Ethylene Polymerization by the Chromium Catalysts Based on Bidentate [O, P=O] or [S, P] Ligands

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ABSTRACT: Novel chromium catalysts based on bidentate phenoxy-phosphinoyl (HO-2R$_1$-4R$_2$-6(Ph$_2$P=O)C$_6$H$_2$: R$_1$ = R$_2$ = H, **3a**; R$_1$ = *t*Bu, R$_2$ = H, **3b**; R$_1$ = R$_2$ = *t*Bu, **3c**; R$_1$ = R$_2$ = cumyl, **3d**; R$_1$ = anthracenyl, R$_2$ = H, **3e**) and thiophenol-phosphine (HS-2R$_1$-4R$_2$-6(Ph$_2$P)C$_6$H$_2$: R$_1$ = R$_2$ = H, **4a**; R$_1$ = SiMe$_3$, R$_2$ = H, **4b**) were prepared and characterized. Treatment with modified methyaluminoxane, these catalysts displayed moderate to high-catalytic activities for ethylene polymerization. The activities of them were higher than those of the corresponding catalysts based on bidentate phenoxy-phosphine ligands. Both the coordinated donors and the *ortho*-substituent of the ligands played an important role in improving catalytic activity. The effects of reaction parameters, such as cocatalyst and Al/Cr molar ratio as well as reaction temperature, on ethylene polymerization behaviors were investigated in detail for two favorable catalytic systems, **3b**/CrCl$_3$(thf)$_3$ and **4b**/CrCl$_3$(thf)$_3$. Catalyst **4b**/CrCl$_3$(thf)$_3$ displayed higher catalytic activity and better temperature tolerance for ethylene polymerization than **3b**/CrCl$_3$(thf)$_3$. © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 311–319, 2010

KEYWORDS: catalysis; polyolefins; Ziegler-Natta polymerization

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 polymer chemistry.[1–3] Chromium catalysts have played a crucial role due to the widespread commercial application of silica-supported Phillips catalysts.[4–9] In more recent years, a significant amount of attention has been given to the development of homogeneous nonmetallocene chromium catalysts. A number of neutral and anionic ligands were used to stabilize chromium complexes, and some of them have already been shown to afford highly active olefin polymerization catalysts.[10–19] The ligands containing relatively hard nitrogen and oxygen donors have featured in the reported chromium catalysts. For example, chromium catalysts based on monoanionic bidentate phenoxy-amide [O, N] ligands displayed high activities toward ethylene polymerization, and the tridentate phenoxy-amide chromium catalysts containing additional coordinated nitrogen donor [O, N, N] generated low-molecular weight linear polyethylene.[12(a,b)] A family of air-stable chromium catalysts bearing bis(imino)pyridine [N, N, N] displayed high activity and promising temperature tolerance toward ethylene polymerization, and afforded linear polyethylene.[13] Bis(benzimidazolyl)pyridine [N, N, N] chromium catalysts also showed high activities toward ethylene oligomerization and polymerization.[14(a)] Recent researches have suggested that there may be a surprising advantage using the ligands bearing soft phosphorus or sulfur donor. For example, the phosphorus-bridged bisphenoxy chromium complexes were found to be highly active toward ethylene polymerization,[16] and aminebis(phosphine) chromium complexes selectively trimerized ethylene to 1-hexene.[17(a)] Our previous research also indicated that introducing an additional soft donor pendant in the amino-pyrrolide ligands can stabilize the chromium catalysts and increase the activity toward ethylene polymerization.[18(b)]

Monoanionic phenoxy-phosphine containing hard oxygen and soft phosphorus donors has been one of the most attracted ligands to have emerged in olefin polymerization catalysis over the past years. Although encouraging olefin polymerization results have been obtained by bis(phenoxy-phosphine), Group 4 catalysts,[20] the chromium catalysts based on phenoxy-phosphine ligands only exhibited low-catalytic activity.[12(b)] Previously, we reported a new class of bisphenoxy ligands [O, P=O, O] based titanium complexes.[21] We found the neutral P=O donor can improve the catalytic activity toward ethylene polymerization. This result prompted us to introduce the neutral P=O donor into the monoanionic phenoxide ligand anchored chromium catalysts. We hope that the neutral P=O donor could be beneficial for stabilizing chromium catalysts. In addition, previous researches also showed that introducing an extra soft sulfur donor into amino-pyrrolide ligand can improve the performance of the chromium catalyst toward ethylene polymerization.[18(b)] Although favorable results have been obtained using chromium complexes that contain soft phosphorus or sulfur donor, catalyst

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system containing both phosphorus and sulfur donors in the same ligand has yet to be reported. In this article, we reported two new classes of effective bidentate phenoxy-phosphinoyl and thiophenol-phosphine ligands for chromium catalysts for ethylene polymerization. The catalyst based on bidentate [S, P] ligand displayed higher catalytic activity and better temperature tolerance for ethylene polymerization than the catalyst based on bidentate [O, P=O] ligand.

EXPERIMENTAL

General Procedure and Materials

All manipulation of air- and/or moisture-sensitive compounds were carried out under a dry argon atmosphere by using standard Schlenk techniques or under a dry argon atmosphere in an MBraun glovebox unless otherwise noted. All solvents were purified from an MBraun SPS system. The NMR data of the ligands were obtained on a Bruker 300 MHz spectrometer (75 MHz for ^{13}C) at ambient temperature, with $CDCl_3$ as a solvent. The ^{13}C NMR data of the polymers were obtained on a Varian Unity-400 MHz spectrometer at 135 °C, with *O*-$C_6D_4Cl_2$ as a solvent. Elemental analyses were recorded on an elemental Vario EL spectrometer. The DSC measurements were performed on a Perkin-Elmer Pyris 1 differential scanning calorimeter at a rate of 10 °C/min. The weight-average molecular weight (M_w) and the polydispersity index 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 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). The 2.5 M *n*-butyllithium solution in hexane was purchased from Acros. $CrCl_3(thf)_3$ was purchased from Aldrich. Modified methylaluminoxane (MMAO, 7% aluminum in heptane solution, 2 mol/L) was purchased from Akzo Nobel Chemical. Commercial ethylene was directly used for polymerization without further purification. Tetrahydropyranyl (THP) ether **1a-e** and ligands **5a-b**, **6**, and **7** were synthesized according to the reported methods.[21,22] The other reagents and solvents were commercially available.

