could be found for the copolymers with high NBE incorporation (Figure 7a). No resonances ascribed to repeated NBE insertion was observed. The DSC thermograms for the resultant copolymers possessed single  $T_g$ , and  $T_g$  values increased linearly upon increasing the NBE content, strongly suggesting that the resultant copolymer possessed uniform NBE incorporation.

#### CONCLUSIONS

We prepared and characterized a series of novel half-sandwich chromium(III) complexes bearing phenoxy-phosphine [O,P] ligands or phenoxy-phosphine oxide [O,P==O] ligands. X-ray



**Figure 7.** <sup>13</sup>C NMR spectra of E/NBE copolymer with different NBE incorporations produced by **3c** (a: 33.8%, entry 1 and b: 19.7%, entry 4 in Table 3, respectively).

structure analyses showed that these complexes adopt a pseudo octahedral coordination environment with a three-legged piano stool geometry. Using MMAO as a cocatalyst, complexes 3a-3f exhibited moderate to high catalytic activities for ethylene polymerization, depending on ligand structure, and produced high molecular weight polyethylenes. Introducing additional oxygen atom in phenoxy-phosphine ligands resulted in significant change on the aspect of the steric and electronic effects around the metal center, which has an impact on the polymerization behavior. Generally speaking, the [O,P=O] half-sandwich chromium(III) complexes displayed higher catalytic activities than the [O,P] analogues, but they produced much lower molecular weight polymers under similar conditions. It should be noted that complex 3c could efficiently promote ethylene/NBE copolymerization. To the best of our knowledge, this is the rare example of a half-sandwich chromium catalyst for ethylene/NBE copolymerization, which produced high molecular weight poly(ethylene-co-NBE) with high catalytic activity and efficient NBE incorporation.

## EXPERIMENTAL SECTION

General Procedures and Materials. All manipulation of airand/or moisture-sensitive compounds was carried out under a dry argon atmosphere by using standard Schlenk techniques or under a dry argon atmosphere in a MBraun glovebox, unless otherwise noted. All solvents were purified from a MBraun SPS system. The NMR data of the ligands used were obtained on a Bruker-300 MHz spectrometer at ambient temperature, with CDCl<sub>3</sub> as the solvent (dried by MS 4 Å). The NMR data of the copolymers were obtained on a Bruker-400 MHz spectrometer at 135 °C, with o-C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub> as a solvent. Mass spectra were obtained using electron impact (EI-MS). The <sup>19</sup>F NMR spectra of the complexes were recorded on a Bruker 400 MHz spectrometer. <sup>19</sup>F NMR spectra of the complexes were recorded with fluorobenzene as the internal standard ( $\delta_{\rm F} = -112.6$  ppm). UV-vis spectra were taken on a Shimadzu UV-2450 UV-vis spectrophotometer. Magnetic susceptibilities were measured with a SQUID magnetometer (Quantum Design, MPMS-LS). Elemental analyses were recorded on an elemental Vario EL spectrometer. The IR spectra of complexes were recorded on a Bio-Rad FTS-135 spectrophotometer. The weight-average molecular weights  $(M_w)$  and the polydispersity indices (PDIs) of polymer samples were determined at 150 °C 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 polystyrene standard EasiCal PS-1 (PL Ltd.). The 2.20 M n-butyllithium solution in hexane was purchased from Acros. Modified methylaluminoxane (MMAO, 7% aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc. Commercial ethylene was directly used for polymerization without further purification.

**Synthesis of Compounds 1a–1f and 2b–2e.** Various phenoxyphosphine [O,P] ligands and phenoxy-phosphine oxide [O,P=O] ligands bearing different substituents on R<sup>1</sup> and R<sup>2</sup> positions, 2-R<sup>1</sup>-4-R<sup>2</sup>-6-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>2</sub>OH (**3a**: R<sup>1</sup> = R<sup>2</sup> = H; **3b**: R<sup>1</sup> = Ph, R<sup>2</sup> = H; **3c**: R<sup>1</sup> = <sup>t</sup>Bu, R<sup>2</sup> = H; **3d**: R<sup>1</sup> = R<sup>2</sup> = <sup>t</sup>Bu; **3e**: R<sup>1</sup> = F, R<sup>2</sup> = H; **3f**: R<sup>1</sup> = C<sub>6</sub>F<sub>5</sub>, R<sup>2</sup> = H) and 2-R<sup>1</sup>-4-R<sup>2</sup>-6-(Ph<sub>2</sub>P=O)C<sub>6</sub>H<sub>2</sub>OH (**4b**: R<sup>1</sup> = Ph, R<sup>2</sup> = H; **4c**: R<sup>1</sup> = <sup>t</sup>Bu, R<sup>2</sup> = H; **4d**: R<sup>1</sup> = R<sup>2</sup> = <sup>t</sup>Bu; **4e**: R<sup>1</sup> = F, R<sup>2</sup> = H) were prepared according to literature procedures.<sup>31</sup>

