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New *o*-methoxyphenylcyclopentadienylchromium (III) complexes: Synthesis, structures and catalytic properties for ethylene polymerization

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Abstract

Two new ligands 1-(2-methoxyphenyl)-3,4-diphenylcyclopentadiene (**1**) and 1-(2-methoxyphenyl)-2,3,4,5-tetramethylcyclopentadiene (**2**), as well as their corresponding cyclopentadienylchromium complexes η^5-1-(2-methoxyphenyl)-3,4-diphenylcyclopentadienyl chromium dichloride (**3**) and η^5-1-(2-methoxyphenyl)-2,3,4,5-tetramethylcyclopentadienyl chromium dichloride (**4**) were synthesized and characterized. Molecular structures of **3** and **4** were determined by single-crystal X-ray diffraction. Complexes **3** and **4** were tested as catalyst precursors for ethylene polymerization. When activated with $Al(^iBu)_3$ and $Ph_3C^+B(C_6F_5)_4^-$, complex **3** shows reasonable catalytic activity while **4** exhibits high catalytic activity for ethylene polymerization. The effects of temperature and Al/Cr ratio on the catalytic activity were studied. The molecular weight and melting temperature of the produced polyethylenes were determined.

Keywords: Cyclopentadienyl ligands; Chromium complexes; Metallocenes; Ethylene polymerization

1. Introduction

Chromium-based catalysts play a significant role in the coordination polymerization of olefins. It is well known that the chromium-based heterogeneous catalysts such as the Phillips catalyst [1] and the Union Carbide Unipol catalyst [2] are among the most important catalysts for the production of high-density polyethylene (HDPE) and have been put to widespread commercial use. However, the chromium catalyst systems were largely ignored for long time in the development of the homogeneous olefin polymerization catalyst systems that have attracted so much attention in the past decade [3]. It is mainly due to the difficulty of studying the chemistry of Cr (III) as a result of its paramagnetic nature. Recently, some of the most significant advances in Cp-based chromium catalyst systems have been made with the catalysts that bear an additional neutral nitrogen donor, either bridged or unbridged to the Cp unit [4]. Several efficient catalyst precursors for ethylene polymerization are listed in Chart 1. Jolly et al. [5–7] reported that half-sandwich type chromium complexes (**a**) shows good activity for the polymerization of ethylene to give polyethylenes with high molecular weights. Enders et al. [8,9] described cyclopentadienylchromium(III) complexes (**b** and **c**) functionalized by quinolinyl or *N*,*N*-dimethylanilinyl group exhibit high catalytic activity for ethylene polymerization. Most recently, Huang et al. [10] reported the bridged cyclopentadienylchromium complexes (**d**) as effective ethylene polymerization catalysts. So far, the functionalized cyclopentadienylchromium catalysts are mainly limited to the nitrogen donor substituted compounds. Reports concerning oxygen donor substituted cyclopentadienyl chromium catalysts are scarce. Previously, we demonstrated that phenoxy substituted cyclopentadienyl titanium complexes (**e** and **f** in Chart 2) are good catalysts for ethylene polymerization [11,12]. In this paper, we report the synthesis and characterization

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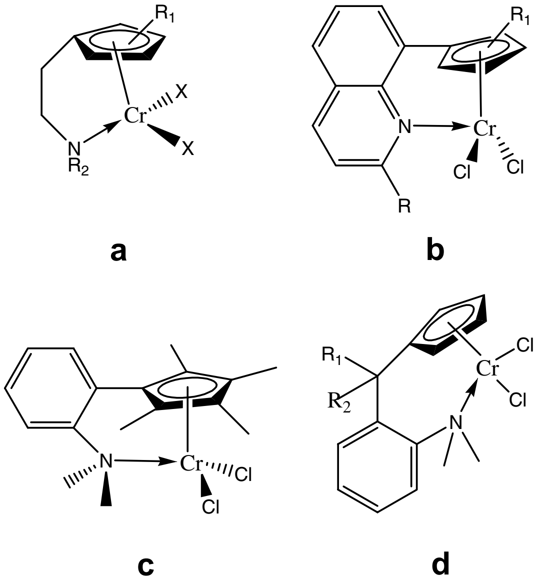
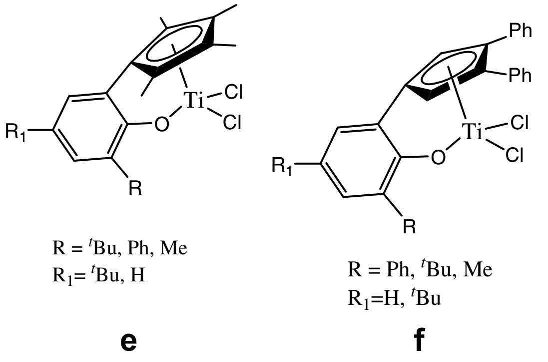