Synthesis of Compounds 2a-e

2-Diphenylphosphanyl Phenol (2a)

To a solution of **1a** (3.7 g, 21 mmol) in hexane (30 mL) was added TMEDA (2.9 g, 25 mmol), *n*-butyllithium (2.5 M in hexane, 10 mL, 25 mmol) at −10 °C. The mixture was allowed to warm to room temperature and stirred for 12 h, giving a yellow precipitate. The appropriate PPh_2Cl (5.5 g, 25 mmol) was added to the suspension dropwise at −10 °C. The mixture was stirred at room temperature for additional 12 h. To the mixture was added water, and extracted with ether. The extract was evaporated under reduced pressure, and then successively dissolved in thf (30 mL) and 5 M HCl (3 mL) added. The mixture was stirred at room temperature for 1 h. The product was neutralized with $NaHCO_3$ to pH = 7, and then extracted with ether. The organic phase was washed with water (2 × 50 mL), dried with Na_2SO_4, and concentrated to give the crude product. The crude product was chromatographed in a silica gel column rapidly to give **2a** as a white solid (3.4 g, 59% yield).

^{1}H NMR ($CDCl_3$): δ 6.26 (br, 1H, Ar-OH), 6.81–6.98 (m, 3H, Ar-H), 7.28–7.37 (m, 11H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 114.5, 120.15, 127.6, 127.7, 127.9, 130.3, 132.2, 133.6, 134.0, 158.2 (d, *J* = 18 Hz). Anal. Calc. for $C_{18}H_{15}OP$: C, 77.69; H, 5.43. Found: C, 77.76; H, 5.39.

*2-*Tert*-butyl-6-diphenylphosphanyl Phenol (2b)*

Compound **2b** was prepared via the same procedure in 63% yield.

^{1}H NMR ($CDCl_3$): δ 1.41 (s, 9H, *t*-Bu), 6.82–6.86 (m, 2H, Ar-H), 7.25–7.26 (m, 1H, Ar-H), 7.34–7.38 (m, 10H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 30.1, 35.4, 120.9, 121.5, 129.0, 129.3, 129.5, 132.5, 133.7, 135.0, 136.5, 158.6 (d, *J* = 20.3 Hz). Anal. Calc. for $C_{22}H_{23}OP$: C, 79.02; H, 6.93. Found: C, 79.09; H, 6.98.

*2,4-Di-*tert*-butyl-6-diphenylphosphanyl Phenol (2c)*

Compound **2c** was prepared via the same procedure in 66% yield.

^{1}H NMR ($CDCl_3$): δ 1.15 (s, 9H, *t*-Bu), 1.41 (s, 9H, *t*-Bu), 6.78–6.81 (m, 1H, Ar-H), 6.86–6.88 (m, 1H, Ar-H), 7.32–7.36 (m, 10H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 30.1, 31.9, 34.8, 35.6, 120.4, 126.7, 129.0, 129.3, 129.5, 129.7, 133.9, 135.8, 142.7, 156.6 (d, *J* = 19.5 Hz). Anal. Calc. for $C_{26}H_{31}OP$: C, 79.97; H, 8.00. Found: C, 79.87; H, 8.05.

2,4-Di-cumyl-6-diphenylphosphanyl Phenol (2d)

Compound **2d** was prepared via the same procedure in 61% yield.

^{1}H NMR ($CDCl_3$): δ 1.53 (s, 6H, cumyl-Me), 1.60 (s, 6H, cumyl-Me), 6.54–6.57 (m, 1H, Ar-H), 7.13–7.33 (m, 21H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 30.1, 31.3, 42.6, 43.1, 123.6, 126.2, 127.0, 128.4, 128.9, 129.2, 131.5, 134.1, 135.1, 136.8, 143.0, 149.4, 151.1, 154.6 (d, *J* = 17.3 Hz). Anal. Calc. for $C_{36}H_{35}OP$: C, 84.02; H, 6.85. Found: C, 79.97; H, 6.93.

2-Anthracenyl-6-diphenylphosphanyl Phenol (2e)

Compound **2e** was prepared via the same procedure in 60% yield.

^{1}H NMR ($CDCl_3$): ^{1}H NMR ($CDCl_3$): δ 6.96–7.66 (m, 19H, Ar-H), 8.06 (d, *J* = 8.1 Hz, 2H, Ar-H), 8.56 (s, 1H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 121.4, 123.9, 124.6, 125.8, 126.5, 126.6, 128.3, 128.9, 129.0, 129.3, 130.4, 131.1, 131.9, 133.9, 134.1, 134.4, 136. 4, 156.2 (d, *J* = 15.6 Hz). Anal. Calc. for $C_{32}H_{23}OP$: C, 84.56; H, 5.10. Found: C, 84.48; H, 5.05.

Synthesis of Compounds 3a-e

2-Diphenylphosphinoyl Phenol (3a)

Compound **3a** (2.5 g, 9 mmol) was dissolved in thf (20 mL), and two drops of H_2O_2 were added to the solution, then the solution was stirred at room temperature for 3 h. The evaporation of the solvent under reduced pressure yielded a crude product, recrystallization from thf/hexane to give **3a** as a white solid (2.4 g, 91% yield).

^{1}H NMR ($CDCl_3$): δ 6.80–6.86 (m, 1H, Ar-H), 6.95–7.05 (m, 2H, Ar-H), 7.38–7.45 (m, 1H, Ar-H), 7.47–7.53 (m, 4H, Ar-H), 7.54–7.62 (m, 2H, Ar-H), 7.65–7.73 (m, 4H, Ar-H). ^{13}C NMR

($CDCl_3$): δ 110.5, 112.0, 118.6, 119.1, 128.6, 131.1, 131.9, 132.1, 134.4, 163.9. Anal. Calc. for $C_{18}H_{15}O_2P$: C, 73.46; H, 5.14; Found: C, 73.55; H, 5.09.

2-Tert-butyl-6-diphenylphosphinoyl Phenol (3b)

Compound **3b** was prepared via the same procedure in 93% yield.

^{1}H NMR ($CDCl_3$): δ 1.41 (s, 9H, *t*-Bu), 6.75–6.86 (m, 2H, Ar-H), 7.42–7.72 (m, 11H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 29.8, 35.6, 110.4, 111.8, 118.8, 129.1, 130.0, 131.7, 132.5, 133.2, 139.2, 163.0. Anal. Calc. for $C_{22}H_{23}O_2P$: C, 75.41; H, 6.62; Found: C, 75.36; H, 6.65.

