Half-titanocene 5-*t*-butyl-2-(1-(arylimino)methyl)quinolin-8-olate chlorides: Synthesis, characterization and ethylene (co-)polymerization behavior

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Abstract: A series of half-titanocene chloride complexes bearing 5-*t*-butyl-2-(1-(arylimino)methyl)quinolin-8-olates, $CpTiLCl_2$, has been synthesized in acceptable yields by the stoichiometric reaction of $CpTiCl_3$ with potassium 5-*t*-butyl-2-(1-(arylimino)methyl)quinolin-8-olates. All half-titanocene complexes were fully characterized by elemental analysis and NMR spectroscopy, and the molecular structures of complexes **C1** and **C2** (what are C1 and C2?) were confirmed by single-crystal X-ray diffraction. When activated with methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), all titanium complexes exhibited good activities (up to 4.8×10^5 $g \cdot mol^{-1}(Ti) \cdot h^{-1}$) towards ethylene polymerization. The obtained polyethylene exhibited ultrahigh molecular weight (up to 11.82×10^5 $g \cdot mol^{-1}$) with narrow polydispersity. Furthermore, effective co-polymerization of ethylene with 1-hexene or 1-octene was achieved with several percentages of co-monomer incorporation in the resultant polyethylenes.

1. Introduction

Still today, the most important thermoplastics are polyethylene-based materials,[1]

which have been mass produced using the now well-known catalytic systems of Zigler-Natta,[2] Phillips[3] and more increasingly metallocenes[4] and half-metallocenes.[5] By retaining the high activities and single-site features of some of the more sophisticated metallocene catalysts,[4a,5a,5b] constrained geometry catalysts (CGC) or so-called half-metallocenes have been commercialized, exhibiting high efficiency and good co-polymerization performance,[5c,5d] however, the critical drawback with metallocence catalysts is the tedious synthetic procedure required which leads to the high cost, as well as other technical problems. To overcome the synthetic problem, non-bridged half-metallocene catalysts have been extensively explored,[6] and more recently, titanium or zirconium complexes bearing multi-dentate ligands related to the FI and PI models have been developed and performed with high activities, but with short lifetimes due to high sensitivity.[7] Other non-bridged half-metallocene complexes based on newly developed multi-dentate anionic ligands have been reported,[8] and importantly the new complex pre-catalysts showed high catalytic activities and good control for copolymerizations.[8d,8e] The ligands can be classified as mono-anionic ancillary ligands with mono-dentate,[9] bi-dentate[10] and di-anionic ligands of tri-dentate coordination;[11] these half-metallocene pre-catalysts have shown varied catalytic activities and controllable properties of the obtained polyethylene by varying the ancillary ligands used.

Recently the influence of fine tuning ligands has been specially considered for titanium complex pre-catalysts. To design the series of anionic tridentate ligands, different substances have been used such as 2-acylquinolin-8-ol,[12,13] 2-acetyl-quinolin-8-ol,[13,14] and 2-propionylquinolin-8-ol.[12,15] The corresponding 2-iminoquinolin-8-olate trichlorotitanium[15a] and half-titanocene dichlorides[13,14,15b] were successfully prepared and investigated for their catalytic behavior in ethylene (co-)polymerizations, which revealed a significant catalytic influence was exerted by the substituent on the ligands, and this was also reflected in the properties of polyethylene obtained. These ligand variations mostly tinkered with the substituents close to the coordinating atoms,[12-15] however, there were a few reports investigating the influence of substituents crossing-over cyclic group to active

