Synthesis and Characterization of Nitrogen-Functionalized Cyclopentadienylchromium Complexes and Their Use as Catalysts for Olefin Polymerization

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A series of nitrogen-functionalized cyclopentadienylchromium complexes (**1**−**9**) have been synthesized, characterized, and then tested as catalyst precursors for olefin polymerization. The structures of complexes **1** and **5** show the nitrogen atom coordinated to the chromium atom, which is confirmed by X-ray crystallography. In the presence of MAO, the complexes exhibited high catalytic activities for the homopolymerization of ethylene and its copolymerization with 1-hexene. It also turned out that both the activity of ethylene polymerization and the incorporation of 1-hexene into the copolymer were highly affected by the substituents on the cyclopentadienyl fragment and bridge group. The effects of temperature variation and Al/Cr ratio on catalytic activity were also studied.

Introduction

Olefin polymerization catalyzed by homogeneous transition metal complexes attracts particular attention in the fields of organometallic chemistry, catalysis, and polymer chemistry. Many reports have been published concerning this topic using various transition metal complexes.[1] Chromium catalysts played a key role in the early development of heterogeneous catalysts for the polymerization of alkenes. It is well known that the chromium-based heterogeneous catalysts such as the Phillips catalyst (Cr_2O_3/SiO_2)[2] and the Union Carbide Unipol catalyst (Cp_2Cr/SiO_2)[3] have been used for the industrial production of high-density polyethylene (HDPE) since the 1950s. In contrast to the Ziegler−Natta system, there are only limited reports in the literature concerning the mechanism and nature of the active species in these chromium catalytic systems. The reason is attributed 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 using precatalysts that bear an additional neutral donor, either bridged or unbridged to the Cp unit.[4−17] There are several examples (**a**−**h**) that have already been used as efficient catalyst precursors for ethylene homo(co)-polymerization, which are listed in Chart 1. Jolly et al.[5−7] reported that half-sandwich type chromium complexes showed excellent activity for the polymerization of ethylene (1.6×10^6 g PE/(mol Cr·h)) to give the polyethylene with narrow molecular weight distributions and high molecular weight. In addition, Ender et al.[8] described cyclopentadienylchromium(III) complexes functionalized by quinoline or *N*,*N*-dimethylaniline for the polymerization of ethylene. Most recently, Yasuda[9] reported the effective polymerization of ethylene and its copolymerization with higher α-olefins using amino-substituted cyclopentadienylchromium complexes. These results revealed that nitrogen donor ligand-substituted cyclopentadienylchromium compounds effectively polymerize olefins. However, reports concerning ligand effects in olefin homo(co)polymerization are scarce.

Previously, our group[18−20] demonstrated that C(R_1)-(R_2)-*o*-PhOMe-substituted Cp(Ind) ligands react with

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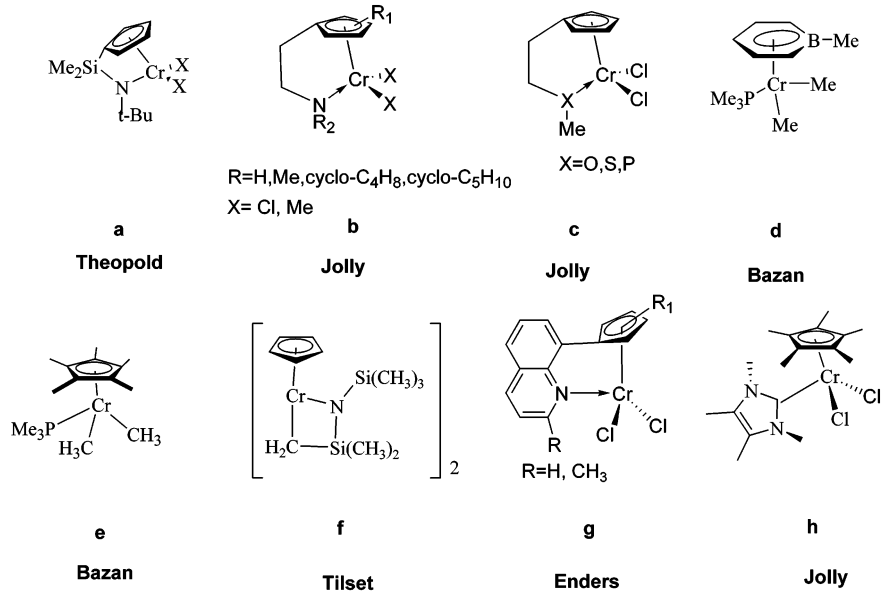
Chart 1



$ZrCl_4$, resulting in a series of novel zirconium complexes. Later, we also reported the reaction of $C(CH_3)_2$-*o*-$PhNMe_2$-substituted Cp ligand with $CrCl_3(THF)_3$, affording a new chromium complex for ethylene polymerization catalyst.[21]

Here we wish to introduce our research results concerning the synthesis of various novel pyridyl- and $C(R_1)(R_2)$-*o*-$PhNMe_2$-substituted cyclopentadienyl chromium complexes and the effect of the cyclopentadienyl fragment and also the bridge fragment on olefin polymerization.

Experimental Details

1. Synthesis of Complexes 1−9. All operations involving air- or moisture-sensitive compounds were carried out under an argon atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF), diethyl ether, toluene, and *n*-hexane were freshly distilled from sodium/benzophenone ketyl under argon prior to use. Methylene chloride was distilled over P_2O_5 under nitrogen. Ethylene for polymerization was used after passing it through phosphorus pentoxide (P_2O_5) powder and KOH pellets. 1-Hexene was distilled over sodium under nitrogen and stored in the prence of activated 4 Å molecular sieves. Methylaluminoxane (MAO) was purchased from Witco.

IR spectra were recorded on a Nicolet MAGNA-IR 550 spectrometer as KBr pellets. ^1H NMR spectra were recorded on a Bruker AVANCE DMX 500 spectrometer in $CDCl_3$. Mass spectra were obtained using the direct insertion probe method on a HP 5989A or Micromass GCT instrument operating at 70 eV. Elemental analyses were performed on an EA-1106.

Synthesis of Complex 1. Ligand **1a** was prepared according to the literature.[22]

To a solution of 1.31 g (6.58 mmol) of ligand **1a** in 20 mL of THF in the flask was added dropwise a solution of butyllithium 5.39 mL (1.22 mol/L, 6.58 mmol) in THF at −78 °C. After complete addition the reaction mixture was stirred for 12 h. The resulting solution was then added to a suspension of $CrCl_3(THF)_3$ (2.47 g, 6.58 mmol) in 45 mL of THF at −78 °C and the mixture stirred overnight. The color of the reaction mixture changed from purple to deep blue. After the solvent was removed under vacuum, toluene was added to precipitate the LiCl, and the organic layer was concentrated to 30 mL. At −30 °C, 0.31 g of dark blue needle crystals were obtained in 24% yield. The sample for X-ray crystallography was further recrystallized from CH_2Cl_2. EI-MS (*m/e*): 320 (100, M), 285 (94, M − Cl), 249 (94, M − 2Cl), 198 (47, M − 2Cl − Cr). IR (cm^{-1}, KBr): 3096m, 3076s, 2969s, 2954m, 2924m, 2872s, 1605s, 1564m, 1486s, 1445s, 1406m, 1385m, 1367m, 1287m, 1164m, 1065m, 1041m, 845s, 832s, 763s. Anal. Calcd for $C_{14}H_{16}Cl_2CrN$: C, 52.35; H, 5.02; N, 4.36. Found: C, 51.95; H, 5.14; N, 4.01. HRMS calcd for $C_{14}H_{16}Cl_2CrN$, 320.0065; found, 320.0065.

