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# Syntheses, Characterization, and Ethylene (Co-)Polymerization Screening of Amidate Half-Titanocene Dichlorides

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A series of amidate half-titanocene dichlorides, Cp′Ti**L**$Cl_2$ [Cp′ = Cp (as $\eta^5$-$C_5H_5$) or Cp* (as $\eta^5$-$C_5Me_5$), **L** = *N*-(2-methylquinolin-8-yl)-*p*-R-benzamides; **C1**: Cp′ = Cp, R = OMe; **C2**: Cp′ = Cp, R = Me; **C3**: Cp′ = Cp, R = H; **C4**: Cp′ = Cp, R = F; **C5**: Cp′ = Cp, R = Cl; **C6**: Cp′ = Cp*, R = OMe; **C7**: Cp′ = Cp*, R = Me], have been synthesized by the stoichiometric reaction of Cp′Ti$Cl_3$ with the corresponding potassium amidates. All complexes are fully characterized by elemental and NMR analyses. The molecular structures of complexes **C2** and **C4** are confirmed by single-crystal X-ray diffraction, and the amidate moieties coordinate the titanium center by imino and alkoxide groups. The systems **C1**−**C7**/MAO show much higher activities toward ethylene polymerization than CpTi$Cl_3$/MAO or Cp*Ti$Cl_3$/MAO systems. The procatalysts (**C6** and **C7**) bearing a Cp* ligand exhibit higher activities than their analogues (**C1**−**C5**) containing a Cp ligand, while the amidate ligands containing electron-donating groups positively affect the catalytic behavior. Both increasing the ratio of MAO to titanium and reducing reaction temperature enhance the productivities; however, the molecular weights of the resultant polymers decrease with higher activities. Moreover, the **C6**/MAO system performs with high activity in the copolymerization of ethylene and 1-hexene or 1-octene.

## 1. Introduction

Polyolefins, the most popularly used synthetic polymer, have been synthesized by employing commercial catalysts of Ziegler−Natta,[1] Phillip,[2] and metallocene type.[3] The constrained-geometry compounds (CGC) of half-metallocene catalysts represent single-site catalysts that are particularly considered due to the properties of the resultant polyolefins such as controlled molecular weight, specific tacticity, and narrow molecular weight distribution, as well as better comonomer incorporation.[4] Since the 1990s, inspired by fast developments in coordination and organometallic chemistry, more and more transition metal procatalysts have been designed and investigated for olefin polymerization.[5] Examples of chelating ligands are amidinate,[6] amide,[7] and alkoxy,[8]

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from which two significant procatalysts named as FI[9] and PI[10] catalysts have drawn much attention due to their high activities and their unique abilities to control polymer microstructures. The catalytic behavior of these procatalysts and also the properties of the resultant polyolefin could be fine-tuned by modifying the substituents of the complexes' ligands.[11] Attempts to combine the merits of the individual systems have led to the successful development of a series of nonbridged half-metallocene procatalysts, Cp′M(**L**)Xn (M = Ti, Zr, Hf; **L** = anionic ligand; X = halogen or alkyl),[12] which exhibited promising catalytic behavior and overcame the synthetic problems associated with metallocene[3] and/or CGC procatalysts.[4] Therefore, the half-titanocene Cp′M(L)Xn procatalysts containing a dianionic[13] or monoanionic[14] amidate ligands have been investigated in our group.

In view of the ease of synthesis and ligand variation, the title amidate metal complexes[15] have been synthesized and characterized. Unexpectedly, *N*-(2-methylquinolin-8-yl)-*p*-R-benzamidates act in the imine/alkoxide coordination of the $\mu_2$-OCN mode of the amidate moiety; however, the quinolinyl group does not coordinate to the titanium atom. All title procatalysts (**C1**−**C7**) show high activities toward ethylene polymerization, and the representative procatalyst (**C6**) exhibits a high activity in the copolymerization of ethylene with 1-hexene or 1-octene. Herein the syntheses and characterizations of the title complexes are reported in detail along with their catalytic behavior in olefin polymerization.

## 2. Results and Discussions

**2.1. Synthesis and Characterization of Half-Titanocene Complexes.** All *N*-(2-methylquinolin-8-yl)benzamide derivatives are prepared according to previously reported methods.[13b,16] These compounds could be deprotonated with potassium hydride in tetrahydrofuran (THF) at room temperature, and the resultant potassium compounds react further with one equivalent of Cp′TiCl$_3$ (Cp′ = Cp or Cp*) in THF to afford red solutions. Brown crystals of analytically pure amidate half-titanocene complexes, Cp′Ti**L**Cl$_2$ (**C1**−**C7**: Cp′ = Cp or Cp*; **L** = *N*-(2-methylquinolin-8-yl)-*p*-R-benzamides) (Scheme 1), are isolated in good yields (77.2−89.0%), and their molecular structures are consistent with the $^1$H and $^{13}$C NMR spectra (see Experimental Section). Regarding the proton resonances of their $^1$H NMR spectra, the protons of the amidate ligand appear between 10.5 and 10.9 ppm, but disappear in the title complexes due to the formation of Ti−N bonds. In all complexes, the protons' resonances are shifted to high-field because of an electron-density decrease in the aromatic rings upon coordination with titanium.