species.[16] On variation of the different alkyl-substituents of the 2-(1-alkyl-2-benzimidazolyl)-6-(1- (arylimino)ethyl)pyridylmetal [Fe(II) or Co (II)] dichlorides,[16] it was noted that the use of less bulky substituents resulted in higher catalytic activities in ethylene oligomerization – not sure this is relevant to this paper!. Subsequently, 5-*t*-butyl-2-acylquinolin-8-ol was prepared for comparison with the analog 2-acylquinolin-8-ol,[12,13] and a series of 5-*t*-butyl-2-(1-(arylimino)methyl)quinolin-8-ol derivatives were prepared by the reaction of 5-*t*-butyl-2-acylquinolin-8-ol with different anilines. Following the literature procedure,[13] the title half-titanocene complexes were synthesized in reasonable isolated yields. Upon activation with either MAO or MMAO, these titanium complexes showed good catalytic activities towards ethylene polymerization, and moreover for the co-polymerization of ethylene with 1-hexene or 1-octene. The synthesis and characterization of the 5-*t*-butyl-2-(1-(arylimino)methyl)quinolin-8-ol derivatives and their titanium complexes are reported along with their catalytic performances for ethylene homo- (co-)polymerization.

2. Results and discussion

2.1 Synthesis and characterization of half-titanocene complexes (C1–C6)

The 5-*t*-butyl-2-(1-(arylimino)methyl)quinolin-8-ol derivatives (**L1**–**L5**) were prepared in decent yields by the condensation reaction of 5-*t*-butyl-8-hydroxyquinoline-2-carbaldehyde with various anilines (scheme 1). All the organic compounds were characterized by the FT-IR, ^{1}H and ^{13}C NMR spectroscopy, and by elemental analysis. The organic compounds were deprotonated by reaction with a stoichiometric amount of KH to form the potassium 5-*t*-butyl-2-(1-(arylimino)methyl)quinolin-8-olates, which were then reacted with (η^5-C$_5$H$_5$)titanium trichloride (CpTiCl$_3$) to afford the desired half-titanocene dichloride complexes. These titanium complexes were fully characterized and the molecular structures of the complexes **C1** and **C2** were confirmed by single crystal X-ray diffraction studies.
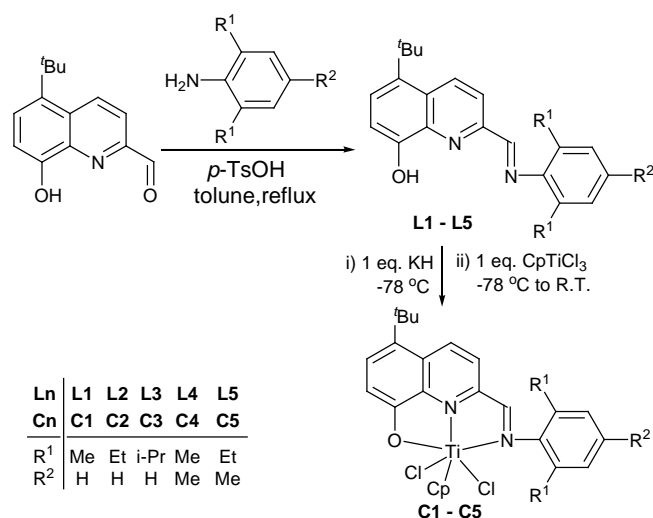
Scheme 1 Synthesis of complexes **C1 – C5**

2.2 Molecular structures

Single crystals of complexes **C1** and **C2** suitable for X-ray diffraction analyses were individually obtained from their toluene solutions on layering with *n*-hexane at room temperature. The molecular structures revealed a pseudo octahedral geometry around the titanium center comprising the tridentate ligand, two chlorine atoms and one η^5-Cp ring. The molecular structures are illustrated in Fig. 1 and Fig. 2 and the selected bond lengths and angles are tabulated in Table 1.
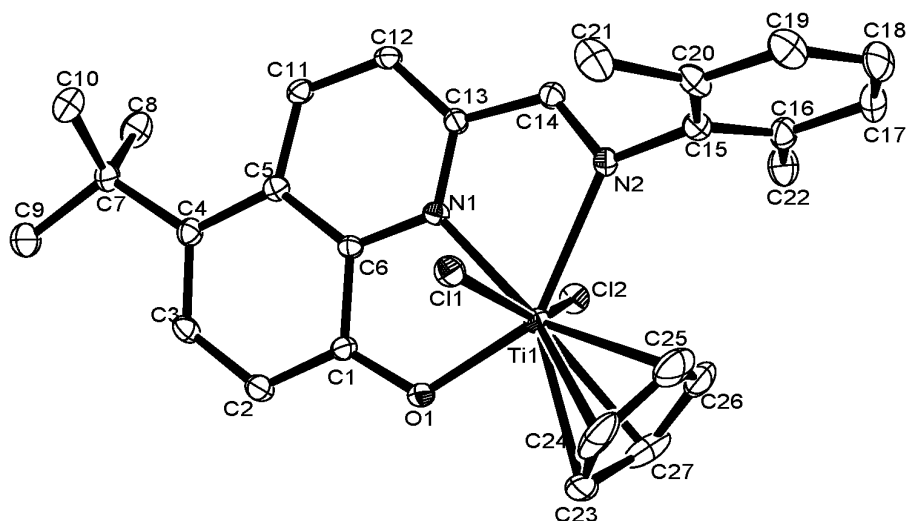