2,4-Di-tert-butyl-6-diphenylphosphanyl Phenol (3c)

Compound **3c** was prepared via the same procedure in 91% yield.

^{1}H NMR ($CDCl_3$): δ 1.16 (s, 9H, *t*-Bu), 1.43 (s, 9H, *t*-Bu), 6.78–6.83 (m, 1H, Ar-H), 7.45–7.50 (m, 5H, Ar-H), 7.51–7.54 (m, 2H, Ar-H), 7.65–7.72 (m, 4H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 29.6, 31.4, 34.1, 35.4, 108.9, 110.3, 126.1, 128. 6, 131.9, 132.4, 133.1, 138.0, 140.5, 160.9. Anal. Calc. for $C_{26}H_{31}O_2P$: C, 76.82; H, 7.69. Found: C, 76.90; H, 7.73.

2,4-Di-cumyl-6-diphenylphosphinoyl Phenol (3d)

Compound **3d** was prepared via the same procedure in 90% yield.

^{1}H NMR ($CDCl_3$): δ 1.57 (s, 6H, cumyl-Me), 1.67 (s, 6H, cumyl-Me), 6.65 (dd, *J* = 2.4 Hz, 14.1 Hz, 1H, Ar-H), 7.10–7.23 (m, 10H, Ar-H), 7.39–7.53 (m, 11H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 29.5, 30.8, 42.5, 109.5, 110.9, 125.3, 125.8, 126.7, 128.0, 128.6, 130.5, 132.0, 132.4, 137.5, 140.4, 150.3, 160.3. Anal. Calc. for $C_{36}H_{35}O_2P$: C, 81.48; H, 6.65; Found: C, 81.53; H, 6.70.

2-Anthracenyl-6-diphenylphosphinoyl Phenol (3e)

Compound **3e** was prepared by the same procedure in 93% yield.

^{1}H NMR ($CDCl_3$): δ 7.06–7.84 (m, 19H, Ar-H), 8.04 (d, *J* = 9 Hz, 2H, Ar-H), 8.51 (s, 1H, Ar-H), 11.17 (s, 1H, Ar-OH). ^{13}C NMR ($CDCl_3$): δ 111.5, 112.8, 119.4, 123.6, 124.8, 125.5, 126.0, 126.8, 127.6, 128.1, 129.0, 129.3, 130.7, 131.9, 132.5, 133.0, 138.0, 162.4. Anal. Calc. for $C_{32}H_{23}O_2P$: C, 81.69; H, 4.93; Found: C, 81.72; H, 4.98.

Synthesis of *In-Situ* Chromium Catalysts (Ligand/$CrCl_3(thf)_3$)

In-situ chromium catalysts were generated by mixing the ligands with $CrCl_3(thf)_3$ (1 equiv) in toluene, followed by removal of the solvent in reduced pressure. The resulting complexes were dissolved in toluene and tested as the catalyst for ethylene polymerization.[12(a),16,18(b)]

Synthesis of Complexes A–C

Bis(2-*tert-butyl-6-diphenylphosphinoyl-phenoxy Tetrahydrofuran Chromiumdichloride) (A)*

To a stirred solution of **3b** (0.60 g, 1.7 mmol) in dried thf (20 mL) at −78 °C, a 2.5 *M* *n*-butyllithium hexane solution (0.68 mL, 1.7 mmol) was added dropwise over 5 min. The mixture was allowed to warm to room temperature and stirred for 2.5 h. The mixture was added dropwise to $CrCl_3(thf)_3$ (0.63 g, 1.7 mmol) in dried thf (30 mL) at −78 °C with stirring over 30 min. The mixture was allowed to warm to room temperature and stirred overnight. The evaporation of the solvent in vacuum yielded a crude product. The crude product was added 30 mL dried hexane and the mixture was stirred for 10 min at 60 °C and then filtered. The deep red solution was cooled to −35 °C slowly to give the crystals of complex **A** (0.72 g, 78% yield).

2,4-Di-cumyl-6-diphenylphosphinoyl-phenoxy bis(tetrahydrofuran) chromiumdichloride (**B**) and 2-anthracenyl-6-diphenylphosphinoyl-phenoxy bis(tetrahydrofuran) chromiumdichloride (**C**) were prepared by the same procedure in 75 and 69% yield, respectively.

Ethylene Polymerization

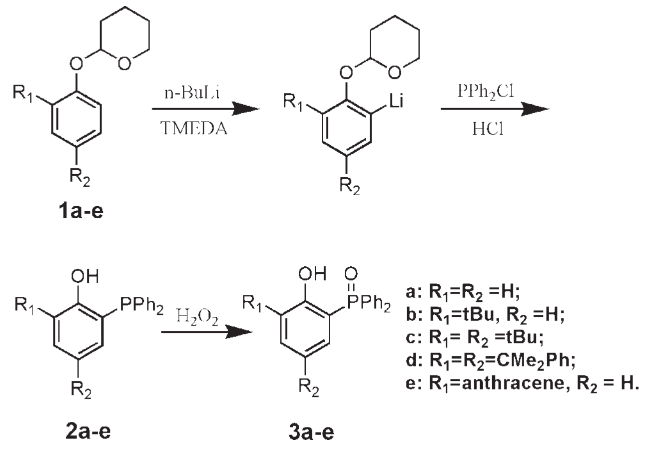
The polymerization was carried out in a 150 mL Schlenk flask equipped with a mechanical stirrer. The flask was repeatedly evacuated and refilled with nitrogen, and finally filled with ethylene gas (ambient pressure) from a Schlenk line. MMAO and toluene were added via a gastight syringe. The catalyst, dissolved in toluene under a dry nitrogen atmosphere, was transferred into the Schlenk flask, and ethylene consumption was noted as a function of time from the gas burette. The polymerization was initiated by the addition of a heptane solution of MMAO into the reactor with vigorous stirring. After the prescribed reaction time, the reaction was stopped, and then the resulted mixture was poured into a solution of hydrochloric acid/ethanol (10 vol %) to precipitate the polymer. The resulted polyethylene was recovered by filtration, washed with ethanol, and dried in a vacuum oven at 60 °C.