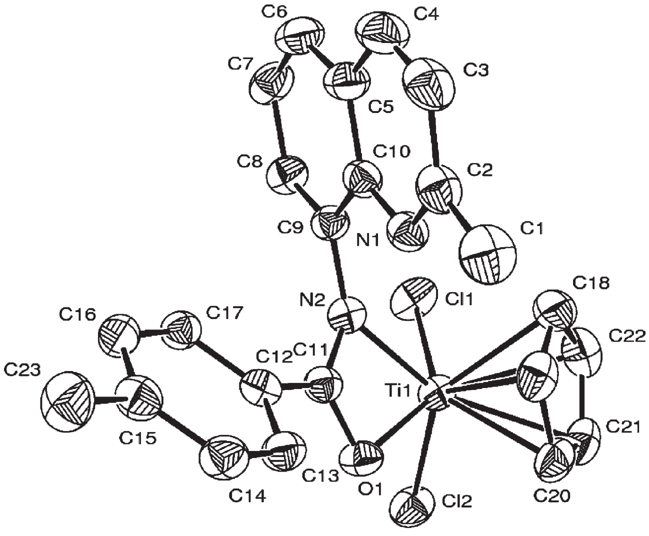
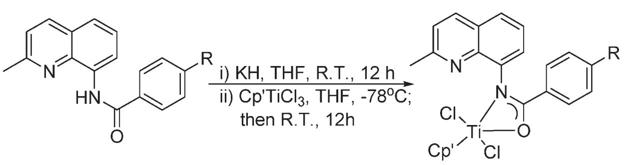


**Figure 1.** ORTEP view of the molecular structure of **C2** (ellipsoids enclose 50% electronic density; H atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ti1−O1 = 2.0697(2), Ti1−C11 = 2.512(3), Ti1−N2 = 2.117(2), Ti1−C18 = 2.332(3), Ti1−C19 = 2.341(3), Ti1−C20 = 2.348(3), Ti1−C21 = 2.352(3), Ti1−C22 = 2.341(3), Ti1−Cl1 = 2.2944(1), Ti1−Cl2 = 2.2906(9), C11−N2 = 1.309(3), C11−O1 = 1.296(3); N2−Ti1−Cl1 = 86.16(7), N2−Ti1−Cl2 = 129.76(7), N2−Ti1−O1 = 62.26(8), Cl1−Ti1−O1 = 136.97(6), Cl2−Ti1−O1 = 86.63(6), Cl1−Ti1−Cl2 = 93.42(4), N2−C11−O1 = 112.4(2).

**Scheme 1. Synthesis of Complexes C1−C7**



|  | C1 | C2 | C3 | C4 | C5 | C6 | C7 |
|---|---|---|---|---|---|---|---|
| R | OMe | Me | H | F | Cl | OMe | Me |
| Cp' | Cp | Cp | Cp | Cp | Cp | Cp* | Cp* |

Crystals of compounds **C2** and **C4** suitable for single-crystal X-ray analysis were grown by slow diffusion of heptane into toluene solutions of compounds **C2** and **C4**. The molecular structure of compound **C2** is illustrated in Figure 1, with selected bond lengths and angles, and the structure of its analogue **C4** is shown in the Supporting Information.

Considering the centroid of Cp as a single coordination site, the molecular structure of complex **C2** (Figure 1) consists of a distorted square-pyramid configuration, in which the Cp group lies in the apical site and the amidate moiety acts as a bidentate ligand together with the two chlorides in the bottom plane. The sum of the metallocyclic bond angles is 359.6°, indicating the coplanarity of titanium with all atoms of the bidentate amidate group in a $\eta^2$ fashion. The bonding motif of the amidate ligand is a nonsymmetric one bonded via the imine/alkoxide mode, which is in contrast to the coordination manner of amidate found in tridentate titanium complexes.[13,17] The C−O bond (C11−O1 1.296(3) Å),

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**Table 1. Ethylene Polymerization with C6/MAO**[a]

| entry | Al/Ti | $t$ (min) | $T$ (°C) | PE (g) | activity (kg·mol$^{-1}$(Ti)·h$^{-1}$) | $T_m$[b] (°C) | $M_w$[c] (kg·mol$^{-1}$) | $M_w/M_n$[c] |
|---|---|---|---|---|---|---|---|---|
| 1 | 500 | 10 | 30 | 0.713 | 856 | 128.1 | 54.7 | 17 |
| 2 | 1000 | 10 | 30 | 1.33 | 1600 | 127.7 | 42.2 | 15 |
| 3 | 1500 | 10 | 30 | 1.81 | 2170 | 125.3 | 30.5 | 13 |
| 4 | 2000 | 10 | 30 | 1.53 | 1840 | 126.8 | 25.3 | 12 |
| 5 | 1500 | 10 | 40 | 1.55 | 1860 | 125.6 | 5.81 | 1.7 |
| 6 | 1500 | 10 | 50 | 1.44 | 1730 | 125.3 | 5.55 | 1.8 |
| 7 | 1500 | 10 | 60 | 0.754 | 905 | 125.0 | 4.80 | 1.6 |
| 8 | 1500 | 5 | 30 | 1.17 | 2810 | 125.2 | 22.3 | 7.1 |
| 9 | 1500 | 30 | 30 | 2.63 | 1050 | 125.8 | 40.8 | 17 |