Chart 1.



R = ^{t}Bu, Ph, Me
R$_1$= ^{t}Bu, H

R = Ph, ^{t}Bu, Me
R$_1$=H, ^{t}Bu

Chart 2

of two oxygen donor substituted cyclopentadiene ligands 1-(2-methoxyphenyl)-3,4-diphenylcyclopentadiene (**1**) and 1-(2-methoxyphenyl)-2,3,4,5-tetramethylcyclopentadiene (**2**), and their chromium complexes η^5-1-(2-methoxyphenyl)-3,4-diphenylcyclopentadienylchromium dichloride (**3**) and η^5-1-(2-methoxyphenyl)-2,3,4,5-tetramethylcyclopentadienylchromium dichloride (**4**), as well as the catalytic performance of complexes **3** and **4** for ethylene polymerization.

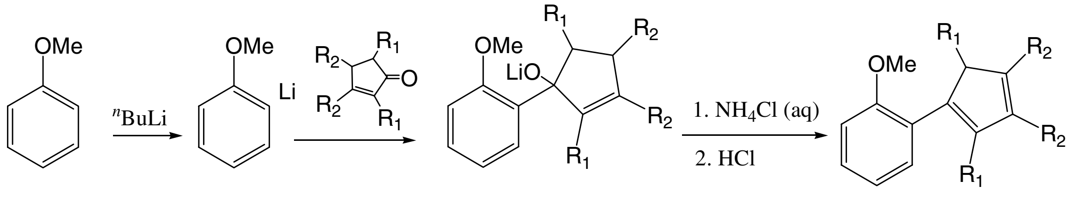
2. Results and discussion

2.1. Synthesis of ligands

Ligand **1** was prepared by the reaction of 3, 4-diphenyl-2-cyclopentenone with lithium salt of anisole in toluene at room temperature followed by hydrolysis and dehydration (Scheme 1). The lithium salt of anisole was obtained by the reaction of anisole with *n*-BuLi without solvent at 80 °C. The lithium salt of anisole could not be obtained when the reaction was carried out in the presence of a solvent such as Et_2O or THF. Ligand **2** was synthesized by the same procedure with 2,3,4,5-tetramethyl-2- cyclopentenone as starting material. Ligands **1** and **2** can also be synthesized in Et_2O or THF in similar yields. **1** and **2** were characterized by elemental analysis and ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR spectroscopic analysis indicates that **2** exists as a mixture of three isomers. Similar behavior has been observed before for the *N*,*N*-dimethylaminophenyl-tetramethylcyclopentadiene ligand system [9] and the tetramethylcyclopentadienylphenol ligand system [12]. The same phenomenon was not found for ligand **1** which exists as one isomer.