High-pressure polymerization experiments were carried out 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 24 h at 150 °C 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 given pressure throughout the polymerization run by continuously feeding the ethylene gas. After the prescribed reaction time, the stirring motor was stopped and the reactor was vented, then the resulting mixture was poured into a solution of hydrochloric acid/ethanol (10 vol %) to precipitate the polymer. The polyethylene thus obtained was recovered by filtration, washed with ethanol, and dried in a vacuum oven at 60 °C.

RESULTS AND DISCUSSION

Ethylene Polymerization by Chromium Catalysts Based on Bidentate [O, P=O] Ligands

The synthetic route for phenoxy-phosphinoyl [O, P=O] ligands **3a–e** used in this study is depicted in Scheme 1. THP ether **1a–e** were lithiated with *n*-BuLi/TMEDA and quenched with PPh_2Cl. The protective group could be easily removed to give **2a–e** by the addition of hydrochloric acid.



SCHEME 1 Synthesis of ligands **3a–e**.

Compounds **2a–e** were further oxidated to ligands **3a–e** using H_2O_2. All the ligands were identified by elemental analysis and NMR spectra.

Phenoxy-phosphinoyl *in-situ* chromium catalysts **3a–e**/$CrCl_3(thf)_3$ were investigated as the catalysts for ethylene polymerization in the presence of MMAO under the mild conditions (25 °C, Al/Cr = 2000/1, 1 atm ethylene pressure). Phenoxy-phosphine catalysts **2a–e**/$CrCl_3(thf)_3$ were also studied for comparison. The polymerization results are collected in Figure 1. The metal precursor alone did not support significant catalysis (80 kg PE/$mol_{Cr} \cdot h$), while **2a–e**/$CrCl_3(thf)_3$ also displayed low-catalytic activities for ethylene polymerization ($\leq$106 kg PE/$mol_{Cr} \cdot h$). Catalyst **3a**/$CrCl_3(thf)_3$ was not active for ethylene polymerization, whereas, **3b**/$CrCl_3(thf)_3$ exhibited an activity of 264 kg PE/$mol_{Cr} \cdot h$ which was not only higher than the activity obtained by **3a**/$CrCl_3(thf)_3$, but also the value of corresponding **2b**/$CrCl_3(thf)_3$ (106 kg PE/$mol_{Cr} \cdot h$). These results suggest that monoanionic phenoxy-phosphinoyl is effective ligand for chromium catalysts and both the additional neutral P=O donor and the *ortho*-substituent of the ligand play an important role in improving catalytic activity. Catalyst **3c**/$CrCl_3(thf)_3$ displayed an activity of 236 kg PE/$mol_{Cr} \cdot h$ for ethylene polymerization. The activity is comparable with the value of **3b**/$CrCl_3(thf)_3$, indicating that the *para*-substituent in the phenoxide donor had little influence on the catalytic activity. Catalyst **3d–e**/$CrCl_3(thf)_3$ with bulky *ortho*-substitute cumyl or anthracenyl displayed lower activities than **3b**/$CrCl_3(thf)_3$. This result is different from the phenoxy-amide chromium catalysts, in which introducing a bulky *ortho*-substitute can dramatically increase the catalytic activity.[12(b)] In all experiments, the catalytic activity was valued based on the solid polymer obtained, while GC analysis of the soluble fraction indicated a small amount of α-olefins by oligomerization of ethylene was present in the reaction mixtures.

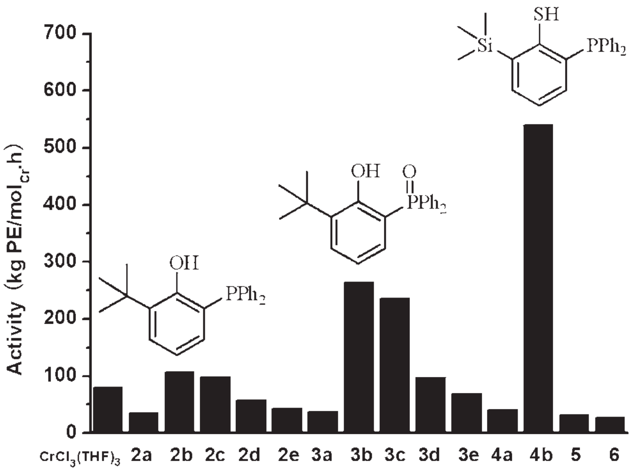
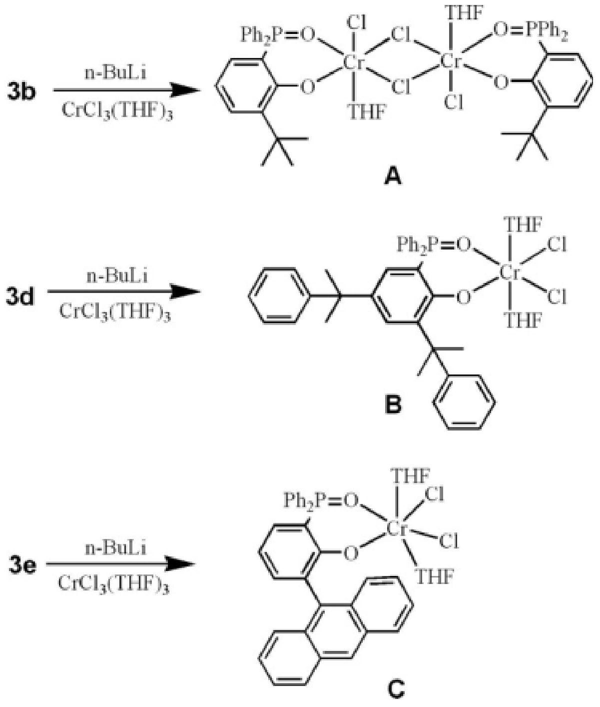


FIGURE 1 Ethylene polymerization results using the *in-situ* catalysts (5 μmol ligand, 5 μmol $CrCl_3(thf)_3$; Al/Cl = 2000/1; 25 °C; 10 min; V_{total} = 50 mL; 1 atm ethylene pressure).