[a] Conditions: 5 $\mu$mol of Ti; 10 atm of ethylene; toluene (total volume 100 mL). [b] Determined by DSC. [c] Determined by GPC.

somewhat shorter than a normal one, together with the C−N bond (C11−N2 1.309(3) Å), suggests a delocalized bonding motif within the amidate backbone where the negative charge is mostly localized on the nitrogen atom. The Ti−N bond (Ti1−N2 2.117(2) Å) and Ti−O bond (Ti1−O1 2.0697(2) Å) are similar to previous amidate-based titanium complexes.[15a,c,d] The Cp ring is planar (maximum deviation from the plane of 0.003 Å for C20) with a typical Ti−Cp$_{cent}$ distance of 2.017 Å. The dihedral angle of the planes defined by the Cp ring and the chelating ring is 23.7°, while the dihedral angles between the chelating ring and the phenyl group or quinoline ring are 35.9° or 61.1°, respectively. Two chlorine atoms are located *cis* to each other, while the Ti−Cl bonds are almost identical (Ti1−Cl1 2.2944(1) Å and Ti1−Cl2 2.2906(9) Å) with an angle of 93.4°. The molecular structures of complexes **C2** and **C4** (see Supporting Information) are quite similar without distinct differences in structural features.

**2.2. Catalytic Behavior toward Ethylene Polymerization. Influences of Al/Ti Molar Ratio, Reaction Temperature, and Time on the Catalytic Behavior of C6.** The reaction conditions in ethylene polymerization have been optimized for procatalyst **C6**. Good catalytic performances are observed in the presence of MAO or MMAO as the cocatalyst, of which MAO gives better results than MMAO. For example, for the molar ratio of Al/Ti = 1500:1 under 10 atm of ethylene pressure, the catalytic activity is 1560 kg mol$^{-1}$(Ti) h$^{-1}$ using MMAO, while the system with MAO gives an activity of 2170 kg mol$^{-1}$(Ti) h$^{-1}$ (entry 3, Table 1). Therefore detailed investigations have been carried out employing MAO through varying the ratios of Al/Ti, reaction temperature, and time, and the results are tabulated in Table 1.

According to observations at different Al/Ti ratios ranging from 500 to 2000 (entries 1−4, Table 1), the maximum activity is shown at an Al/Ti molar ratio of 1500 (entry 3, Table 1). Such a phenomenon can be well clarified by the influence of the Al concentration on the termination of polymer chains.[5f,18] In addition, the obtained polyethylene exhibits lower $M_w$ values when the ratio of Al:Ti is increased, because the chain transfer increases with high Al concentration.[18,19]

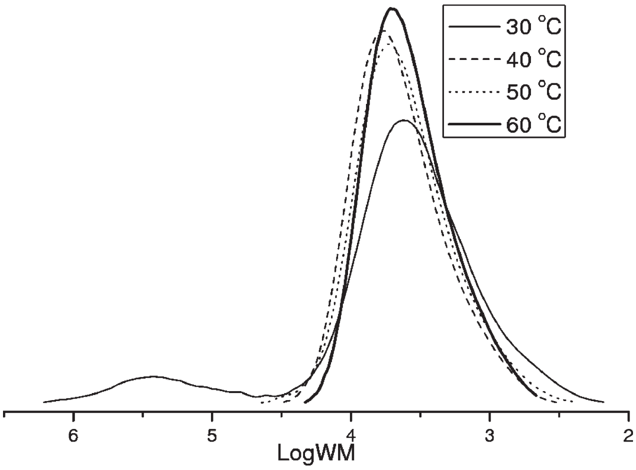

**Figure 2.** GPC profiles of PEs obtained from entries 3 and 5−7 in Table 1.

**Table 2. Ethylene Polymerization with C1−C7/MAO**[a]

| entry | procat. | PE (g) | activity (kg·mol$^{-1}$(Ti)·h$^{-1}$) | $T_m$[b] (°C) | $M_w$[c] (kg·mol$^{-1}$) | $M_w/M_n$[c] |
|---|---|---|---|---|---|---|
| 1 | **C1** | 1.28 | 1540 | 127.7 | 231 | 4.3 |
| 2 | **C2** | 1.11 | 1330 | 129.3 | 188 | 5.5 |
| 3 | **C3** | 0.966 | 1160 | 130.8 | 336 | 8.6 |
| 4 | **C4** | 0.815 | 978 | 131.8 | 437 | 4.1 |
| 5 | **C5** | 0.840 | 1080 | 132.1 | 180 | 5.6 |
| 6 | **C6** | 1.81 | 2170 | 125.3 | 30.5 | 13 |
| 7 | **C7** | 1.72 | 2060 | 126.7 | 20.1 | 5.8 |
| 8 | $CpTiCl_3$ | 0.235 | 282 | 129.0 | 99.2 | 3.0 |

[a] Conditions: 5 $\mu$mol of Ti; 10 atm of ethylene; Al/Ti = 1500; 30 °C; 10 min; total volume, 100 mL. [b] Determined by DSC. [c] Determined by GPC.