Synthesis of Complexes 3a-3f and 4b-4c. Synthesis of Chromium Complex 3a Cp[O-6-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>]CrCl. A suspension of CpLi (0.15 g, 2.00 mmol) in THF (10 mL) was slowly added to a purple suspension of CrCl<sub>3</sub>(THF)<sub>3</sub> (0.75 g, 2.00 mmol) in THF (20 mL) at 0 °C. 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 added to a solution of 1a (0.56 g, 2.00 mmol) in dried THF (20 mL) at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2.5 h and then added slowly to the above reaction mixture at -78 °C. The obtained reaction mixture was allowed to warm to room temperature and was stirred overnight. During the reaction, the color of the reaction mixture changes from blue to green. Next, the reaction mixture was filtered by cannula filtration, and the filtrate was concentrated in vacuo to about 5 mL. Then, hexane (20 mL) was added into the system at room temperature. Green solids were precipitated from the solution, which were isolated via filtration and washed several times by cold hexane to yield 0.57g (66%) of complex 3a. Compounds 3b-3f and 4b-4c were prepared in similar methods. FT-IR (KBr, cm<sup>-1</sup>): 3050, 1582, 1548, 1480, 1453, 1440, 1303, 1263, 1243, 1185, 1155, 1125, 1096, 1058, 1026, 850, 813, 744, 693. EI-MS (70 eV):  $m/z = 428 [M^+]$ . Anal. Calcd for C<sub>23</sub>H<sub>19</sub>ClCrOP: C, 64.27; H, 4.46. Found: C, 64.13; H, 4.50. UV-vis (hexane): 267, 298 nm. Magnetic measurement:  $\mu_{\text{eff}}$  (300 K) = 3.15  $\mu_{\text{B}}$ .

Synthesis of Chromium Complex **3b** Cp[O-2-Ph-6-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>3</sub>]-CrCl. The complex was carried out according to the same procedure as that of **3a**, except that 2-Ph-6-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>3</sub>OH (0.71 g, 2.0 mmol) was used in place of 6-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>OH. Pure products were obtained as dark green crystals (0.74 g, 73%). FT-IR (KBr, cm<sup>-1</sup>): 3055, 1577, 1553, 1496, 1480, 1448, 1434, 1400, 1290, 1251, 1201, 1182, 1159, 1095, 1021, 1007, 851, 822, 749, 694, 627. EI-MS (70 eV): m/z = 504[M<sup>+</sup>]. Anal. Calcd for C<sub>29</sub>H<sub>23</sub>ClCrOP: C, 68.85; H, 4.58. Found: C, 68.98; H, 4.54. UV-vis (hexane): 253, 291 nm. Magnetic measurement:  $\mu_{\text{eff}}$  (300 K) = 3.12  $\mu_{\text{B}}$ .

Synthesis of Chromium Complex 3c  $Cp[O-2-{}^{t}Bu-6-(Ph_2P)C_6H_3]$ -CrCl. The complex was carried out according to the same procedure as that of 3a, except that 2- ${}^{t}Bu-6-(Ph_2P)C_6H_3OH$  (0.67 g, 2.0 mmol) was used in place of 6-(Ph\_2P)C\_6H\_4OH. Pure products were obtained as dark green crystals (0.66 g, 68%). FT-IR (KBr, cm<sup>-1</sup>): 3050, 2952, 1577, 1549, 1483, 1457, 1436, 1402, 1382, 1353, 1294, 1260, 1251, 1191, 1110, 1096, 1081, 871, 844, 755, 741, 693. EI-MS (70 eV): m/z = 484 [M<sup>+</sup>]. Anal. Calcd for C<sub>27</sub>H<sub>27</sub>ClCrOP: C, 66.74; H, 5.60. Found: C, 66.61; H, 5.65. UV–vis (hexane): 265, 306 nm. Magnetic measurement:  $\mu_{\text{eff}}$  (300 K) = 3.24  $\mu_{\text{B}}$ .