To further elucidate the structure of the catalyst and the steric hindrance influence on the catalytic activity, we tried to isolate and characterize the catalysts. Chromium complexes based on phenoxy-phosphinoyl ligands were prepared by the reaction of $CrCl_3(thf)_3$ with one equivalent of the lithium salts of the corresponding ligands, as shown in Scheme 2. Attempted characterization of these complexes by NMR resulted in failure because of its severe line broadening in the spectra, which indicates that the complexes are paramagnetic species. Fortunately, the crystals (**A**–**C**) suitable for X-ray structure determination were obtained by diffusion of hexane into a dichloromethane solution. Their molecular structures were shown in Figures 2–4. Crystal **B** consists of two crystallographically independent molecules in the unit cell and there is only few difference between each other. One molecule is omitted for clarity in Figure 3.



SCHEME 2 Synthesis of chromium complexes **A**–**C**.

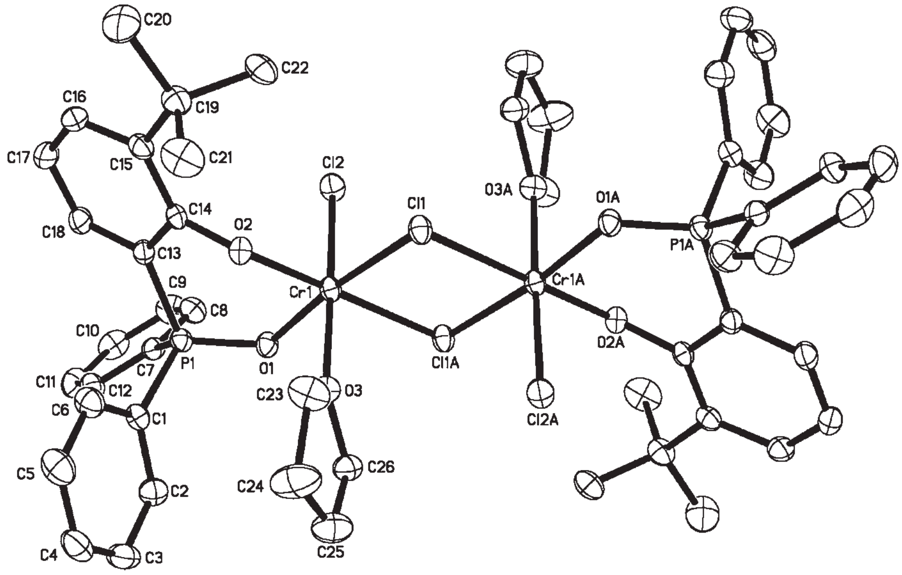


FIGURE 2 Molecular structure of complex **A** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Cr(1)—O(1), 1.9611(18); Cr(1)—O(2), 1.9078(18); Cr(1)—O(3), 2.0620(19); Cr(1)—Cl(1), 2.3969(8); Cr(1)—Cl(1A), 2.3998(8); Cr(1)—Cl(2), 2.3003(8); O(1)—Cr(1)—O(2), 92.51(8); O(1)—Cr(1)—O(3), 86.68(8); O(2)—Cr(1)—O(3), 87.41(8); O(1)—Cr(1)—Cl(1), 173.78(6); O(2)—Cr(1)—Cl(1), 90.88(6); O(3)—Cr(1)—Cl(1), 88.27(6); O(1)—Cr(1)—Cl(2), 90.88(6); O(2)—Cr(1)—Cl(2), 93.08(6); O(3)—Cr(1)—Cl(2), 177.53(6); Cl(1)—Cr(1)—Cl(2), 94.15(3); Cl(1)—Cr(1)—Cl(1A), 95.33(3).

As shown in Figure 2, complex **A** reveals chloro-bridged binuclear structure in which each monomer moiety is related by a crystallographic center of symmetry. Each chromium center in complex **A** displays a six-coordinated distorted-octahedral geometry with one additional thf molecule. The two bridging groups are located at the position *trans* to the oxygen atoms of the phenoxy-phosphinoyl ligands and the chlorine atoms occupies a position *trans* to the thf molecules. The nonbonded Cr···Cr distance (3.546 Å) is in the range found in a number of other chloride-bridged chromium complexes (3.64–3.23 Å).[23] Different from **A**, complexes **B** and **C** with bulky *ortho*-phenoxy substituents show octahedral coordination at the chromium center with a single bidentate [O, P=O] ligand and two *cis*-coordinated thf molecules, as shown in Figure 3 (O(1)—Cr—O(2) 91.70°; Cl(1)—Cr—Cl(2) 95.35°) and Figure 4 (O(1)—Cr—O(2) 92.22°; Cl(1)—Cr—Cl(2) 94.66°). The different coordination mode of complexes **A**–**C** are probably associated with the steric crowding of the bulky group around the *ortho*-position, which may hinder

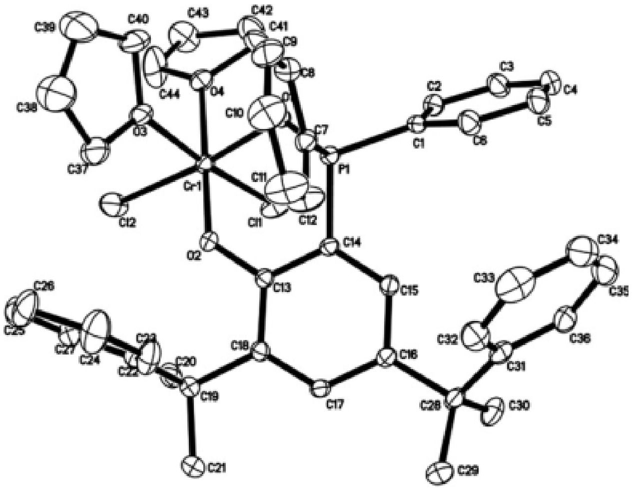


FIGURE 3 Molecular structure of complex **B** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Cr—O(1), 1.9905(19); Cr—O(2), 1.9243(19); Cr—O(3), 2.054(2); Cr—O(4), 2.082(2); Cr—Cl(1), 2.2776(9); Cr—Cl(2), 2.3214(9); O(1)—Cr—O(2), 91.70(8); O(1)—Cr—O(3), 85.63(9); O(1)—Cr—O(4), 85.38(8); O(2)—Cr—O(3), 89.33(8); O(2)—Cr—O(4), 175.74(8); O(3)—Cr—O(4), 87.35(9); O(1)—Cr—Cl(1), 90. 10(6); O (2)—Cr—Cl(1), 93.76(6); O(3)—Cr—Cl(1), 174. 81(7); O(4)—Cr—Cl(1), 89.36(7); O(1)—Cr—Cl(2), 173. 70(6); O(2)—Cr—Cl(2), 91.08(6); O(3)—Cr—Cl(2), 88.75(7); O(4)—Cr—Cl(2), 91.52(6); Cl(1)—Cr—Cl(2), 95.35(4).