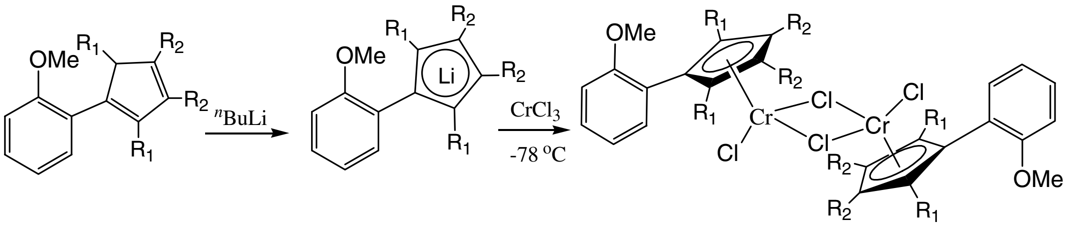
2.2. Synthesis of complexes 3 and 4

Complexes **3** and **4** were synthesized via a straightforward procedure (Scheme 2) from the reaction of $CrCl_3$ with the lithium salt of corresponding ligand. Ligand **1** or **2** was treated with one equivalent of *n*-BuLi, and then a solution of $CrCl_3$ in THF was slowly added at −78 °C. After filtration and concentration of the reaction mixture, complex **3** or **4** was obtained as a green or blue crystalline solid in a moderate yield. The reaction was also tried in toluene and it was found that complexes **3** and **4** could not be obtained for the low solubility of $CrCl_3$ in toluene. Complexes **3** and **4** were found to be air and moisture sensitive in solution, but they are considerably stable in the solid state and could be exposed to air for several days without obvious decomposition. Due to paramagnetic nature, NMR study for complexes **3** and **4** was not feasible. Elemental analysis of complexes **3** and **4** fits their respective structures obtained by X-ray crystallographic study.



R$_1$ = H, R$_2$ = Ph (**1**)
R$_1$ = R$_2$ = Me (**2**)

Scheme 1. Synthetic procedure of ligands **1** and **2**.



R_1 = H, R_2 = Ph (**3**)
$R_1 = R_2$ = Me (**4**)

Scheme 2. Synthetic procedure of complexes **3** and **4**.

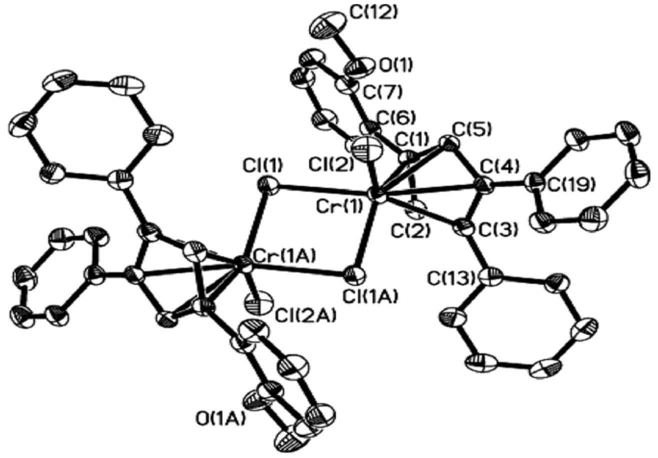


Fig. 1. Structure of complex **3** (thermal ellipsoids are drawn at the 30% probability level).

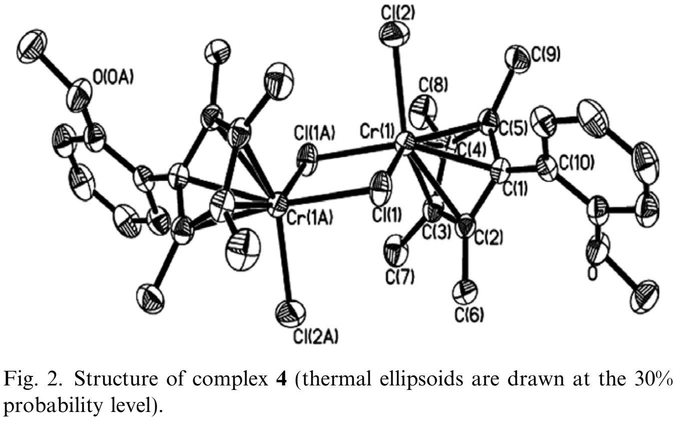


Fig. 2. Structure of complex **4** (thermal ellipsoids are drawn at the 30% probability level).