Fig. 1 ORTEP drawing of the molecular structure of **C1** (ellipsoids enclose 30 % electronic density; **H** atoms were omitted for clarity).
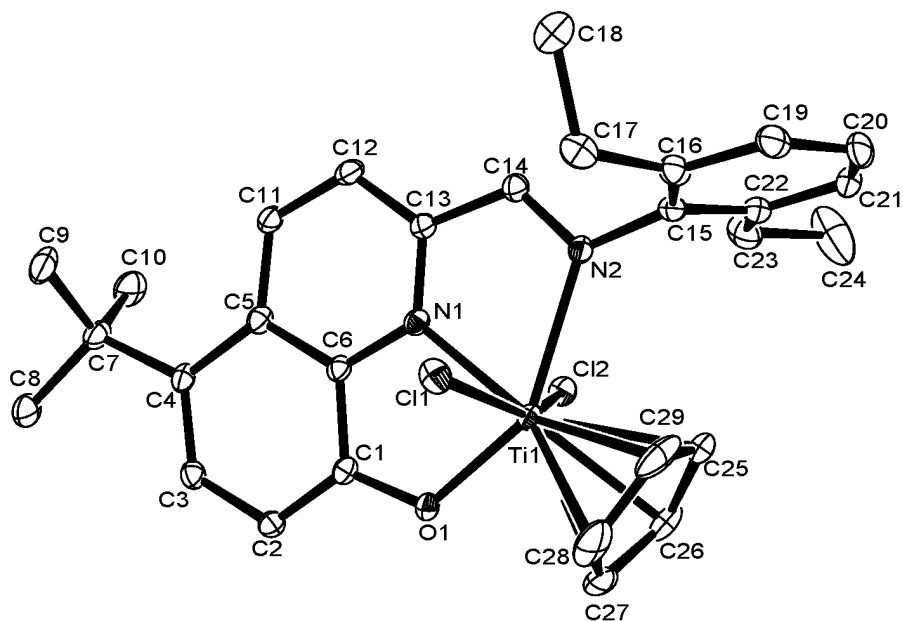
Fig. 2 ORTEP drawing of the molecular structure of **C2** (ellipsoids enclose 30 % electronic density; **H** atoms were omitted for clarity).

Table 1 Selected bond lengths (Å) and angles (°) for **C1** and **C2**

	C1	C2
Bond lengths (Å)		
Ti1–O1	1.967(3)	1.935(3)
Ti1–N1	2.147(3)	2.134(3)
Ti1–N2	2.376(3)	2.364(3)
Ti1–Cl1	2.4285(14)	2.418(12)
Ti1–Cl2	2.4168(13)	2.465(12)
Ti1–Cp	2.076	2.068
Bond angles (°)		
O1–Ti1–N1	76.06(12)	76.83(3)
O1–Ti1–N2	145.70(11)	146.85(3)
N1–Ti1–N2	69.70(11)	70.02(3)
O1–Ti1–Cl1	87.96(9)	90.61 (8)
N1–Ti1–Cl1	76.37(9)	76.95(9)
N2–Ti1–Cl1	82.06(8)	82.58(8)