Synthesis of Chromium Complex **3d**  $Cp[O-2,4^{-t}Bu_2-6-(Ph_2P)-C_6H_2]CrCl$ . The complex was carried out according to the same procedure as that of **3a**, except that 2,4<sup>-t</sup>Bu<sub>2</sub>-6-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>2</sub>OH (0.78 g, 2.0 mmol) was used in place of 6-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>OH. Pure products were obtained as dark green crystals (0.76 g, 70%). FT-IR (KBr, cm<sup>-1</sup>): 3055, 2951, 2867, 1954, 1480, 1463, 1436, 1427, 1385, 1361, 1298, 1251, 1203, 1138, 1111, 1096, 1020, 1008, 998, 916, 879, 835, 814, 771, 744, 698, 654. EI-MS (70 eV): m/z = 541 [M<sup>+</sup>]. Anal. Calcd for C<sub>31</sub>H<sub>35</sub>ClCrOP: C, 68.69; H, 6.51. Found: C, 68.54; H, 6.55. UV– vis (hexane): 265, 306 nm. Magnetic measurement:  $\mu_{eff}$  (300 K) = 3.28  $\mu_{\rm B}$ .

Synthesis of Chromium Complex **3e** Cp[O-2-F-6-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>3</sub>]CrCl. The complex was carried out according to the same procedure as that of **3a**, except that 2-F-6-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>3</sub>OH (0.59 g, 2.0 mmol) was used in place of 6-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>OH. Pure products were obtained as green crystals (0.72 g, 75%). <sup>19</sup>F NMR (376.5 MHz, CDCl<sub>3</sub>):  $\delta$  –138.6. FT-IR (KBr, cm<sup>-1</sup>): 3055, 1596, 1464, 1438, 1315, 1296, 1256, 1232, 1179, 1095, 1063, 1020, 899, 844, 827, 776, 745, 737, 691. EI-MS (70 eV): m/z = 446 [M<sup>+</sup>]. Anal. Calcd for C<sub>23</sub>H<sub>18</sub>ClCrFOP: C, 61.69; H, 4.05. Found: C, 61.81; H, 4.01. UV–vis (hexane): 259, 349 nm. Magnetic measurement:  $\mu_{eff}$  (300 K) = 3.18  $\mu_{B}$ .

Synthesis of Chromium Complex **3f** Cp[O-2-C<sub>6</sub>F<sub>5</sub>-6-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>3</sub>]-CrCl. The complex was carried out according to the same procedure as that of **3a**, except that 2-C<sub>6</sub>F<sub>5</sub>-6-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>3</sub>OH (0.89 g, 2.0 mmol) was used in place of 6-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>OH. Pure products were obtained as blue crystals (0.91 g, 76%). <sup>19</sup>F NMR (376.5 MHz, CDCl3):  $\delta$ -162.2, -153.8. FT-IR (KBr, cm<sup>-1</sup>): 3087, 1582, 1557, 1518, 1493, 1468, 1436, 1413, 1323, 1281, 1263, 1228, 1181, 1098, 1069, 1019, 988, 904, 850, 822, 767, 755, 749, 739, 694, 654. EI-MS (70 eV): *m/z* = 594 [M<sup>+</sup>]. Anal. Calcd for C<sub>29</sub>H<sub>18</sub>ClCrF<sub>5</sub>OP: C, 58.45; H, 3.04. Found: C, 58.62; H, 2.98. UV-vis (hexane): 268, 304 nm. Magnetic measurement:  $\mu_{\text{eff}}$  (300 K) = 3.22  $\mu_{\text{B}}$ .

Synthesis of Chromium Complex **4b** Cp[O-2-Ph-6-(Ph<sub>2</sub>P=O)-C<sub>6</sub>H<sub>3</sub>]CrCl. The complex was carried out according to the same procedure as that of **3a**, except that 2-Ph-6-(Ph<sub>2</sub>P=O)C<sub>6</sub>H<sub>3</sub>OH (0.74 g, 2.0 mmol) was used in place of 6-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>OH. Pure products were obtained as blue crystals (0.76 g, 73%). FT-IR (KBr, cm<sup>-1</sup>): 3054, 2956, 1768, 1581, 1554, 1494, 1484, 1447, 1438, 1411, 1313, 1297, 1261, 1204, 1123, 1065, 1050, 1022, 998, 861, 814, 752, 726, 696. EI-MS (70 eV): m/z = 520 [M<sup>+</sup>]. Anal. Calcd for C<sub>29</sub>H<sub>23</sub>ClCrO<sub>2</sub>P: C, 66.74; H, 4.44. Found: C, 66.91; H, 4.49. UV-vis (hexane): 265, 334 nm. Magnetic measurement:  $\mu_{eff}$  (300 K) = 3.27  $\mu_{\rm B}$ .