Regarding the thermal stability of complex **C6**, its activities significantly decrease with elevated reaction temperature from 30 to 60 °C (entries 3, 5−7, Table 1). In contrast to the current system, half-titanocene chlorides bearing tridentate *N*-(2-benzimidazolylquinolin-8-yl)benzamidates exhibit higher activities on elevating the temperature and possess good thermal stability.[13b] The multidentate coordination of ligands is helpful in the thermal stability of half-titanocene complexes and their active species. This observation that the activity decreases at high temperature was also found in the catalytic system of $Cp_2TiCl_2$ due to the bimolecular disproportionation termination.[20] In terms of the molecular weights of the resultant polyethylenes (PEs), remarkable differences have been found between reactions at 30 °C and those above 40 °C. At 30 °C, the **C6**/MAO system affords PEs with a bimodal molecular weight distribution, while PEs with a monomodal distribution are obtained at 40 °C or above (Figure 2). The influence of reaction temperatures or activators on the molecular weight distribution is also observed in α-diimine

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**Table 3. Copolymerization of Ethylene with 1-Hexene or 1-Octene with C6/MAO**[a]

| entry | 1-hexene (mol $L^{-1}$) | 1-octene (mol $L^{-1}$) | polymer (g) | activity (kg·$mol^{-1}$(Ti)·$h^{-1}$) | $T_m$[b] (°C) | $M_w$[c] (kg·$mol^{-1}$) | $M_w/M_n$[c] |
|---|---|---|---|---|---|---|---|
| 1 | 0.1 | 0 | 1.98 | 2380 | 112.9 | 223 | 7.7 |
| 2 | 0.2 | 0 | 1.86 | 2230 | 108.4 | 195 | 3.3 |
| 3 | 0.5 | 0 | 1.78 | 2140 | 104.0 | 473 | 4.6 |
| 4 | 1.0 | 0 | 1.22 | 1460 | 94.4 | 299 | 2.6 |
| 5 | 0 | 0.1 | 1.71 | 2050 | 109.8 | 257 | 3.5 |
| 6 | 0 | 0.2 | 1.44 | 1730 | 105.3 | 268 | 2.8 |
| 7 | 0 | 0.5 | 1.23 | 1480 | 104.7 | 239 | 1.8 |
| 8 | 0 | 1.0 | 1.07 | 1280 | 93.5 | 230 | 3.4 |
| 9[d] | 0.5 | 0 | 0.158 | 31.6 | 110.9 | 54.5 | 1.6 |

[a] Conditions: 5 μmol of catalysts; 10 atm of ethylene; 10 min; Al/Ti = 1500; 30 °C; toluene (total volume 100 mL). [b] Determined by DSC. [c] Determined by GPC. [d] 1 atm of ethylene; 60 min; toluene (total volume 50 mL).

nickel or bis(imine)pyridine iron complexes.[21] It is assumed that the active species above 40 °C are uniform; however, those active sites could not be prolonged in ethylene insertions for high molecular weight PEs. Due to the highly exothermal nature of the polymerization reaction, we had difficulties controlling the reaction temperature below 30 °C. The catalytic system produces highly active species for ethylene polymerization at 30 °C; however, active species would probably be changed into multiactive sites and PEs with a bimodal distribution would be obtained because of reaction temperature fluctuations during the exothermal polymerization. Regarding the lifetime of the **C6**/MAO system (entries 3, 8, and 9, Table 1), the activities decreased with extending the reaction time to 5, 10, or 30 min.

**Ligands' Environmental Effect on the Catalytic Behavior of Procatalysts C1−C7.** Using the optimized conditions from above (10 atm of ethylene, 30 °C, and Al/Ti 1500), the procatalysts **C1**−**C7** have been examined to understand the substituent effects of the ligands. For comparison, the polymerization using $CpTiCl_3$ was also conducted. The results are collected in Table 2. In general, all procatalysts show high activities in the range 978 to 2170 kg·$mol^{-1}$(Ti)·$h^{-1}$ (entries 1−7, Table 2), while $CpTiCl_3$ gave an activity of 282 kg·$mol^{-1}$(Ti)·$h^{-1}$.