Table 1
Selected bond lengths and angles

Complex 3			
Cr(1)–C(1)	2.259(3)	Cl(2)–Cr(1)–Cl(1)	95.17(5)
Cr(1)–C(2)	2.238(3)	Cp(cent)–Cr(1)–Cl(1)	120.9
Cr(1)–C(3)	2.304(4)	Cp(cent)–Cr(1)–Cl(2)	124.2
Cr(1)–C(4)	2.230(3)	Cr(1)–Cp(cent)–C(1)	90.3
Cr(1)–C(5)	2.202(3)	Cr(1)–Cp(cent)–C(2)	90.1
Cr(1)–Cl(1)	2.3680(12)	Cr(1)–Cp(cent)–C(3)	92.7
Cr(1)–Cl(2)	2.2795(13)	Cr(1)–Cp(cent)–C(4)	88.9
Cr(1)–Cl(1A)	2.3582(10)	Cr(1)–Cp(cent)–C(5)	87.9
Cr(1)–Cp(cent)	1.893	Cr(1)–Cl(1)–Cr(1A)	88.99(4)
C(1)–C(6)	1.467(5)	Cl(1)–Cr(1)–Cl(1A)	91.01(4)
Complex 4			
Cr(1)–C(1)	2.228(3)	Cl(1)–Cr(1)–Cl(2)	96.25(5)
Cr(1)–C(2)	2.243(3)	Cp(cent)–Cr(1)–Cl(1)	123.4
Cr(1)–C(3)	2.237(3)	Cp(cent)–Cr(1)–Cl(2)	122.4
Cr(1)–C(4)	2.205(4)	Cr(1)–Cp(cent)–C(1)	89.7
Cr(1)–C(5)	2.245(3)	Cr(1)–Cp(cent)–C(2)	90.7
Cr(1)–Cl(1)	2.3716(11)	Cr(1)–Cp(cent)–C(3)	90.5
Cr(1)–Cl(2)	2.2808(12)	Cr(1)–Cp(cent)–C(4)	88.7
Cr(1)–Cl(1A)	2.3736(10)	Cr(1)–Cp(cent)–C(5)	90.4
Cr–Cp(cent)	1.875	Cr(1)–Cl(1)–Cr(1A)	90.74(3)
C(1)–C(10)	1.490(4)	Cl(1)–Cr(1)–Cl(1A)	89.26(3)

2.3. Crystal structures of 3 and 4

The molecular structures of complexes **3** and **4** were determined by X-ray crystal structure analysis. The ORTEP drawings of the molecular structures are shown in Figs. 1 and 2, respectively. The selected bond lengths and angles are summarized in Table 1. There is a CH_2Cl_2 molecule in the unit cells of both complexes **3** and **4**. One more thing that should be mentioned is that the Cl atoms of the CH_2Cl_2 molecule in the unit cell of complex **4** are disordered. Both complexes **3** and **4** (Figs. 1 and 2) exist in dimeric form connected through two chloride bridges in the solid state, and the two molecular units comprising the dimer are each constrained by a crystallographic center of inversion. Each chromium atom is bonded to one Cp ligand, one terminal chloride atom and two bridging chloride atoms, completing the familiar pseudo-octahedral coordination environment of a three-legged piano stool. Bond distances from each chromium atom to the non-equivalent bridging chlorides for **3** (2.3680 Å, 2.3582 Å) and **4** (2.3716 Å, 2.3736 Å) are elongated from the Cr–Cl (terminal) distances of **3** (2.2795 Å) and **4** (2.2808 Å), respectively. The Cr–Cl(bridging)–Cr and Cl(bridging)–Cr–Cl(bridging) angles for **3** and **4** are 88.99°, 91.01° and 90.74°, 89.26°, respectively. The two chromium atoms and two bridging chlorides are coplanar and the mean deviations from the planes are 0 Å for both complexes. The Cr–Cp(cent) distances are 1.893 Å for **3** and 1.875 Å for **4**. The Cr–C(ring) distances are in the range 2.202–2.304 Å for **3** and 2.205–2.245 Å for **4**. The angle (57.3°) between the Cp ring plane and the phenyl ring plane in