Synthesis of Chromium Complex 4c Cp[O-2-<sup>t</sup>Bu-6-(Ph<sub>2</sub>P= O)C<sub>6</sub>H<sub>3</sub>]CrCl. The complex was carried out according to the same procedure as that for 3a, except that 2-<sup>t</sup>Bu-6(Ph<sub>2</sub>P=O)C<sub>6</sub>H<sub>3</sub>OH (0.70 g, 2.0 mmol) was use in place of 6-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>OH. Pure products were obtained as dark blue crystals (0.75 g, 75%). FT-IR (KBr, cm<sup>-1</sup>): 3088, 3058, 2978, 2939, 2897, 1575, 1552, 1483, 1460, 1437, 1407, 1386, 1350, 1291, 1264, 1198, 1185, 1166, 1121, 1051, 1022, 1010, 997, 876, 854, 813, 799, 766, 755, 730, 693. EI-MS (70 eV): m/z =500 [M<sup>+</sup>]. Anal. Calcd for C<sub>27</sub>H<sub>27</sub>ClCrO<sub>2</sub>P: C, 64.61; H, 5.42. Found: C, 64.77; H, 5.48. UV-vis (hexane): 266, 294 nm. Magnetic measurement:  $\mu_{\text{eff}}$  (300 K) = 3.18  $\mu_{\text{B}}$ .

Synthesis of Chromium Complex 4d Cp[O-2,4-<sup>t</sup>Bu<sub>2</sub>-6-(Ph<sub>2</sub>P= O)C<sub>6</sub>H<sub>2</sub>]CrCl. The complex carried out according to the same procedure as that for 3a, except that 2,4-<sup>t</sup>Bu<sub>2</sub>-6(Ph<sub>2</sub>P=O)C<sub>6</sub>H<sub>3</sub>OH (0.81 g, 2.0 mmol) was used in place of 6(Ph<sub>2</sub>P=O)C<sub>6</sub>H<sub>4</sub>OH. Pure products were obtained as blue solids (0.88 g, 79%). FT-IR (KBr, cm<sup>-1</sup>): 3078, 3058, 2954, 2904, 2867, 1770, 1594, 1536, 1406, 1438, 1426, 1385, 1361, 1301, 1253, 1202, 1120, 1059, 1021, 1011, 998, 916, 884, 871, 839, 807, 787, 775, 755, 726, 692. EI-MS (70 eV): m/z =557 [M<sup>+</sup>]. Anal. Calcd for C<sub>31</sub>H<sub>35</sub>ClCrO<sub>2</sub>P: C, 66.72; H, 6.32. Found: C, 66.54; H, 6.27. UV-vis (hexane): 266, 306 nm. Magnetic measurement:  $\mu_{eff}$  (300 K) = 3.21  $\mu_{B}$ .

Synthesis of Chromium Complex 4e Cp[O-2-F-6-(Ph<sub>2</sub>P=O)C<sub>6</sub>H<sub>3</sub>]-CrCl. The complex was carried out according to the same procedure as that of **3a**, except that 2-F-6-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>3</sub>OH (0.62 g, 2.0 mmol) was used in place of 6-(Ph<sub>2</sub>P–O)C<sub>6</sub>H<sub>4</sub>OH. Pure products were obtained as blue solids (0.68 g, 75%). <sup>19</sup>F NMR (376.5 MHz, CDCl3):  $\delta$  –134.8. FT-IR (KBr, cm<sup>-1</sup>): 3057, 2961, 1599, 1465, 1441, 1309, 1264, 1234, 1191, 1120, 1068, 1014, 998, 855, 811, 743, 725, 704, 695. EI-MS (70 eV): m/z = 462 [M<sup>+</sup>]. Anal. Calcd for C<sub>23</sub>H<sub>18</sub>ClCrFO<sub>2</sub>P: C, 59.56; H, 3.91. Found: C, 59.68; H, 4.01. UV–vis (hexane): 265, 317 nm. Magnetic measurement:  $\mu_{eff}$  (300 K) = 3.26  $\mu_{\rm B}$ .

**X-ray Crystallography.** Single crystal of complexes **3b**, **3c**, **3e**, and **4c** suitable for X-ray structure determination were grown from hexane solution at -20 °C in a glovebox, thus maintaining a dry,  $O_2$ -free environment. The intensity data were collected with the  $\omega$  scan mode (186 K) on a Bruker Smart APEX diffractometer with CCD detector using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Lorentz, polarization factors were made for the intensity data, and absorption corrections were performed using SADABS. 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.

**Ethylene (Co)polymerization.** A typical procedure was performed as follows: the prescribed amounts of toluene and MMAO and NBE if necessary were added into the autoclave (200 mL, stainless steel), 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 metal complex. The polymerization was terminated with the addition of EtOH, and the resultant polymer was adequately washed with EtOH containing HCl and then dried under vacuum for several hours.

#### ASSOCIATED CONTENT

# **Supporting Information**

Crystal data and structure refinements of complexes **3b**, **3c**, **3e**, and **4c** and X-ray diffraction data for **3b**, **3c**, **3e**, and **4c** (as CIF and PDF files). This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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