Synthesis of Complex 2. Ligand **2a** was prepared according to the literature.[22]

Synthetic procedure for **2** was the same as that for **1**, except that ligand **2a** (0.91 g, 4.27 mmol) was used in place of ligand **1a** (butyllithium 3.50 mL, 4.27 mmol; $CrCl_3(THF)_3$ 1.61 g, 4.30 mmol; THF 70 mL). At −30 °C, 0.34 g of dark blue needle crystals were obtained in 24% yield. EI-MS (*m/e*): 334 (67, M), 299 (43, M − Cl), 264 (56, M − 2Cl), 212 (32, M − 2Cl − Cr). IR (cm^{-1}, KBr): 3089s, 2960s, 2922m, 2873m, 1661w, 1562w, 1474s, 1454s, 1429s, 1380s, 1347m, 1295m, 1261m, 1231w, 1153m, 1098s, 1039s, 1018s, 928w, 888w, 826s, 779s, 692m. Anal. Calcd for $C_{15}H_{18}Cl_2CrN$: C, 53.75; H, 5.41; N, 4.18. Found: C, 53.25; H, 5.36; N, 3.90.

Synthesis of Complex 3. Ligand **3a** was prepared according to the literature.[22]

Synthetic procedure for **3** was the same as that for **1**, except that ligand **3a** (0.86 g, 3.84 mmol) was used in place of ligand **1a** (butyllithium 3.14 mL, 3.84 mmol; $CrCl_3(THF)_3$ 1.44 g, 3.84 mmol; THF 70 mL). At −30 °C, 0.17 g of dark blue needle crystals were obtained in 13% yield. EI-MS (*m/e*): 346 (55, M), 311 (52, M − Cl), 276 (100, M − 2Cl), 224 (31, M − 2Cl − Cr). IR (cm^{-1}, KBr): 3118w, 3084s, 2946s, 2867s, 1602s, 1478s, 1444s, 1427s, 1403m, 1338m, 1301m, 1268w, 1229w, 1107w, 1066m, 1022m, 852s, 822s, 769s, 667m, 646m, 520m, 428m. Anal. Calcd for $C_{16}H_{18}Cl_2CrN$: C, 55.35; H, 5.23; N, 4.03. Found: C, 54.90; H, 5.01; N, 3.71.

Synthesis of Complex 4. Ligand **4a** was prepared according to the literature.[22]

Synthetic procedure for **4** was the same as that for **1**, except that ligand **4a** (1.31 g, 5.48 mmol) was used in place of ligand

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1a (butyllithium 4.49 mL, 5.48 mmol; $CrCl_3(THF)_3$ 2.05 g, 5.48 mmol; THF 70 mL). At −30 °C, 0.42 g of dark blue needle crystals were obtained in 21% yield. EI-MS (*m/e*): 360 (50, M), 325 (34, M − Cl), 288 (100, M − 2Cl), 238 (14, M − 2Cl − Cr). IR (cm^{-1}, KBr): 3449m, 3112w, 3084s, 3073s, 2949s, 2926s, 2857s, 1603s, 1564m, 1477s, 1461s, 1443s, 1406w, 1340w, 1301w, 1266w, 1226w, 1166w, 1106w, 1069w, 1020m, 907w, 853s, 826s, 769s, 692w, 645w, 508w, 447w, 432w, 409w. Anal. Calcd for $C_{17}H_{20}Cl_2CrN$: C, 56.52; H, 5.58; N, 3.88. Found: C, 55.93; H, 5.59; N, 3.82.

Synthesis of Complex 5. The novel ligand **5a** was prepared by the following procedure. A solution of 6,6′-dimethylbenzofulvene (7.84 g, 50.7 mmol) in 50 mL of Et_2O was added to the solution of 2-methylpyridine lithium in Et_2O, which was prepared from 2-methylpyridine (4.72 g, 50.7 mmol) in 100 mL of *n*-hexane and n-BuLi (41.5 mL, 50.7 mmol) in *n*-hexane. The mixture was stirred overnight and hydrolyzed. After workup, **5a** was obtained as pale orange crystals, yield = 76% (8.7 g). ^1H NMR (δ, ppm, $CDCl_3$): 8.50 (m, 1H), 7.81 (d, 1H, J = 7.8 Hz), 7.50 (m, 1H), 7.30 (m, 2H), 7.23 (m, 1H), 7.07 (m, 1H), 6.62 (d, 1H, J = 7.8 Hz), 6.01 (t, 1H, J = 1.9 Hz), 3.29 (s, 2H), 3.26 (d, 2H, J = 1.9 Hz), 1.39 (s, 6H). EI-MS (*m/e*): 249 (73, M), 234 (100, M − CH_3), 219 (4, M − $2CH_3$), 157 (50, M − CH_3 − pyridyl), 115 (39, C_9H_7). IR (cm^{-1}, KBr): 3070m, 3000m, 2985m, 2970m, 1600m, 1580m, 1485s, 1460s, 1435s, 1396m, 1375m, 1355m, 1290m, 1245s, 1150m, 1085m, 1050m, 1025s, 770s, 750s, 725s. Anal. Calcd for $C_{18}H_{19}N$: C, 86.70; H, 7.68; N, 5.62. Found: C, 86.18; H, 7.91; N, 5.68.

To a solution of 2.35 g (9.47 mmol) of ligand **5a** in 20 mL of THF in the flask was added dropwise a solution of butyllithium (7.76 mL, 1.22 mol/L, 9.47 mmol) in THF at −78 °C. After complete addition the reaction mixture was stirred for 12 h at room temperature. Then the resulting solution was added to a suspension of $CrCl_3(THF)_3$ (3.54 g, 9.47 mmol) in 45 mL of THF at −78 °C. The mixture was warmed slowly to room temperature and stirred for 14 h. The color of the reaction mixture changed from purple to deep blue. After the solvent was removed in vacuo, toluene was added to precipitate the LiCl, and the organic layer was concentrated to 30 mL. At −30 °C, 0.38 g of dark blue needle crystals was obtained in 11% yield. The sample for X-ray crystallography was further recrystallized from CH_2Cl_2. EI-MS (*m/e*): 370 (45, M), 334 (17, M − Cl), 298 (24, M − 2Cl), 248 (100, M − Cr − 2Cl), 232 (7, M − Cr − 2Cl − Me). IR (cm^{-1}, KBr): 3450w, 3051w, 3074m, 2978w, 2962m, 2923w, 2870w, 1720w, 1704w, 1658w, 1602s, 1563m, 1545m, 1475s, 1447s, 1433s, 1385m, 1367m, 1341m, 1297m, 1251m, 1209m, 1160m, 1102w, 1052w, 1019m, 996w, 837w, 812s, 775s, 748s, 645w, 620w, 556m, 480m, 452m. Anal. Calcd for $C_{18}H_{18}Cl_2CrN$: C, 58.23; H, 4.89; N, 3.77. Found: C, 57.87; H, 4.91; N,3.65.