Their catalytic activities vary in the order **C6** (R = OMe and Cp′ = Cp*) > **C7** (Me and Cp*) > **C1** (OMe and Cp) > **C2** (Me and Cp) > **C3** (H and Cp) > **C5** (Cl and Cp) > **C4** (F and Cp). In terms of steric influence, the bulky Cp* enhances the activity of its procatalyst (**C6** vs **C1**, and **C7** vs **C2**) because the active species are better protected in the polymerization process.[18] On the other hand, the electron-donating substituents of the amidates and Cp* could increase the electron density of titanium and stabilize the active species, which are favorable for the alkyl−Ti bond and a *cis*-located vacant coordination site for ethylene, therefore resulting in a better activity.[18,22] In addition, the molecular weights of the resultant PEs are also catalyst-dependent; the $M_w$ values of PEs by procatalysts **C1**−**C5** (180−437 kg·$mol^{-1}$) are far higher than that produced by $CpTiCl_3$ (99.2 kg·$mol^{-1}$). Concerning the same ancillary ligands, the procatalysts bearing Cp* produced lower molecular weight PEs than those ligated by Cp (**C6** vs **C1**, and **C7** vs **C2**). Less resistance around the active species would be favorable for producing polyolefins with higher molecular weights. It is supposed that in the titanium cyclopentadienylamide catalytic systems, chain-increasing processes occupy more space in the coordination sphere of titanium than chain transfer. Therefore bulky ligands occupying more space around titanium disfavor chain propagation, but increase the chain transfer and result in PEs with lower molecular weights.

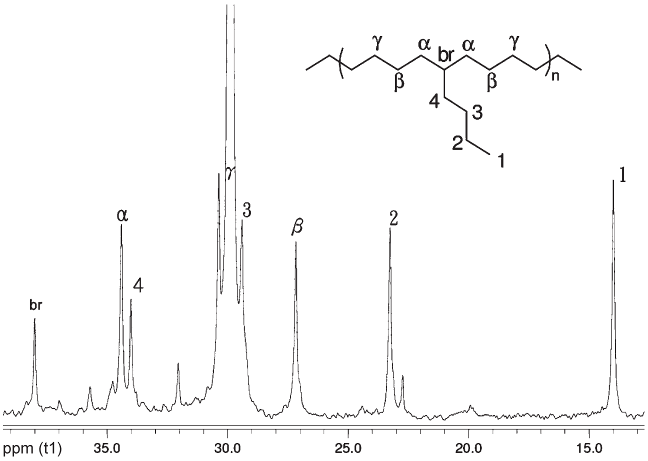

**Figure 3.** $^{13}C$ NMR spectrum of ethylene/1-hexene copolymer by the **C6**/MAO system (entry 3, Table 3).

### 2.3. Copolymerization of Ethylene/1-Hexene and Ethylene/1-Octene.

In addition to ethylene polymerization for PEs, the copolymerization of ethylene with 1-hexene or 1-octene was also investigated, using the representative example of procatalyst **C6**. The detailed copolymerization of ethylene/1-hexene or octene by **C6**/MAO has been successfully carried out, and the results are illustrated in Table 3.

In comparison with its ethylene polymerization activity (2170 kg·$mol^{-1}$(Ti)·$h^{-1}$, entry 6, Table 2), the positive effect of comonomer is observed at low concentration of 1-hexene (entries 1 and 2, Table 3); however, the activities decreased with a further increase of the concentration of 1-hexene (entries 3 and 4, Table 3). This is similar to observations for the imino-indolate half-titanocenes.[14] DSC analysis shows melting points of the obtained polymers in the range 103 to 94 °C, and the $^{13}C$ NMR spectrum (Figure 3) of the resultant poly(ethylene-*co*-1-hexene) (entry 3, Table 3) reveals a typical spectrum of linear low-density polyethylene (LLDPE) with a 14.7 mol % 1-hexene incorporation. Comparing the properties of the copolymers obtained by our previous half-titanocene procatalysts,[13b] although reaction parameters are not the same, reaction conditions for each catalytic system were optimized, and the current system produced copolymers with higher 1-hexene incorporation. Less crowding around titanium in the systems employed herein is a plausible cause for this. The 1-hexene incorporation ability herein

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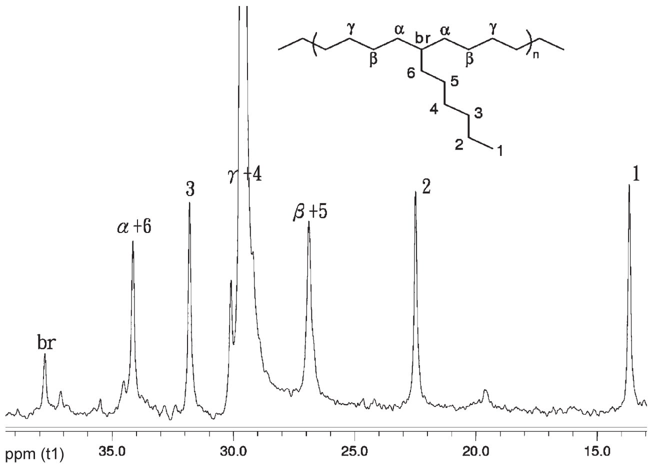

**Figure 4.** $^{13}$C NMR spectrum of ethylene/1-octene copolymer by the **C6**/MAO system (entry 7, Table 3).

is also higher than those reported by others.[23,24] At a fixed 1-hexene concentration, increasing ethylene pressure leads to higher productivity and produces polymers with higher molecular weight (entry 1 vs 9, Table 3).