Table 2
Summary of ethylene polymerization catalyzed by complex **3** and **4** (activated by Al(^{i}Bu)$_3$ and Ph$_3$C$^+$[B(C$_6$F$_5$)$_4$]$^-$)[a]

No.	Cata.	Al:Cr	T (°C)	Yield (g)	Activity [b]	Mη[c] × 10^{-4}	T_m (°C)[d]
1	**3**	300	100	0.22	0.04	8.09	127.9
2	**3**	300	80	0.63	0.13	11.64	126.3
3	**3**	300	60	0.34	0.07	10.83	126.7
4	**3**	200	80	0.28	0.06	9.52	125.9
5	**3**	400	80	0.37	0.07	10.17	127.4
6	**4**	300	100	6.04	1.21	6.13	125.2
7	**4**	300	80	6.86	1.37	6.03	126.0
8	**4**	300	60	2.58	0.52	7.01	125.4
9	**4**	200	80	4.28	0.86	8.41	124.7
10	**4**	400	80	2.45	0.49	7.46	125.3

[a] Polymerization conditions: solvent 50 mL of toluene, catalyst 1 μmol (2 μmol Cr), B/Cr ratio 1.5, time 30 min, ethylene pressure 5 bar.
[b] 10^3 kg PE/ mol Cr h bar.
[c] Measured in decahydro-naphthalene at 135 °C.
[d] Determined by DSC at a heating rate of 10 °C min^{-1}.

complex **4** is larger than that (26.6°) in **3**, which should be attributed to the repulsion of the Me groups on the Cp ring in complex **4**.

2.4. Ethylene polymerization studies

Complexes **3** and **4** were studied as ethylene polymerization catalysts and the results are summarized in Table 2. Upon activation with Al(^{i}Bu)$_3$ and Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$, complex **3** shows reasonable catalytic activity while **4** exhibits high catalytic activity for ethylene polymerization, producing polyethylene with moderate molecular weight and melting temperature. No oligomer was obtained from the polymerization solution for both catalysts. The catalytic activity of **3** and **4** and the molecular weight of the obtained polyethylene are much higher than those reported for simple cyclopentadienylchromium-based catalyst systems [13,14] and more similar to the results obtained from constrained geometry cyclopentadienylchromium catalyst systems [8,9]. These results imply that the catalytic active species formed from complexes **3** and **4** during the polymerization reaction might have similar structures to that formed from complex **c** in Chart 1, and the oxygen atom in the catalytic active species might coordinate to the chromium atom. A similar mononuclear cyclopentadienylchromium complex with a coordinated ether side-chain has been reported before [6]. However, our attempts to obtain the crystal structure of the catalytic active species or to get IR spectroscopic evidence to verify the structure of the catalytic active species were unsuccessful. On the basis of common knowledge about the olefin polymerization mechanism and the relationship between catalyst structure and property, it could be known that the coordination of the oxygen atom to the chromium atom would increase the stability of the chromium cation and weaken the interaction between the cationic chromium center and the anionic cocatalyst, therefore increase the catalytic activity of the catalyst. In addition, the coordination of the oxygen atom to the chromium atom would also lower the rate of the chain termination by β-H elimination, and hence increase the molecular weight of the produced polyethylene. If it was not the case, the electron-withdrawing methoxyphenyl group on the cyclopentadienyl ring would lower the catalytic activity of the catalysts, and the catalytic activity of **4** should be lower than that of simple pentametnylcyclopentadienylchromium-based catalysts. It is expected that complex **4** shows higher catalytic activity than **3** since the four electron-donating Me groups on the Cp ring of **4** would increase its catalytic activity [12]. The catalytic activity of complexes **3** and **4** is low at room temperature and increases at elevated temperatures. For both complexes, the catalytic activity increases with the increase in Al/Cr ratio and reaches the highest catalytic activity with the Al/Cr ratio of 300. Further increase in the Al/Cr ratio results in a decrease in the catalytic activity. It is possible that excessive Al(^{i}Bu)$_3$ would consume some of Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$, which results in that the catalyst could not be efficiently activated [15]. It is also worth noting that the less active catalyst **3** gives higher molecular weight polyethylene, which could be explained by that the slow chain propagation in **3** will ensure to have sufficient monomer to coordinate to the catalyst metal center and thus suppress the chain termination through β-H elimination [11].