Synthesis of Complex 6. The novel ligand **6a** was prepared following the procedure described for ligand **5a**. A solution of 6-methyl-6′-ethylbenzofulvene (8.10 g, 52.6 mmol) in 50 mL of Et_2O was added to the solution of 2-methylpyridine lithium in Et_2O, which was prepared from 2-methylpyridine (4.90 g, 52.6 mmol) in 100 mL of *n*-hexane and n-BuLi (43.1 mL, 52.6 mmol) in hexane. The mixture was stirred overnight and hydrolyzed. After workup, **6a** was obtained as pale orange crystals in a 47% (6.46 g) yield. ^1H NMR (δ, ppm, $CDCl_3$): 8.50 (m, 1H), 7.75 (d, 1H, J = 7.8 Hz), 7.50 (t, 1H, J = 7.4 Hz), 7.30 (m, 2H), 7.25 (t, 1H, J = 7.4 Hz), 7.00 (m, 1H), 6.62 (d, 1H, J = 7.8 Hz), 6.01 (m, 1H), 3.26 (m, 2H), 3.25 (s, 2H), 1.89 (m, 2H), 1.25 (s, 3H), 0.75 (m, 3H). EI-MS (*m/e*): 263 (28, M), 248 (29, M − Me), 234 (100, M − Et), 218 (7, M − Me − Et). IR (cm^{-1}, KBr): 3075w, 3004w, 2966s, 2928s, 2894m, 2874m, 1586s, 1565m, 1472s, 1457s, 1432s, 1393m, 1379m, 1297m, 1275m, 1153w, 1088w, 1051w, 976m, 916w, 766s, 749m, 725m, 653w, 606w, 559w. Anal. Calcd for $C_{19}H_{21}N$: C, 86.65; H, 8.04; N, 5.32. Found: C, 86.32; H, 8.22; N, 4.90.

To a solution of 1.32 g (5.96 mmol) of ligand **6a** in 20 mL of THF in the flask was added dropwise a solution of butyllithium (4.89 mL, 1.22 mol/L, 5.96 mmol) in THF at −78 °C. After complete addition the reaction mixture was stirred for 12 h. Then the resulting solution was added to the suspension of $CrCl_3(THF)_3$ (2.24 g, 5.96 mmol) in 45 mL of THF at −78 °C. The mixture was stirred overnight. The color of the reaction mixture changed from purple to deep blue. After the solvent was removed in vacuo, toluene was added to precipitate the LiCl, and the organic layer was concentrated to 30 mL. At −30 °C, 0.43 g of dark blue needle crystals were obtained in a 19% yield. EI-MS (*m/e*): 384 (31, M), 349 (34, M − Cl), 313 (24, M − 2Cl), 262 (100, M − Cr − 2Cl), 234 (50, M − Cr − 2Cl − Et), 218 (18, M − Cr − 2Cl − Me − Et). IR (cm^{-1}, KBr): 3094w, 3070m, 2960s, 2937m, 2876m, 1603s, 1565m, 1530w, 1474s, 1454s, 1443s, 1427s, 1377s, 1350m, 1316w, 1294m, 1262w, 1236w, 1211w, 1144m, 1118w, 1098m, 1051s, 1021m, 841s, 772s, 738s, 669w, 648w, 560w, 475w, 452s, 434m. Anal. Calcd for $C_{19}H_{20}Cl_2CrN$: C, 59.23; H, 5.23; N, 3.64. Found: C, 59.30; H, 5.16; N, 3.57.

Synthesis of Complex 7. A 6.17 g (30.81 mmol) sample of *ortho*-bromo-*N*,*N*-dimethylaniline and 50 mL of dry *n*-hexane were put into the flask. The temperature of the reaction mixture was maintained below −5 °C. A solution of butyllithium (16.75 mL, 1.84 M, 30.81 mmol) was slowly added dropwise while stirring. After addition was completed, the temperature was maintained at 25 °C for 12 h. The lithium salt was separated by filtration and washed with dry *n*-hexane.

The lithium salt was dissolved in 100 mL of dry diethyl ether, and to this a solution of 3.27 g (30.81 mmol) of 6,6-dimethylfulvene in 10 mL of dry diethyl ether was added dropwise. The temperature of the reaction mixture was maintained at −5 °C, and after complete addition the reaction mixture was stirred overnight at room temperature. Ice water (30 mL) was then added to hydrolyze the lithium salt. The organic phase was separated, and to this was added 4 mL of concentrated HCl and 15 mL of ice water. Then organic phase was extracted with diethyl ether three times to remove the unreacted fulvene and other byproducts.

The aqueous phase was cooled to −5 °C and the pH adjusted to 13 with 25% KOH. The organic phase was separated, and the aqueous phase was extracted with diethyl ether. The combined organic phases were dried with anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The resulting residue was distilled to give a light yellow oil, **7a** (1.03 g; yield 14% (94−95 °C/1 mmHg)). ^1H NMR (δ, ppm, $CDCl_3$): 7.34 (dt, 1H, J = 7.9 Hz, J = 1.7 Hz, Ph *o*-H), 7.28 (dd, 1H, J = 7.9 Hz, J = 1.7 Hz, Ph *m*-H), 7.22 (m, 1H, Ph *m*-H), 7.12 (m, 1H, Ph *p*-H), 6.25 (m, 3H, Cp), 2.96 (m, 2H, Cp), 2.35 (s, 6H, $N(CH_3)_2$), 1.67 (s, 6H, $C(CH_3)_2$).