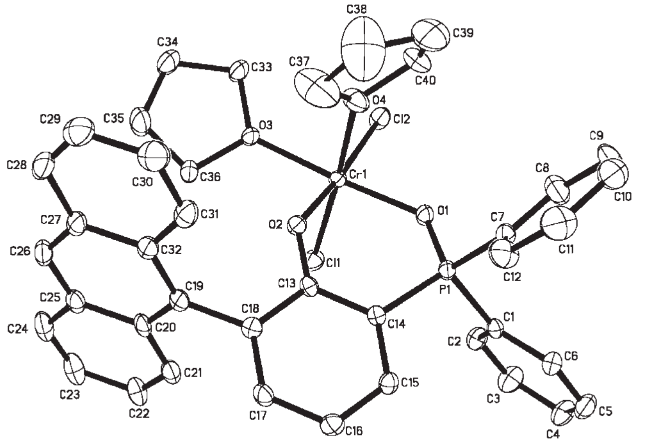
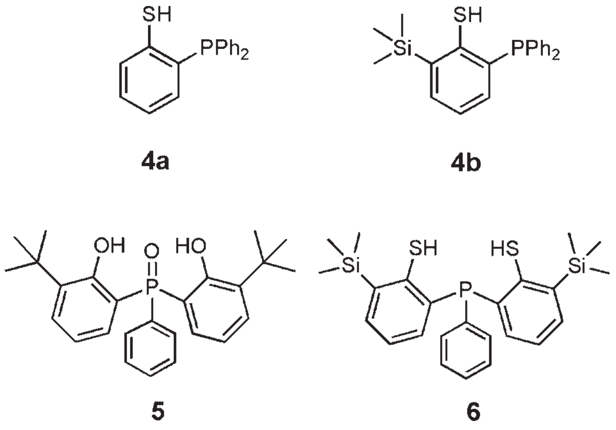


FIGURE 4 Molecular structure of complex **C** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Cr—O(1), 1.956(3); Cr—O(2), 1.917(3); Cr—O(3), 2.038(3); Cr—O(4), 2.077(3); Cr—Cl(1), 2.2889(14); Cr—Cl(2), 2.3247(14); O(1)—Cr—O(2), 92.22(13); O(1)—Cr—O(3), 175.00(14); O(1)—Cr—O(4), 89.42(15); O(2)—Cr—O(3), 86.96(13); O(2)—Cr—O(4), 85.66(14); O(3)—Cr—O(4), 85.60(15); O(1)—Cr—Cl(1), 92.74(10); O(2)—Cr—Cl(1), 90.75(10); O(3)—Cr—Cl(1), 92.20(11); O(4)—Cr—Cl(1), 175.89(11); O(1)—Cr—Cl(2), 90.51(10); O(2)—Cr—Cl(2), 173.81(10); O(3)—Cr—Cl(2), 89.84(10); O(4)—Cr—Cl(2), 88.82(11); Cl(1)—Cr—Cl(2), 94.66(6).



SCHEME 3 Ligands **4a-b**, **5**, and **6** used in this study.

the adjacence of two molecules and restrain the formation of the chloro-bridge. Although **B** and **C** exhibit similar coordination structure, there are also some differences between them. For example, the Cr—O(1) and Cr—O(2) bond distances in **B** (1.990 and 1.924 Å) are slightly longer than those in **C** (1.956 and 1.917 Å, respectively). The phosphor atom lying 0.539 Å out of the phenoxy ring plane in **B**, whereas they are coplanar in **C**. In complex **C**, the anthracenyl moiety is oriented approximately orthogonally to the phenoxy ring (~77.68°), which is slightly shorter than that in corresponding phenoxy-amide chromium complex (~85°).[12(b)]

Complexes **A**–**C** displayed catalytic activity of 278, 111, and 76 kg PE/mol$_{Cr}$·h, respectively, for ethylene polymerization under the mild conditions. The catalytic activities are consistent with the values obtained by *in-situ* catalysts under the same conditions. Complex **A** displayed much higher catalytic activity than **B** and **C**. The effect of the ligand environments on the productivity is similar to the results obtained by *in-situ* process. These results suggest that the identical catalytic species were generated in these two systems. We assumed the low-catalytic activities of complexes **B** and **C** were probably due to bulky *ortho*-substitute in complexes. Considering the steric protection to the active site afforded by diphenylphosphinoyl in phenoxy-phosphinoyl complexes, a further bulky *ortho*-anthracenyl substituent in close proximity to the active site in **B** and **C** may hinder the access of ethylene to the active site and restrain the growth of the polymer chain, and thus lead to the low-catalytic activity.

Ethylene Polymerization by Chromium Catalysts Based on Bidentate [S, P] Ligands

The aforementioned results revealed that the catalytic activities of the phenoxy-phosphine based chromium catalysts could be readily tuned via modification of the coordination donors. Therefore, thiophenol-phosphine ligands **4a–b** (Scheme 3) were designed and synthesized by changing the hard oxygen donor to soft sulfur donor to further explore the potential of soft sulfur donor-based ligand systems. The polymerization results are also shown in Figure 1. Catalyst **4a**/$CrCl_3(thf)_3$ was not active for ethylene polymerization just like **3a**/$CrCl_3(thf)_3$. It is noteworthy that **4b**/$CrCl_3(thf)_3$ displayed a high-catalytic activity of 540 kg PE/mol$_{Cr}$ · h for ethylene polymerization, which is higher than both the values of corresponding **2b**/$CrCl_3(thf)_3$ (106 kg PE/mol$_{Cr}$ · h) and **3b**/$CrCl_3(thf)_3$ (264 kg PE/mol$_{Cr}$ · h). The catalytic activity of **4b**/$CrCl_3(thf)_3$ was much higher than the value of corresponding *ortho-tert*-butyl phenoxy-amide chromium catalysts reported by Gibson and coworkers under the similar conditions, although it was still lower than the activity of the *ortho-anthracene* one.[12(b)] This result reveals that bulky thiophenol-phosphine is more effective ligand for chromium catalysts and both the soft sulfur and phosphorus donors in the ligand were essential for the high-catalytic activity. Based on the encouraging results of **3b** and **4b**, bisanionic ligands **5** and **6** (Scheme 3) were also prepared and tested via the *in-situ* catalyst polymerization. Compared with **3b**/$CrCl_3(thf)_3$ and **4b**/$CrCl_3(thf)_3$ systems, however, **5**/$CrCl_3(thf)_3$ and **6**/$CrCl_3(thf)_3$ only possessed low-catalytic activity as shown in Figure 1, which indicates that bisanionic [O, P=O, O] and [S, P, S] were not suitable ligands for efficient chromium catalysts.