3. Experimental

3.1. General comments

Reactions with organometallic reagents were carried out under argon atmosphere (ultra-high purity) using standard schlenk techniques [16]. Solvents were dried and distilled prior to use [17]. Polymerization grade ethylene was further purified by passage through columns of 10 A molecular sieves and MnO. Al(^{i}Bu)$_3$, *n*-BuLi and CrCl$_3$ were purchased from Aldrich. 2,3,4,5-tetramethyl-2-cyclopentenone [18], 3,4-diphenyl-2-cyclopentenone [19], and

$Ph_3C^+B^-(C_6F_5)_4$ [20] were prepared according to literature procedures. NMR spectra were measured using a Varian Mercury-300 NMR spectrometer.

*3.2. Synthesis of 1-(2-methoxyphenyl)-3,4-diphenylcyclopentadiene (**1**)*

8.3 mL of anisole (76 mmol) was slowly added to 76 mmol of pure *n*-BuLi and the mixture was heated to 80 °C for 48 h to form the lithium salt of anisole. The lithium salt was washed with *n*-hexane and dissolved in toluene (100 mL). To the solution 3,4-diphenyl-2-cyclopentenone (17.8 g, 76 mmol) was added at −15 °C and the mixture was stirred at room temperature overnight. The reaction mixture was hydrolyzed with 100 mL of H_2O and then acidified with 20 mL of concentrated HCl. The organic layer was separated, dried over $MgSO_4$, filtered and concentrated by distillation under reduced pressure. Pure product (13.8 g, 53.4%) was obtained by column chromatography over silica (hexanes/CH_2Cl_2, 3:2) as yellowish crystalline solid. Anal. Calcd for $C_{24}H_{20}O$ (324.415): C, 88.77, H, 6.16. Found: C, 88.72, H, 6.22%. ^1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 6.95–7.56 (m, 15H, Cp, Ph), 3.93 (s, 3H, OMe), 4.06 (s, 2H, Cp), ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 157.26, 142.57, 141.97, 139.17, 137.78, 137.26, 136.07, 128.75, 128.67, 128.46, 128.13, 128.06, 128.02, 127.24, 126.59, 125.10, 120.95, 111.42, 55.51, 47.26.

*3.3. Synthesis of 1-(2-methoxyphenyl)-2,3,4,5-tetramethylcyclopentadiene (**2**)*

Ligand **2** was prepared in the same manner as **1** with 76 mmol of 2,3,4,5-tetramethyl-2-cyclopentenone as starting material. Pure product (7.9 g, 45.6%) was obtained as yellow oil. Anal. Calcd for $C_{16}H_{20}O$ (228.329): C, 84.16, H, 8.83. Found: C, 84.07, H, 8.91%. ^1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.25 (m, 4H, Ph), 3.79 (s, 3H, OCH_3), 3.40 (q, 1H, CpH), 1.91 (s, 3H, C_5Me_4), 1.86 (s, 6H, C_5Me_4), 0.88 (d, 3H, C_5Me_4), ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 157.26, 140.86, 140.31, 138.06, 134.54, 131.35, 127.35, 126.60, 120.17, 110.72, 55.39, 50.09, 14.29, 12.84, 12.01, 11.27.

*3.4. Synthesis of η^5-1-(2-methoxyphenyl)-3,4-diphenylcyclopentadienyl chromium dichloride dimer (**3**)*

To a solution of 0.37 g (1.1 mmol) of **1** in 15 mL of THF was added dropwise a solution of *n*-BuLi (1.1 mL, 1.0 M) in *n*-hexane at −78 °C. After the addition the reaction mixture was stirred for 12 h at room temperature. Then the resulting solution was added to a suspension of $CrCl_3$ (0.17 g, 1.1 mmol) in 45 mL of THF at room temperature and the mixture was stirred for 12 h. The color of the reaction mixture turned from purple to blue during the reaction. The precipitate was filtered off and the solvent was removed to leave a blue solid. Recrystallization from CH_2Cl_2/Hexane (1:2) gave pure **3** as green crystals (0.24 g, 50.5%). Anal. Calcd for $(C_{24}H_{19}Cl_2CrO)_2$ (892.44): C, 64.59, H, 4.29. Found: C, 64.48, H, 4.22%.