Butyllithium (2.27 mL, 1.84 mol/L, 4.18 mmol) in THF was dropwise added to a solution of ligand **7a** (0.95 g, 4.18 mmol) in 20 mL of THF at −78 °C. After complete addition the reaction mixture was stirred for 4 h. The resulting solution was then added to a suspension of $CrCl_3(THF)_3$ (1.57 g, 4.18 mmol) in 45 mL of THF at 25 °C, and the mixture stirred overnight. The color of the reaction mixture changed from purple to deep blue. After evaporation of the solvent, toluene was added to remove the LiCl, and the organic layer was concentrated to 30 mL and cooled to − 30 °C to give dark blue needle crystals, 338 mg (23%). EI-MS (*m/e*): 348 (1, M), 312 (100, M − Cl), 276 (15, M − 2Cl), 262 (3, M − 2Cl − CH_3), 226 (11, M − 2Cl − Cr), 196 (50, M − 2Cl − Cr − $2CH_3$). IR (cm^{-1}, KBr): 3110.0m, 3094.0m, 3080.8m, 3022.7m, 2971.2m, 2922.3m, 2867.7m, 2819.4s, 2779.2s, 1635.5s, 1482.5m, 1465.2m, 1441.5m, 1402.3m, 1368.0s, 1290.7vs, 1258.9vs, 1114.5s, 1065.0m, 1038.2m, 979.2s, 902.9s, 884.0s. Anal. Calcd for $C_{16}H_{20}Cl_2CrN$: C, 55.03; H, 5.77; N, 4.01. Found: C, 53.83; H, 5.77; N, 3.57. HRMS calcd for $C_{16}H_{20}Cl_2CrN$, 348.0378; found, 348.0377.

Synthesis of Complex 8. Ligand **8a** was synthesized in a fashion similar to **7a**. Thus, the reaction of *ortho*-bromo-*N*,*N*-dimethylaniline (14.66 g, 73.27 mmol), butyllithium (39.82 mL, 73.27 mmol), and 6,6-methylethylfulvene (10.70 g, 30.81 mmol)

Table 1. Crystal Data and Structure Refinement Parameters for 1 and 5

	1	5
empirical formula	$C_{14}H_{16}NCl_2Cr$	$C_{18}H_{18}NCl_2Cr$
fw	321.18	371.23
temp (K)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)/*n*
unit cell dimens		
a (Å)	13.2436(14)	10.2893(12)
b (Å)	12.3830(13)	11.8211(13)
c (Å)	17.5497(18)	13.6801(15)
α (deg)	90	90
β (deg)	97.777(2)	96.693(2)
γ (deg)	90	90
volume (Å^3)	2851.6(5)	1652.6(3)
Z	8	4
calcd density (Mg/m^3)	1.496	1.492
absorp coeff (mm^{-1})	1.158	1.010
F(000)	1320	764
cryst size (mm)	0.479 × 0.266 × 0.200	0.538 × 0.228 × 0.221
θ range for data collection (deg)	1.81 to 28.34	2.28 to 28.24
limiting indices	$-13 \le h \le 17$, $-16 \le k \le 16$, $-23 \le l \le 23$	$-12 \le h \le 13$, $-15 \le k \le 15$, $-12 \le l \le 18$
no. of reflns collected/ unique	17 123/6586 [*R*(int) = 0.0961]	9824/3815 [*R*(int) = 0.0760]
completeness to *θ* = 28.24	92.5%	93.4%
absorp corr	SADABS	SADABS
max. and min. transmn	1.00000 and 0.51557	1.00000 and 0.76545
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/ params	6586/16/454	3815/6/271
goodness-of-fit on F^2	0.849	0.891
final *R* indices [$I>2\sigma(I)$]	R1 = 0.0439, wR2 = 0.0832	R1 = 0.0470, wR2 = 0.0926
R indices (all data)	R1 = 0.0778, wR2 = 0.0914	R1 = 0.0763, wR2 = 0.1005
largest diff peak and hole (e·Å^{-3})	0.586 and −0.472	0.519 and −0.387

afforded a light yellow oil, **8a**, obtained in 37% yield (138−140 °C/1 mmHg). ^{1}H NMR (*δ*, ppm, $CDCl_3$): 7.36 (dt, 1H, *J* = 7.8 Hz, *J* = 1.7 Hz, Ph), 7.28−7.12 (m, 3H, Ph), 6.25−5.99 (m, 3H, Cp), 2.95 (m, 2H, Cp), 2.30 (s, 6H, $N(CH_3)_2$), 1.91 (m, 2H, $C(CH_2)$), 1.47 (s, 3H, $C(CH_3)$), 0.97 (m, 3H, $C(CH_2CH_3)$). ESI-MS (*m*/*e*): 241.3 (100, M). IR (cm^{-1}, KBr): 3059m, 3012vs, 2968vs, 2931s, 2875s, 2618w, 2778m, 1598m, 1573w, 1485s, 1452vs, 1378m, 1354m, 1290m, 1190m, 1161w, 1142w, 1083w.

Complex **8** was synthesized as described below to afford **7** as dark blue crystals, obtained in a 10% yield (95 mg). EI-MS (*m*/*e*): 362 (1, M), 326 (69, M − Cl), 311 (8, M − Cl − CH_3), 290 (17, M − 2Cl), 276 (4, M − 2Cl − CH_3), 239 (23, M − 2Cl − Cr), 225 (6, M − 2Cl − Cr − CH_3), 210 (44, M − 2Cl − Cr − 2CH_3), 196 (100, M − 2Cl − Cr − CH_3 − CH_2CH_3). IR (cm^{-1}, KBr): 3137m, 3087s, 2945vs, 2923vs, 2861m, 1490w, 1464s, 1444vs, 1402w, 1071m, 1010w, 977w. HRMS calcd for $C_{17}H_{22}Cl_2CrN$, 362.0534; found, 362.0534.

Synthesis of Complex 9. Ligand **9a** was synthesized similarly to **7a**, resulting in a light yellow oil in a 75% yield. ^{1}H NMR (*δ*, ppm, $CDCl_3$): 7.47 (m, 1H), 7.21−7.12 (m, 3H), 6.35 (m, 1H), 6.25 (m, 1H), 6.01 (m, 1H), 2.93 (m, 2H), 2.46 (m, 2H), 2.28 (s, 6H), 2.18 (m, 2H), 1.53−1.42 (m, 6H). EI-MS-(*m*/*e*): 267.2 (100, M), 252.2 (6, M − CH_3), 238.2 (2, M − 2CH_3), 223.1 (1, M − $N(CH_3)_2$), 202.2 (6, M − Cp), 65.0 (1, Cp). IR (cm^{-1}, KBr): 3057m, 2931vs, 2854vs, 2817s, 2776s, 1593w, 1512w, 1485s, 1451s, 1375w, 1354m, 1291m.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes 1 and 5