Influence of Reaction Parameters on Ethylene Polymerization by 3b/$CrCl_3(thf)_3$ and 4b/$CrCl_3(thf)_3$ Systems

We focused on *in-situ* chromium catalytic systems **3b**/$CrCl_3(thf)_3$ and **4b**/$CrCl_3(thf)_3$, which displayed the highest catalytic activity for ethylene polymerization among the tested ones. Ethylene polymerization behaviors of **3b**/$CrCl_3(thf)_3$ and **4b**/$CrCl_3(thf)_3$ were investigated in detail and the typical results are summarized in Table 1. The effects of various cocatalysts on the ethylene polymerization were first studied. In addition to MMAO, diethyl aluminum chloride ($AlEt_2Cl$) and triethylaluminum (TEA) were also used as the cocatalyst. The catalytic activity was strongly influenced by the chosen cocatalysts. The systems activated with MMAO (entries 1–2) showed higher activities than the ones activated with $AlEt_2Cl$ (entries 3–4), whereas little ethylene consumption was observed and trace amount of polymer was obtained by the systems activated with TEA (entries 5–6).

The influence of reaction conditions such as Al/Cr molar ratio and reaction temperature on polymerization was further investigated in detail in the presence of MMAO. For the two systems, the increasing Al/Cr molar ratio resulted in a gradual increase of the catalyst activities, as shown in Figure 5, whereas the molecular weight of the resultant polyethylenes decreased with increasing cocatalyst dosage via chain transfer to aluminum (entries 1–2 and 7–10). The effects of reaction temperature on the catalytic activities were studied with an Al/Cr molar ratio of 2000/1 and the temperature dependence can be seen from Figure 6. The catalytic activity of **3b**/$CrCl_3(thf)_3$ decreased above room temperature, revealing that the catalyst active species decay at elevated temperature. Contrarily, **4b**/$CrCl_3(thf)_3$ displayed the promising temperature tolerance toward ethylene polymerization. The catalytic activity first increased with temperature and reached a maximum value at ~55 °C, and then gradually decreased,

TABLE 1 Ethylene Polymerization Results by **3b**/$CrCl_3(thf)_3$ and **4b**/$CrCl_3(thf)_3$[a]

Entry	Ligand	Cocatalyst	Al/Cr (molar ratio)	Temperature (°C)	P (atm)	Time (min)	Polymer Yield (g)	Activity[b]	M_w[c] (10^3)	M_w/M_n[c]	T_m[d] (°C)
1	**3b**	MMAO	2,000	25	1	10	0.22[e]	264	4.0	2.9	125
2	**4b**	MMAO	2,000	25	1	10	0.45	540	20.1	3.5	126
3	**3b**	$AlEt_2Cl$	2,000	25	1	10	0.04	48	6.3	5.6	125
4	**4b**	$AlEt_2Cl$	2,000	25	1	10	0.11	132	25.3	13.1	131
5	**3b**	TMA	2,000	25	1	10	Trace	–	–	–	–
6	**4b**	TMA	2,000	25	1	10	Trace	–	–	–	–
7	**3b**	MMAO	1,000	25	1	10	0.19	228	12.7	7.0	126
8	**4b**	MMAO	1,000	25	1	10	0.29	348	45.3	7.5	128
9	**3b**	MMAO	3,000	25	1	10	0.26	312	2.2	2.1	123
10	**4b**	MMAO	3,000	25	1	10	0.49	588	12.5	2.5	127
11	**3b**	MMAO	2,000	55	1	10	0.06	72	1.7	2.0	122
12	**4b**	MMAO	2,000	55	1	10	0.61	732	10.2	2.3	126
13	**4b**	MMAO	2,000	75	1	10	0.28	336	7.2	5.2	127
14	**3b**	MMAO	2,000	25	1	30	0.51	204	6.7	2.0	126
15	**4b**	MMAO	2,000	25	1	30	1.18	472	50.5	5.0	130
16[f]	**3b**	MMAO	2,000	25	10	30	2.13	426	8.6	1.9	127
17[f]	**4b**	MMAO	2,000	25	10	30	5.80	1,160	66.2	4.6	130

[a] Conditions: 5 μmol ligand, 5 μmol $CrCl_3(thf)_3$; $V_{total} = 50$ mL.
[b] Activity in kg PE/mol_{Cr}·h.
[c] GPC data in trichlorobenzene versus polystyrene standards.
[d] Melting temperature determined by DSC.
[e] 2.6 methyl branches per 1000 C, 1.7 vinyls per 1000 C.
[f] 10 μmol ligand, 10 μmol $CrCl_3(thf)_3$; $V_{total} = 100$ mL.

which indicates that ligand **4b** can restrain the chromium center from deactivation. The molecular weights of the resultant polymers decreased with the reaction temperature for the both systems (entries 11–13). Although the activities of the two catalytic systems decreased with prolonged reaction time (entries 14–15 vs. 1–2), the catalytic activity of **4b**/$CrCl_3(thf)_3$ for 30 min (472 kg PE/$mol_{Cr}\cdot$h) was still comparable with that for 10 min (540 kg PE/$mol_{Cr}\cdot$h), revealing that **4b**/$CrCl_3(thf)_3$ possess long lifetime for ethylene polymerization. Increasing the ethylene pressure can obviously enhance productivity (entries 16–17). Catalyst **4b**/$CrCl_3(thf)_3$ shows a higher catalytic activity of 1160 kg PE/$mol_{Cr}\cdot$h than **3b**/$CrCl_3(thf)_3$ (426 kg PE/$mol_{Cr}\cdot$h) at 10 atm ethylene pressure, which is similar to the results at atmosphere pressure.