Similarly, the ethylene/1-octene copolymerization was also studied, and the results are summarized in Table 3. A comparison of the ethylene/1-hexene copolymerization with ethylene/1-octene copolymerization reveals slightly lower activities (entry $n$ vs entry $n + 4$, $n = 1-4$, Table 3). DSC analysis of the resultant copolymers shows melting points from 93 to 110 °C. Figure 4 shows the $^{13}$C NMR spectrum of ethylene/1-octene copolymer produced by the **C6**/MAO system (entry 7, Table 3), and it indicates a 16.3 mol % incorporation of 1-octene.

## 3. Conclusions

The amidate half-titanocene dichlorides, $Cp'Ti(\mathbf{L})Cl_2$ ($Cp'$ = Cp or Cp*; **L** = amidate ligand, **C1**−**C7**), have been synthesized and fully characterized, including single-crystal X-ray diffraction for **C2** and **C4**. All procatalysts show high activities toward ethylene polymerization in the presence of MAO. The procatalysts bearing substituted cyclopentadienyl groups give higher activity, while the use of stronger electron-donating groups of arylamidates enhances the catalytic activities of the corresponding procatalysts. It is likely there is a single active species above 40 °C, which produces PEs with narrow molecular weights. Regarding the results with procatalyst **C6**, the copolymerization of ethylene with 1-hexene or 1-octene produced copolymers incorporating branching of about 15%.

## 4. Experimental Section

**4.1. General Considerations.** All manipulations of air- and/or moisture-sensitive compounds were performed under a nitrogen atmosphere in a glovebox or using standard Schlenk techniques. *N*-(2-Methylquinolin-8-yl)benzamide derivatives were prepared as already reported.[13b,16] Methylaluminoxane (MAO, 1.46 M in toluene) was purchased from Albemarle. Potassium hydride (KH) was bought from Beijing Chemical Regent Company and washed with hexane before use to remove any mineral oil. Tetrahydrofuran (THF), toluene, hexane, and heptane were refluxed over sodium and benzophenone, distilled, and then stored under a nitrogen atmosphere. Dichloromethane ($CH_2Cl_2$) was distilled over calcium hydride and stored under a nitrogen atmosphere. Highly pure ethylene was purchased from Beijing Yansan Petrochemical Co. and used as received. IR spectra were recorded on a Perkin-Elmer FT-IR 2000 spectrometer using KBr disks in the range 4000−400 cm$^{-1}$. Elemental analysis was performed on a Flash EA 1112 microanalyzer. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard. DSC trace and melting points of polyethylenes were obtained from the second scanning run on a Perkin-Elmer DSC-7 at a heating rate of 10 °C/min. $^1$H NMR and $^{13}$C NMR spectra of the polymers were recorded on a Bruker DMX-300 MHz instrument at 110 °C in deuterated 1,2-dichlorobenzene with TMS as an internal standard. Molecular weights and polydispersity indices (PDI) of (co)polyethylene were determined using a PL-GPC220 instrument at 135 °C in 1,2,4-trichlorobenzene with polystyrene as the standard.

**4.2. Synthesis of Complexes C1−C7.** **$\eta^5$-Cyclopentadienyl[*N*-(2-methylquinolin-8-yl)-*p*-methoxybenzamide]titanium Dichlorides (C1).** To a stirred solution of 4-methoxy-*N*-(2-methylquinolin-8-yl)benzamide (0.585 g, 2.00 mmol) in dried THF (30 mL) at room temperature was added KH (0.080 g, 2.00 mmol). The mixture was allowed to stir for 12 h, and a yellow suspension was obtained. At −78 °C, 20 mL of a $CpTiCl_3$ (0.438 g, 2.00 mmol) solution in THF was added dropwise over a 30 min period. The resultant mixture was allowed to warm to room temperature and stirred for an additional 12 h. The residue, obtained by removing the solvent under vacuum, was extracted with toluene (3 × 20 mL). The combined filtrates were concentrated under vacuum to reduce the volume to 5 mL and then filtered to give a red solid (0.781 g, 1.64 mmol, yield 82.0%). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.02 (d, $J$ = 8.4 Hz, 1H, quin), 7.65 (d, $J$ = 7.7 Hz, 2H, quin), 7.47 (dd, $J_1$ = 7.7 Hz, $J_2$ = 7.8 Hz, 1H, quin), 7.29 (d, $J$ = 8.4 Hz, 2H, aryl), 7.22 (d, $J$ = 8.4 Hz, 1H, quin), 7.04 (s, 5H, Cp), 6.57 (d, $J$ = 8.3 Hz, 2H, aryl), 3.69 (s, 3H, $OCH_3$), 2.59 (s, 3H, $CH_3$). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 173.8, 162.8, 158.3, 142.6, 141.9, 136.4, 131.0, 127.6, 126.3, 126.0, 125.9, 123.5, 122.2, 121.5, 113.5, 55.4, 25.4. Anal. Calcd for $C_{23}H_{20}Cl_2N_2O_2Ti$: C, 58.13; H, 4.24; N, 5.90. Found: C, 58.03; H, 4.28; N, 5.53.