1[a]		5	
Bond Lengths			
Cr(2)−N(2)	2.108(2)	Cr−N(1)	2.118(2)
Cr(2)−Cl(4)	2.2838(9)	Cr−Cl(1)	2.2740(10)
Cr(2)−Cl(3)	2.2964(9)	Cr−Cl(2)	2.2984(9)
Cr(2)−C(19)	2.212(3)	Cr−C(9)	2.223(3)
C(19)−C(20)	1.503(4)	C(9)−C(10)	1.506(4)
C(20)−C(21)	1.539(4)	C(10)−C(11)	1.531(4)
C(21)−(C22)	1.496(4)	C(11)−C(12)	1.503(4)
N(2)−C(22)	1.348(3)	N(1)−C(12)	1.349(3)
N(2)−C(26)	1.337(4)	N(1)−C(16)	1.352(4)
C(20)−C(27)	1.549(4)	C(1)−C(2)	1.396(5)
C(20)−C(28)	1.513(4)	C(1)−C(9)	1.417(4)
Bond Angles			
N(2)−Cr(2)−Cl(4)	89.79(6)	N(1)−Cr−Cl(1)	90.83(7)
N(2)−Cr(2)−Cl(3)	97.02(7)	N(1)−Cr−Cl(2)	97.90(6)
Cl(4)−Cr(2)−Cl(3)	99.93(4)	Cl(1)−Cr−Cl(2)	97.66(4)
C(26)−N(2)−C(22)	118.0(2)	C(12)−N(1)−C(16)	117.7(2)
C(26)−N(2)−Cr(2)	114.79(19)	C(16)−N(1)−Cr	116.71(19)
N(2)−Cr(2)−C(19)	88.77(9)	N(1)−Cr−C(9)	88.74(9)
Cr(2)−C(19)−C(20)	121.23(19)	C(10)−C(9)−Cr	121.3(2)
C(19)−C(20)−C(21)	109.1(2)	C(9)−C(10)−C(11)	109.7(2)
C(20)−C(21)−C(22)	117.0(3)	C(12)−C(11)−C(10)	115.7(3)
C(21)−C(22)−N(2)	120.8(3)	N(1)−C(12)−C(11)	119.5(3)
C(22)−N(2)−Cr(2)	126.62(19)	C(12)−N(1)−Cr	125.47(18)
C(28)−C(20)−C(27)	109.1(3)	C(18)−C(10)−C(17)	107.2(3)

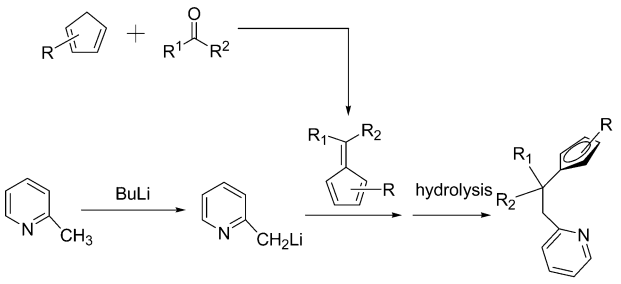
[a] The data are for one of the two independent molecules present in the unit cell.

Complex **9** was synthesized similarly to **7**. Dark blue crystals were afforded in 13% yield (103 mg). EI-MS (*m*/*e*): 388 (1, M), 352 (100, M − Cl), 316 (18, M − 2Cl), 266 (24, M − 2Cl − Cr), 251.2 (13, M − 2Cl − Cr − CH_3), 222 (5, M − 2Cl − Cr − $N(CH_3)_2$). IR (cm^{-1}, KBr): 3137m, 3087s, 2945vs, 2923vs, 2861m, 1490w, 1464s, 1444vs, 1402w, 1071m, 1010w, 977w. HRMS calcd for $C_{19}H_{24}Cl_2CrN$, 388.0691; found, 388.0722.

X-ray Crystallography of the New Complexes 1 and 5. The dark green crystals of **1** and **5** were mounted on a glass fiber. All measurements were made on a Bruker AXSD8 diffractometer with graphite monochromatic Mo Kα (=0.71073 Å) radiation. All data were collected at 20 °C using the scan techniques. All structures were solved by direct methods and refined using Fourier techniques. An absorption correction based on SADABS was applied. All non-hydrogen atoms were refined by full-matrix least-squares on F^2. Hydrogen atoms were located and refined by the geometry method. The cell refinement, data collection, and reduction were done by Bruker SAINT and SMART. The structure solution and refinement were performed by SHELXSL-97. For further crystal data and details of measurements see Table 2.

2. Polymerization Procedure. A 100 mL flask equipped with an ethylene inlet, magnetic stirrer, and vacuum line was filled with the appropriate volume of freshly distilled solvent, the comonomer (1-hexene, in the case of copolymerization), and MAO. The flask was placed in an oil bath at the desired temperature, and ethylene was introduced for 10 min to saturate the toluene solution. The polymerization reaction was started by adding a solution of the catalyst precursor via a syringe and was carried out under 1 atm pressure of ethylene for 30 min and then quenched with 3% HCl in ethanol. The polymer was precipitated in the ethanol, filtered, and washed with EtOH, and was then dried overnight in a vacuum oven at 80 °C. ^{13}C NMR spectra were recorded on a Varian GEMINI-300 spectrometer in 1,2-dichlorobenzene at 130 °C. Molecular weight and molecular weight distribution (M_w/M_n) values were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with a polystyrene gel column (TSK gel GM-H_{HR}-H HT×2) at 140 °C using *o*-dichlorobenzene containing 0.05 w/v 2,6-di-*tert*-butyl-*p*-cresol as solvent. The molecular

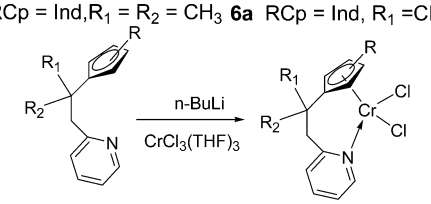
Scheme 1. Route for the Synthesis of Cyclopentadienylchromium Complexes 1−6



1a R = H, $R_1 = R_2 = CH_3$ **2a** R = H, $R_1 = CH_3$, $R_2 = CH_2CH_3$

3a R = H, R_1, R_2=  **4a** R = H, R_1, R_2 = 

5a RCp = Ind, $R_1 = R_2 = CH_3$ **6a** RCp = Ind, $R_1 = CH_3$, $R_2 = CH_2CH_3$



1 R = H, $R_1 = R_2 = CH_3$ **2** R = H, $R_1 = CH_3$, $R_2 = CH_2CH_3$

3 R = H, R_1, R_2=  **4** R = H, R_1, R_2 = 

5 RCp = Ind, $R_1 = R_2 = CH_3$ **6** RCp = Ind, $R_1 = CH_3$, $R_2 = CH_2CH_3$

weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

Results and Discussion

1. Synthesis and Characterization of Complexes 1−9. The route of the synthesis of the pyridyl-substituted cyclopentadienyl chromium complexes **1**−**6** is illustrated in Scheme 1.

The pyridyl-substituted cyclopentadienyl ligands are readily accessible from the reaction of 6,6-dialkylfulvenes with the appropriate 2-methylpyridyllithium salts.[22] Using the same procedure, two new pyridyl-substituted indenyl ligands, **5a** and **6a**, were obtained.

The reaction of these ligands with $CrCl_3(THF)_3$ leads to the new half-sandwich chromium complexes **1**−**6**, which were isolated in moderate yield. The complexes **1**−**4** are blue in toluene solution and black-green in CH_2Cl_2 solution. However, the complexes **5** and **6** dissolve only in CH_2Cl_2.

The molecular structures of complexes **1** and **5** were determined by X-ray diffraction. Crystal data and relevant structural parameters are listed in Table 1.