All the polymers obtained have been analyzed by GPC. As shown in Table 1, the molecular weight of the resultant

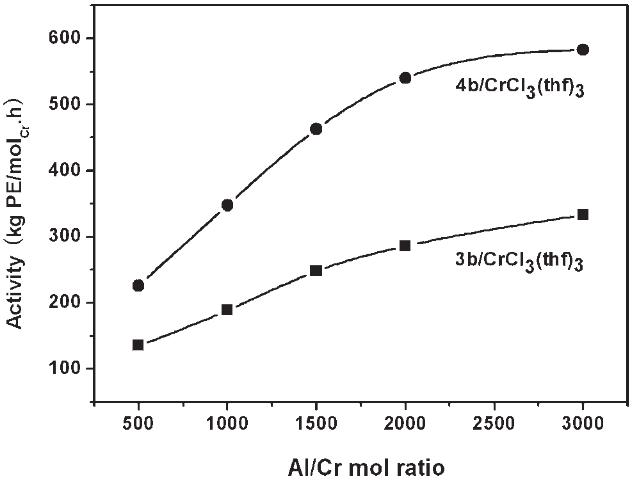


FIGURE 5 Plots of the activity of **3b**/$CrCl_3(thf)_3$ and **4b**/$CrCl_3(thf)_3$ versus Al/Cr molar ratio (5 μmol ligand, 5 μmol $CrCl_3(thf)_3$; 25 °C; 10 min; $V_{total} = 50$ mL; 1 atm ethylene pressure).

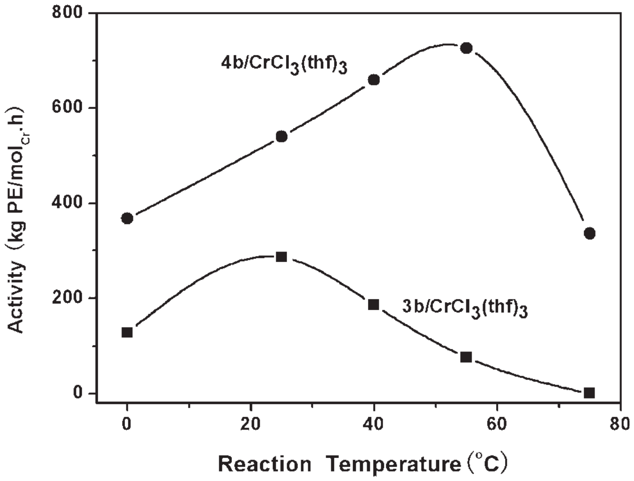


FIGURE 6 Plots of the activity of **3b**/$CrCl_3(thf)_3$ and **4b**/$CrCl_3(thf)_3$ versus the polymerization reaction temperature (5 μmol ligand, 5 μmol $CrCl_3(thf)_3$; Al/Cr = 2000/1; 10 min; $V_{total} = 50$ mL; 1 atm ethylene pressure).

polyethylenes obtained by **4b**/$CrCl_3(thf)_3$ were higher than the ones produced by **3b**/$CrCl_3(thf)_3$ under the same conditions. The results may be ascribed to the fact that soft donors [S, P] chelate **4b** could stabilize the chromium complex and diminish the rate of chain termination compared with the hard donors [O, P=O] chelate **3b**. On examination of the GPC data, most of the traces showed unimodal behavior and some of them displayed bimodal or even polymodal behavior. The melting temperatures (T_ms) of the resulting polyethylene were determined by DSC. For different catalyst systems and various reaction conditions, the T_ms of the polymers range between 122 and 131 °C, which are higher than the values obtained by tridentate amino-pyrrolide chromium catalysts (112–118 °C).[18(b)] The typical polyethylenes obtained by **3b**/$CrCl_3(thf)_3$ (entry 1) and **4b**/$CrCl_3(thf)_3$ (entry 2) have been further characterized by high temperature ^{13}C NMR spectra. Three kinds of terminal groups: methyl, vinyl, and isopropyl were detected for the polyethylene obtained by **3b**/$CrCl_3(thf)_3$, while only methyl terminal group was found in the polyethylene produced with **4b**/$CrCl_3(thf)_3$.[24] As we know, the methyl and isopropyl end groups expresses the occurrence of chain transfer to aluminum. The vinyl end group shows β-hydrogen elimination or β-hydrogen transfer to the monomer. The apparent nondependence of molecular weight of the polyethylene obtained by **3b**/$CrCl_3(thf)_3$ on ethylene pressure (entry 16 vs. 14) is a strong indication for chain transfer by β-hydrogen transfer to the monomer rather than to the metal.[18(b),25] In contrast to the case of **3b**/$CrCl_3(thf)_3$, it is difficult to observe the vinyl end group for the polyethylene produced with **4b**/$CrCl_3(thf)_3$ probably due to less β-hydrogen elimination or β-hydrogen transfer reaction.

CONCLUSIONS

Novel bidentate phenoxy-phosphinoyl [O, P=O] and thiophenol-phosphine [S, P] have been synthesized, and found to be effective ligands of the chromium catalysts for ethylene polymerization. The chromium catalysts based on bidentate [O, P=O] and [S, P] ligands displayed higher activities than those based on corresponding bidentate [O, P] ligands. Both the coordinated donor and the *ortho*-substituent in the ligand considerably affect catalytic activity for ethylene polymerization. Catalytic activities of **3b**/$CrCl_3(thf)_3$ and **4b**/$CrCl_3(thf)_3$ systems and the molecular weights of the polyethylene obtained are also considerably influenced by the reaction parameters such as cocatalyst, Al/Cr molar ratio and polymerization temperature. Catalyst **4b**/$CrCl_3(thf)_3$ displayed higher catalytic activity and better temperature tolerance for ethylene polymerization than **3b**/$CrCl_3(thf)_3$. For **3b**/$CrCl_3(thf)_3$, chain transfer to the aluminum and β-hydrogen transfer to the monomer occurred during the polymerization, whereas the chain transfer to aluminum is the dominating chain transfer way for **4b**/$CrCl_3(thf)_3$. To our best knowledge, **4b**/$CrCl_3(thf)_3$ is the first example of chromium catalyst system, which is based on the ligand containing both the soft sulfur and phosphorous donors.

The crystal date and structure refinement of complexes **A**–**C**; ^{13}C NMR spectra and GPC traces of the typical polyethylene samples are obtained. This material is available in the Supporting Information.

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