**$\eta^5$-Cyclopentadienyl[*N*-(2-methylquinolin-8-yl)-*p*-methylbenzamide]titanium Dichlorides (C2).** Using the same procedure for the synthesis of **C1**, **C2** was obtained as a red solid in 80.5% yield (0.739 g, 1.61 mmol). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.01 (d, $J$ = 8.3 Hz, 1H, quin), 7.64 (d, $J$ = 7.8 Hz, 2H, quin), 7.46 (dd, $J_1$ = 7.9 Hz, $J_2$ = 7.6 Hz, 1H, quin), 7.27−7.16 (m, 3H, quin and aryl), 7.05 (s, 5H, Cp), 6.89 (d, $J$ = 8.0 Hz, 2H, aryl), 2.58 (s, 3H, $CH_3$), 2.21 (s, 3H, $CH_3$). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 174.4, 158.3, 143.0, 142.4, 141.8, 136.4, 129.5, 128.8, 128.1, 127.5, 126.5, 125.9, 123.5, 122.1, 121.5, 25.3, 21.6. Anal. Calcd for $C_{23}H_{20}Cl_2N_2OTi$: C, 60.16; H, 4.39; N, 6.10. Found: C, 60.13; H, 4.66; N, 5.92.

**$\eta^5$-Cyclopentadienyl[*N*-(2-methylquinolin-8-yl)benzamide]titanium Dichlorides (C3).** Using the same procedure for the synthesis of **C1**, **C3** was obtained as a red solid in 77.2% yield (0.687 g, 1.54 mmol). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.00 (d, $J$ = 8.4 Hz, 1H, quin), 7.68 (d, $J$ = 7.4 Hz, 1H, quin), 7.63 (d, $J$ = 7.9 Hz, 1H, quin), 7.46 (dd, $J_1$ = 7.8 Hz, $J_2$ = 7.8 Hz, 1H, quin), 7.33 (d, $J$ = 7.6 Hz, 2H, aryl), 7.28−7.23 (m, 1H, quin), 7.19−7.16 (m, 1H, aryl), 7.08 (d, $J$ = 7.7 Hz, 2H, aryl), 7.04 (s, 5H, Cp). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 174.7, 158.3, 142.1, 141.6, 136.4, 132.1, 130.0, 128.9, 128.3, 127.9, 127.5, 127.3, 126.2, 125.9, 125.3, 123.5, 122.1. Anal. Calcd for $C_{22}H_{18}Cl_2N_2OTi$: C, 59.36; H, 4.08; N, 6.29. Found: C, 59.10; H, 4.26; N, 6.29.

**$\eta^5$-Cyclopentadienyl[*N*-(2-methylquinolin-8-yl)-*p*-fluorobenzamide]titanium Dichlorides (C4).** Using the same procedure for the synthesis of **C1**, **C4** was obtained as a red solid in 84.0% yield

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(0.778 g, 1.68 mmol). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.11−8.07 (m, 1H, quin), 8.02 (d, $J$ = 8.4 Hz, 1H, quin), 7.70 (d, $J$ = 7.4 Hz, 1H, quin), 7.66 (d, $J$ = 8.1 Hz, 1H, quin), 7.52−7.47 (m, 1H, quin), 7.37−7.33 (m, 1H, aryl), 7.25−7.23 (m, 1H, aryl) 7.03 (s, 5H, Cp), 6.77 (d, $J$ = 8.2 Hz, 2H, aryl), 2.57 (s, 3H, $CH_3$). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 173.6, 158.4, 141.9, 141.4, 136.5, 131.1, 131.0, 129.1, 128.3, 127.6, 126.2, 126.1, 126.0, 125.4, 123.6, 122.3, 122.2, 25.3. Anal. Calcd for $C_{22}H_{17}Cl_2FN_2OTi$: C, 57.05; H, 3.70; N, 6.05. Found: C, 57.03; H, 3.96; N, 5.99.

**$\eta^5$-Cyclopentadienyl[*N*-(2-methylquinolin-8-yl)-*p*-chlorobenzamide]titanium Dichlorides (C5).** Using the same procedure for the synthesis of **C1**, **C5** was obtained as red solid in 79.5% yield (0.763 g, 1.59 mmol). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.02 (d, $J$ = 8.0 Hz, 2H, quin), 7.70 (d, $J$ = 7.3 Hz, 1H, quin), 7.65 (d, $J$ = 8.0 Hz, 1H, quin), 7.54−7.47 (m, 1H, quin), 7.28−7.26 (m, 2H, aryl), 7.06 (d, $J$ = 7.9 Hz, 2H, aryl), 7.03 (s, 5H, Cp), 2.57 (s, 3H, $CH_3$). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 173.8, 164.2, 158.4, 157.4, 141.8, 136.5, 129.9, 129.1, 129.0, 128.7, 128.3, 128.2, 123.6, 122.6, 122.2, 25.3. Anal. Calcd for $C_{22}H_{18}Cl_3N_2OTi$: C, 55.09; H, 3.57; N, 5.84. Found: C, 54.93; H, 3.76; N, 5.88.