The structures with the atom-numbering schemes are shown in Figures 1 and 2, and selected bond lengths and angles are listed in Table 2. The crystals of complex **1** contain two independent molecules, which differ in the arrangement of the fragment bridging the ring and the N-donor atom, and the data shown are for only one molecule.

It is shown that the crystal system and space group of two complexes are monoclinic and $P2(1)/n$. The nitrogen−chromium distance in complex **1** (2.108 Å) is somewhat shorter than that in complex **5** (2.118 Å), but the Cl−Cr−Cl angle in complex **1** (99.93°) is somewhat bigger than that in complex **5** (97.66°). Furthermore, the Cr−N bond distance in pyridyl-substituted cyclopentadienylchromium complexes is longer than that of quinoyl-substituted complexes (2.088 Å) and shorter than that of aniline-substituted complexes (2.251 Å).[8] In both cases the Cr−N distance of 2.1−2.2 Å confirms that the N-donor atom coordinated to the metal. In complex **1**, the length of $Cr-C_{18}$ is shortest among the lengths of Cr−C of the five-membered-ring moiety. This phenomenon suggests that the metal atom is not located exactly below the centers of the five-membered rings but is shifted slightly toward the tethered donor ligands.

The IR spectra of these complexes also prove that the nitrogen atom is complexed to the chromium atom.

The routes employed for the syntheses of the α,α-dialkyl-*ortho*-*N*,*N*-dimethylbenzylcyclopentadienylchromium complexes **7**−**9** are illustrated in Scheme

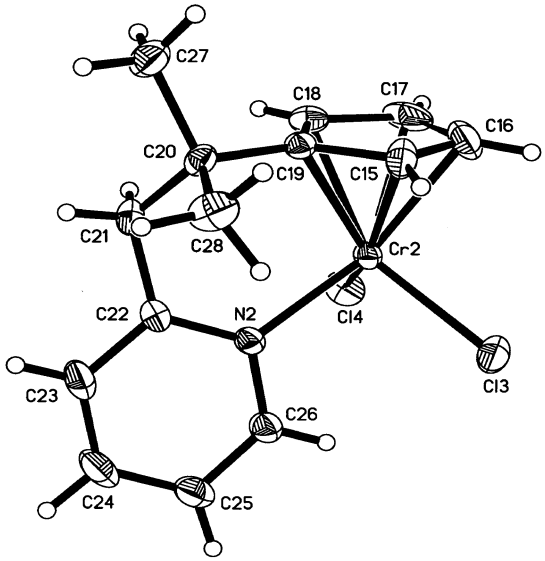


Figure 1. Molecular structure of complex **1**.

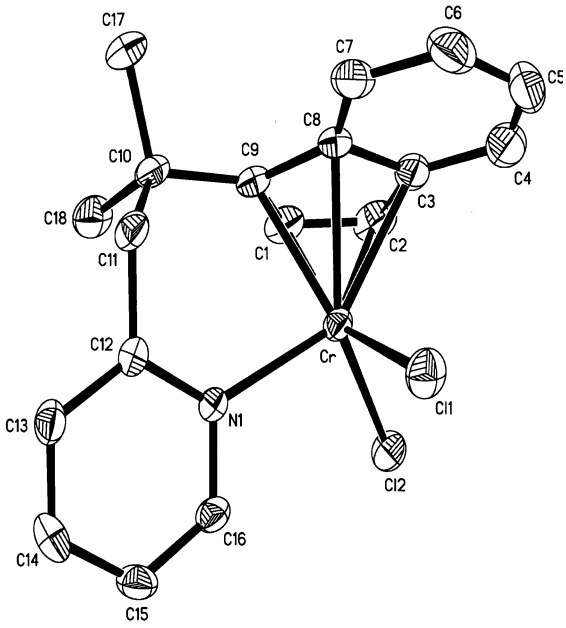


Figure 2. Molecular structure of complex **5**.

Scheme 2. Route for the Synthesis of Cyclopentadienylchromium Complexes 7−9

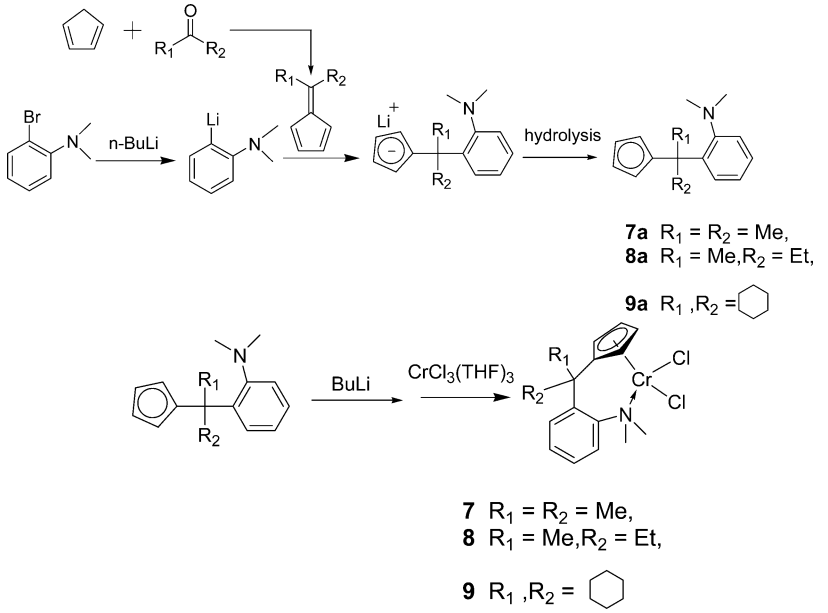


Table 3. Polymerizations of Ethylene Using Cyclopentadienylchromium Complexes 1−9[a]

entry	catalyst	amt of Cr (μmol)	MAO:Cr	T_p (°C)	amt of PE (g)	activity (10^5g PE mol Cr^{-1} h^{-1})	M_w ($\times 10^4$)	M_w/M_n
1	**1**	5.05	2000:1	25	0.4625	1.83	1.29	2.12
2	**1**	5.05	1000:1	25	0.3548	1.40	2.34	2.08
3	**1**	10.10	1000:1	25	0.7406	1.47		
4	**2**	5.05	2000:1	25	2.1400	8.48	1.82	2.80
5	**3**	5.05	2000:1	25	2.2552	8.92	1.59	3.12
6	**3**	5.05	1000:1	25	1.4281	5.65	4.28	2.52
7	**3**	5.05	2000:1	50	1.6953	6.71	1.04	4.74
8	**3**	5.05	1000:1	50	1.2114	4.79	2.42	2.81
9	**4**	5.05	2000:1	25	3.1293	11.9	3.33	2.34
10	**5**	5.05	2000:1	25	3.4042	13.5	3.87	2.47
11	**6**	5.05	2000:1	25	5.0557	20.0	5.52	2.23
12	**6**	5.05	1000:1	25	3.3636	13.3	12.8	3.23
13	**6**	5.05	2000:1	50	4.4369	17.6	1.88	5.13
14	**6**	5.05	1000:1	50	2.6285	10.4	4.26	3.36
15	**7**	5.05	2000:1	25	0.4541	1.80	1.54	2.46
16	**7**	5.05	2000:1	50	0.4361	1.73		
17	**7**	5.05	1000:1	25	0.2821	1.12		
18	**7**	5.05	1000:1	7	0.3818	1.51		
19	**7**	5.05	100:1	25	0.0250	0.10		
20	**7**	25.2	100:1	25	0.8071	0.64		
21	**8**	5.05	2000:1	25	0.3225	1.28	1.12	3.24
22	**8**	5.05	1000:1	25	0.2114	0.84		
23	**9**	5.05	2000:1	25	0.2409	0.96	1.07	3.67
24	**9**	5.05	1000:1	25	0.1916	0.76		