*3.5. Synthesis of η^5-1-(2-methoxyphenyl)-2,3,4,5-tetramethylcyclopentadienyl chromium dichloride dimer (**4**)*

Reaction of the lithium salt of **2** (0.35 g, 1.53 mmol) with $CrCl_3$ (0.24 g, 1.53 mmol) in THF (40 mL) was carried out in the same way as described above for the synthesis of **3**. Pure **4** (0.18 g, 35.1%) was obtained as blue crystals. Anal. Calcd for $(C_{16}H_{19}Cl_2CrO)_2$ (700.45): C, 54.87, H, 5.47. Found: C, 54.78, H, 5.29%.

*3.6. X-ray structure determinations of **3** and **4***

Single crystals of **3** and **4** suitable for X-ray structural analysis were obtained from solutions in mixed CH_2Cl_2/hexane (V/V = 1/2). Data were collected at 293(K) on the Bruker SMART-CCD diffractometer (graphite-monochromated MoKα-radiation: $\lambda = 0.71073$ Å). Details of the crystal data, data collections, and structure refinements are summarized in Table 3. Both structures were solved by direct methods [21] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in idealized position. All calculations were performed using the SHELXTL [22] crystallographic software packages.

Table 3
Crystal data and structural refinements details for **3** and **4**

	3	**4**
Molecular formula	$C_{25}H_{21}Cl_4CrO$	$C_{17}H_{21}Cl_4CrO$
Molecular weight	531.22	435.14
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.677(2)	8.3829(17)
b (Å)	10.795(2)	8.6849(18)
c (Å)	11.182(2)	14.439(3)
α (°)	79.04(3)	75.313(3)
β (°)	78.94(3)	82.170(3)
γ (°)	72.25(3)	83.892(4)
V (Å^3)	1192.7(4)	1004.5(4)
Z	2	2
D_c (g cm^{-3})	1.479	1.439
$F(000)$	542	446
Abs coefficient (mm^{-1})	0.943	1.102
Scan type	$\omega - 2\theta$	$\omega - 2\theta$
Collect range (deg)	$3.22 \leqslant 2\theta \leqslant 27.49$	$2.43 \leqslant 2\theta \leqslant 28.26$
Number of reflections	7940	6339
Number of independent reflections	4722	4481
R_{int}	0.0318	0.0348
Number of data/restraints/parameters	4772/12/304	4481/0/213
$R(I > 2sigma(I))$	0.0486	0.0579
$R_w(I > 2sigma(I))$	0.1495	0.1642
Goodness of fit	1.068	1.012
Largest difference in peak and hole (e Å^{-3})	0.459 and −0.659	0.897 and −0.523

3.7. Polymerization reactions

A dry 250 mL steel autoclave was charged with 50 mL of toluene, thermostated at desired temperature and saturated with ethylene (1.0 bar). The polymerization reaction was started by injection of a mixture of catalyst and $Al(^iBu)_3$ in toluene (5 mL) and a solution of $Ph_3C^+B(C_6F_5)_4^-$ in toluene (5 mL) at the same time. The vessel was repressurized to needed pressure with ethylene immediately and the pressure was kept by continuously feeding monomer. After 30 min, the polymerization was quenched by injecting acidified methanol [HCl (3 M):methanol = 1:1]. The polymer was collected by filtration, washed with water, methanol, and dried in vacuo at 60 °C to a constant weight.

Acknowledgement

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Appendix A. Supplementary material

CCDC 292293 and 292292 contains the supplementary crystallographic data for **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.04.044.

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