**$\eta^5$-Pentamethylcyclopentadienyl[*N*-(2-methylquinolin-8-yl)-*p*-methoxybenzamide]titanium Dichlorides (C6).** Using the same procedure for the synthesis of **C1**, **C6** was obtained as a red solid in 89.0% yield (0.970 g, 1.78 mmol). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.93 (d, $J$ = 8.4 Hz, 1H, quin), 7.87 (d, $J$ = 7.4 Hz, 1H, quin), 7.56 (d, $J$ = 8.0 Hz, 1H, quin), 7.45 (dd, $J_1$ = 8.4 Hz, $J_2$ = 8.4 Hz, quin), 7.30 (d, $J$ = 8.5 Hz, 2H, aryl), 7.09 (d, $J$ = 8.4 Hz, 1H, quin), 6.53 (d, $J$ = 8.5 Hz, 2H), 3.67 (s, 3H, $CH_3$), 2.49 (s, 3H, $CH_3$), 2.34 (s, 15H, $CH_3$). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 174.8, 162.4, 157.1, 141.9, 136.5, 136.0, 134.1, 130.5, 129.1, 126.1, 122.4, 116.3, 114.0, 112.9, 55.5, 25.4, 13.8. Anal. Calcd for $C_{28}H_{30}Cl_2N_2O_2Ti$: C, 61.67; H, 5.55; N, 5.14. Found: C, 61.55; H, 5.76; N, 5.18.

**$\eta^5$-Pentamethylcyclopentadienyl[*N*-(2-methylquinolin-8-yl)-*p*-methylbenzamide]titanium Dichlorides (C7).** Using the same procedure for the synthesis of **C1**, **C7** was obtained as a red solid in 85.2% yield (0.901 g, 1.70 mmol). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.95 (d, $J$ = 8.3 Hz, 1H, quin), 7.82 (d, $J$ = 7.3 Hz, 1H, quin), 7.50 (d, $J$ = 8.0 Hz, 1H, quin), 7.42 (dd, $J_1$ = 8.3 Hz, $J_2$ = 8.3 Hz, 1H, quin), 7.35 (d, $J$ = 8.5 Hz, 2H, aryl), 7.09 (d, $J$ = 8.3 Hz, 1H, quin), 6.76 (d, $J$ = 8.5 Hz, 2H, aryl), 2.47 (s, 3H, $CH_3$), 2.35(s, 15H, $CH_3$), 2.21 (s, 3H, $CH_3$). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 174.2, 161.4, 155.1, 141.0, 137.5, 136.0, 134.7, 132.5, 129.8, 128.1, 123.4, 116.5, 114.1, 112.9, 25.4, 21.6, 13.8. Anal. Calcd for $C_{28}H_{30}Cl_2N_2OTi$: C, 63.53; H, 5.71; N, 5.29. Found: C, 63.46; H, 5.75; N, 5.25.

**4.3. Procedures for Ethylene Polymerization and Copolymerization of Ethylene with α-Olefin.** A 250 mL autoclave stainless steel reactor equipped with a mechanical stirrer and a temperature controller is heated under vacuum for at least 2 h at 80 °C. It is allowed to cool to the required reaction temperature under ethylene atmosphere and then charged with toluene (with comonomer), the desired amount of cocatalyst (MAO), and a toluene solution of the catalytic precursor. The total volume is 100 mL. After reaching the reaction temperature, the reactor is sealed and pressurized to 10 atm of ethylene pressure. The ethylene pressure is kept constant during the reaction time by feeding the reactor with ethylene. After the desired reaction time, the polymerization reaction is quenched by addition of a solution of ethanol containing HCl. The precipitated polymer is washed with ethanol several times and dried under vacuum.

**4.4. X-ray Structure Determination.** Crystals of **C2** and **C4** suitable for single-crystal X-ray analysis are obtained by laying heptane on their toluene solutions. Single-crystal X-ray diffraction for **C2** and **C4** are performed on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å) at 173(2) K. Cell parameters are obtained by global refinement of the positions of all collected reflections. Intensities are corrected for Lorentz and polarization effects and empirical absorption. The structures are solved by direct methods and refined by full-matrix least-squares on $F^2$. All non-hydrogen atoms are refined anisotropically. Structure solution and refinement are performed by using the SHELXL-97 package.[25] Crystal data collection and refinement details for all compounds are available in the Supporting Information.

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**Supporting Information Available:** GPC diagrams of corresponding polyolefins, the molecular structure of compound **C4**, crystal data and processing parameters for complexes **C2** and **C4** and their CIF file giving X-ray crystal structural data. These materials are available free of charge via the Internet at http://pubs.acs.org.

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