[a] Polymerization conditions: $P_{ethylene}$ = 1 atm; t_p = 30 min; solvent: toluene; total volume: 50 mL.

2. Ligands are readily accessible from the reaction of 6,6-dialkylfulvenes with the appropriate aryllithium salts. The α,α-dialkyl-*ortho*-*N*,*N*-dimethylbenzylcyclopentadienylchromium complexes are prepared via salt metathesis of the appropriate (cyclopentadienyl)lithium with $CrCl_3(THF)_3$ in THF. However, these complexes are very sensitive to air and moisture.

The complexes **7**−**9** are paramagnetic, and coordination of the N-donor atom to the metal has been confirmed by IR, which was in agreement with that reported by Jolly.[6]

2. Polymerization of Olefin Using Complexes 1−9. 2.1. Polymerization of Ethylene with Chromium Complex. Effect of Steric Bulk of the Cp′ Ring and Different Bridge Fragments between the Cyclopentadienyl Ligand and the Pyridyl (Anilin) Group on the Polymerization of Ethylene. The ethylene polymerization results using complexes **1**−**9** as catalyst precursors in the presence of MAO are summarized in Table 3. It was revealed that these complexes exhibited high catalytic activities for ethylene polymerization, although they were lower than Jolly's results at different polymerization conditions.[6] The catalytic activities increased at higher Al/Cr molar ratios and decreasing polymerization temperatures, which was in agreement with that reported by Jolly.[6] The resultant polymer possessed high molecular weight with unimodal molecular weight distribution and with a melting point (DSC) in the range 125−132 °C.

The catalytic activity and the molecular weight for resultant polyethylene increased in the order **1** < **2** < **3** < **4** < **5** < **6** under the same conditions for pyridyl-substituted cyclopentadienylchromium complexes. The M_w value decreased upon increasing the Al/Cr molar ratio for complexes **3** and **6**, suggesting some extent of chain transfer to Al occurred. The molecular weights of

Table 4. Random Copolymerization of Ethylene with 1-Hexene[a]

entry	catalyst	amt of Cr (μmol)	MAO:Cr	T_p (°C)	1-hexene (mL)	yield (g)	activity (10^5 g mol Cr^{-1} h^{-1})	1-hexene content[b] (mol %)	M_w ($\times 10^5$)	M_w/M_n
1	**1**	5.05	1000:1	25	3	0.4371	1.73	0.47	1.56	2.23
2	**3**	5.05	1000:1	25	3	2.5738	10.19	1.19	2.20	2.71
3	**5**	5.05	1000:1	25	3	3.0538	12.09			
4	**6**	5.05	1000:1	25	3	3.4727	13.74	1.47	3.29	2.12

[a] Polymerization conditions: $P_{ethylene}$ = 1 atm; t_p = 30 min; solvent: toluene; total volume: 50 mL. [b] 1-Hexene content in copolymer determined by ^{13}C NMR spectra.

the polymers decreased by raising the polymerization temperature from 25 to 50 °C because of the frequent β-hydride elimination.

To examine the effects of the Cp′ fragment on the polymerization activity, complexes **1**, **2**, **5**, and **6** were chosen as catalysts for ethylene polymerization. As a result, the indenyl analogue **6**/MAO system reveals a catalytic activity nearly 3 times as high as that of cyclopentienyl analogue **2**/MAO system. The molecular weights of the resulting polymers using complex **6** are 5.52×10^4 with a polydispersity index of 2.23 at 25 °C; on the other hand, complex **2** possessed a lower molecular weight (1.82×10^4) and relatively broader polydispersity index (2.80) with the same conditions. One possible explanation for it is that the more electron-donating nature of the complex increases the propagation rate rather than chain-transfer rate. The same trend was observed for complexes **1** and **5**. Furthermore, it is thus concluded that substitutents on the cyclopentadienyl group affect both the catalytic activity and the molecular weight of the resultant polymer.

To investigate the effect of the bridge between the cyclopentadienyl and pyridyl groups, ethylene polymerization was carried out using complexes **1** and **4**. When the dimethyl group was replaced by the cyclohexyl group, a 7-fold increase in catalytic activity was observed with complex **4** compared with **1** (entries 1 and 9). The same trend was observed for complexes **1** and **3**. This is probably due to the steric bulk of the ligand, bite angle, configuration, conformation, and electronic effects. The cyclohexyl group seems to provide a more appropriate bulkiness or conformation than the methyl substituents for ethylene polymerization. Furthermore, since complex **4** exhibits higher activity than **3**, this implies that steric or conformational effects in the bridge fragment between the cyclopentadienyl ligand and the pyridyl group are more important than electronic effects for catalyst **4**.

The catalytic activity of the anilin-substituted cyclopentadienylchromium complexes for ethylene polymerization decreased in the order **7** > **8** > **9**. We also investigated the effect of the bridge between the cyclopentadienyl and anilin groups for complexes **7**−**9**. The differences in polymerization activity between the **7**/MAO, **8**/MAO, and **9**/MAO systems are relatively small and are known to be the result of different steric properties of the backbone substituents.[23] The activity of the **7**/MAO system is nearly the same as that of the **1**/MAO system. However, the observed catalytic activities of complexes **8** and **9** were lower than complexes **2** and **4**. Although the origin for this effect might not be completely clear in this case, this does not rule out the effect of environments of nitrogen atom in the olefin polymerization.

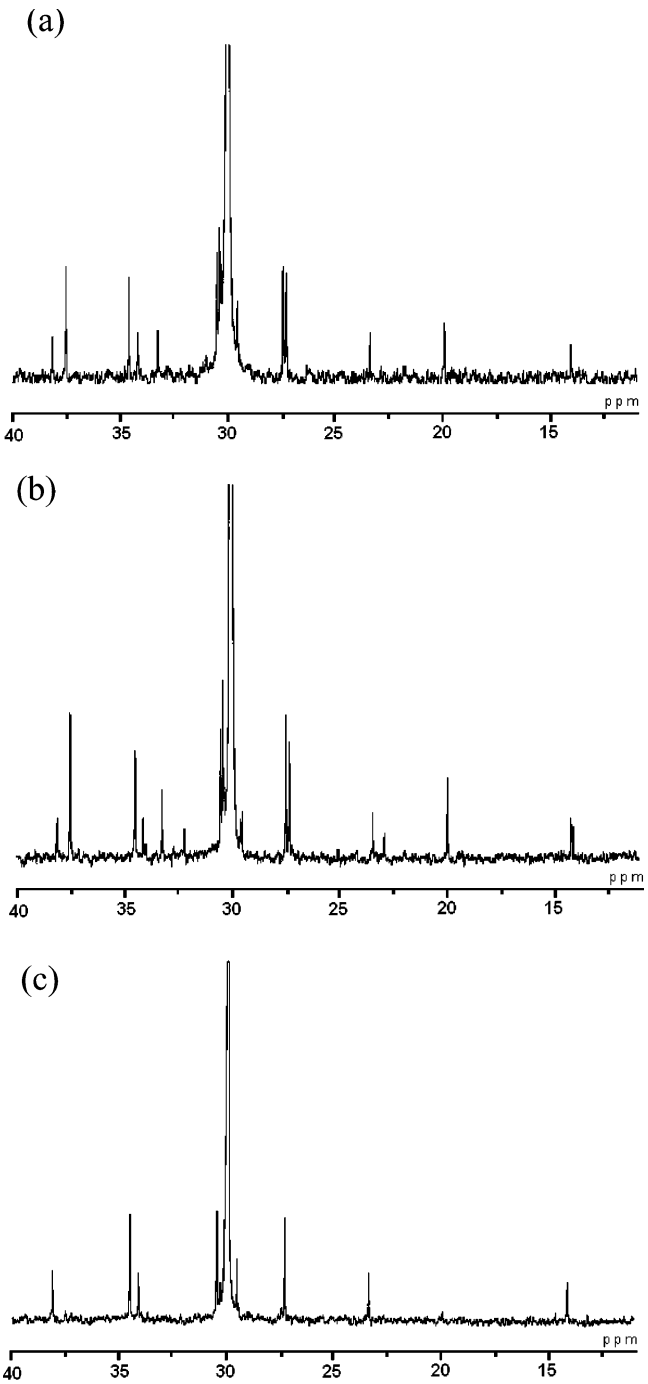


Figure 3. ^{13}C NMR spectrum of ethylene/1-hexene copolymer obtained by **1**, **3**, and **6**/MAO: (a) complex **1**; (b) complex **3**; (c) complex **6**.

(23) (a) Alt, H. G.; Zenk, R. *J. Organomet. Chem.* **1996**, *526*, 295. (b) Deckers, P. J. W.; Hessen, B.; Teuben, J. H. *Organometallics* **2002**, *21*, 5122.

Table 5. Dyad and Triad Distribution of Poly(ethylene-*co*-1-hexene)s[a]

run no.	catalyst	HH	HE	EE	HHH	HHE	EHE	HEH	EEH	EEE
1	**1**	0.00	0.93	99.07	0.00	0.00	0.49	0.00	0.88	98.58
2	**3**	0.00	2.38	97.62	0.00	0.00	1.34	0.00	2.07	96.59
3	**6**	0.01	2.93	97.16	0.00	0.02	1.45	0.00	2.93	95.60

[a] Calculated by ^{13}C NMR spectra. EE = EEE+1/2EEH, EH = 1/2EHH+1/2HEE+EHE+HEH, HH = HHH+1/2HHE.

The ^{13}C NMR spectrum of the PE obtained with the **6**/MAO system indicates the resultant polymer is linear.

2.2. Random Copolymerization of Ethylene with 1-Hexene. These catalytic systems showed the notable characteristics in ethylene polymerization; we are thus encouraged to investigate the copolymerization behavior. Table 4 summarizes the results for ethylene/1-hexene copolymerization by the complexes **1**, **3**, **5**, and **6**/MAO catalytic systems.

From the results of ethylene/1-hexene coplymerization, it is noteworthy that complex **6** exhibits the highest catalytic activity (13.74×10^5 g/mol Cr·h) and 1-hexene incorporation ability (1.47%) among these catalytic systems. It is also noted that the catalytic activity increases in the order **1** (1.73×10^5 g/molCr·h) < **3** (10.19×10^5 g/molCr·h) < **5** (12.09×10^5 g/molCr·h) < **6** (13.74×10^5 g/molCr·h) under the same polymerization conditions. In addition the M_w values for the copolymer prepared by **1**, **3**, and **6** were higher than those for polyethylene [e.g., M_w values for poly(ethylene-*co*-1-hexene) vs polyethylene, **1**: $M_w = 15.6 \times 10^4$ vs 2.34×10^4; **3**: $M_w = 22.0 \times 10^4$ vs 4.28×10^4; **6**: $M_w = 32.9 \times 10^4$ vs 12.8×10^4].

Polymer microstructures are analyzed on the basis of ^{13}C NMR with reference to Randall's report.[24] Typical examples are displayed in Figure 3, which was obtained with **1**, **3**, and **6**/MAO catalytic system. Results of the analysis are given in Table 5. In every case, the content of the ethylene unit is higher than that of the 1-hexene unit. The 1-hexene unit is isolated in the polymer chain because of the low incorporation.

Taking into account the above results, the effect of substituent in both cyclopenatdienyl fragment and different bridge fragment between the cyclopentadienyl ligand and the pyridyl group plays an essential role in both the catalytic activity and the monomer sequence distributions in ethylene/1-hexene copolymerization.

(24) (a) Hsieh, E. T.; Randall, J. C. *Macromolcules* **1982**, *15*, 1402. (b) Randall, J. C. *JMS Rev. Macromol. Chem. Phys*. **1989**, *C29*, 201.

Conclusion

We prepared new half-sandwich cyclopentadienylchromium complexes and examined their catalytic activity for ethylene polymerization and copolymerization with 1-hexene. Among them, the **6**/MAO system exhibits the highest activity for copolymerization of ethylene with 1-hexene and for the homopolymerization of ethylene. As a result of the polymerizations, we can conclude that the environment of the Cp and different bridge fragments between the cyclopentadienyl ligand and the pyridyl (anilin) group plays an important role in this series of complexes for olefin polymerization.

Acknowledgment. This article is dedicated to the late Professor Yanlong Qian in honor of his remarkable contribution in this research field. H.Z. would like to express his heartfelt thanks to Prof. Kotohiro Nomura (NAIST) for GPC analyses. H.Z. thanks Dr. Wang for helpful discussions and Dr. J. J. Murphy for his detailed corrections of the manuscript. This project was supported by special funds for Major State Basic Research Projects (G1999064801), National Natural Science Foundation of China (NNSFC 20372022).

Supporting Information Available: Detailed information on the crystal structure determinations, including tables of data collection parameters, final atomic positional and thermal parameters, and interatomic distances and angles as well as ORTEP diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

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