O1–Ti1–Cl2	90.82(9)	87.64(8)
N1–Ti1–Cl2	76.30(9)	74.57(9)
N2–Ti1–Cl2	83.39(9)	83.25(8)
Cl1–Ti1–Cl2	152.10(5)	151.10(4)
Cp–Ti1–N1	150.74	150.31
Cp–Ti1–N2	107.21	107.88
Cp–Ti1–O1	104.67	102.91
Cp–Ti1–Cl1	109.4	102.91
Cp–Ti1–Cl2	102.50	103.49

In the structure of complex **C1** (Fig. 1), all the carbon atoms in Cp ring group are coplanar and the distance between the centroid of the Cp ring and titanium atom is 2.076 Å, however, the $Ti-C_{Cp}$ bond lengths are slightly deviated within the range 2.377(5) Å to 2.391(6) Å ($\Delta Ti-C$ = 0.014 Å). The two Ti-N bonds (Ti1-N1 = 2.147(3) Å, Ti1-N2 = 2.376(3) Å) are consistent with observations for the analogous imino quinolin-8-olate titanium complexes,[13,14] and the Ti1-O1 bond length is 1.967(3) Å. The bond lengths of Ti1-Cl1 (2.4285(14) Å) and Ti-Cl2 (2.4168(13) Å) are slightly different, whilst the angle Cl1-Ti1-Cl2 is 152.10(5)°. Two chelating planes θ Ti1-O1-C1-C6-N1 and θ Ti1-N1-C13-C14-N2 form a dihedral angle at 2.26 °, illustrating near co-planarity.

The molecular structure of complex **C2** (Fig. 2) is very similar to that of complex **C1**, however, the two chelating planes θ Ti1-O1-C1-C6-N1 and θ Ti1-N1-C13-C14-N2 are even closer to being coplanar with the dihedral angle of 0.49°. The dihedral angle of the aryl-imine and the quinoline ring is 81.04° for **C2**, which is slightly larger than that in complex **C1** (77.44°).

2.3 Ethylene polymerization

The complex **C3** was used to select a suitable alkylaluminium reagent, and the co-catalysts MAO and MMAO were found to be most active for this catalytic system. Further investigations were thus conducted separately with either MMAO or MAO.

2.3.1 Polymerization and co-polymerization results by MMAO systems

The catalytic system of **C3/MMAO** was explored to optimize the reaction parameters on catalytic activity, *ie* molar ratios of Al/Ti, reaction time and temperature (Table 2) were all varied.

Table 2 Ethylene polymerization results by the **C3**/**MMAO** systems[a]

Run	Al/Ti	T/°C	t(min)	Polym(g)	Act[b]	$M_w{}^{c,d}$	$M_w/M_n{}^d$	$T_m{}^e$(°C)
1	2000	40	30	0.80	3.20	4.94	2.46	135.0
2	2500	40	30	0.82	3.28	5.94	2.61	134.3
3	3000	40	30	0.92	3.68	7.17	2.77	134.1
4	3500	40	30	0.84	3.36	6.03	3.45	134.6
5	4000	40	30	0.67	2.68	6.08	3.05	134.9
6	3000	20	30	0.43	1.72	8.34	2.66	133.4
7	3000	30	30	0.60	2.40	8.05	2.96	133.9
8	3000	50	30	0.74	2.96	5.68	2.91	136.2
9	3000	60	30	0.59	2.36	4.35	2.49	135.5
10	3000	40	5	0.22	5.28	5.43	1.43	134.4
11	3000	40	15	0.57	4.56	5.68	1.97	133.9

[a] Conditions: 5 $u$mol **C3**, toluene (total volume 100 mL), 10 atm. [b] Activity: 10^5 g·mol^{-1}(Ti)·h^{-1}, [c] 10^5 g·mol^{-1}. [d] Determined by GPC. [e] Determined by DSC.

On varying the Al/Ti molar ratio from 2000 to 4000 (runs 1-5, Table 2) at 40 °C, the best catalytic activity was observed at 3.68×10^5 g·mol^{-1}(Ti)·h^{-1} for the Al/Ti ratio 3000; the higher the activity of the system, the higher was the molecular weight of the obtained polyethylene. In general, the polydispersity of the obtained polyethylene was remained relatively narrow; the tendency for wider distributions (from 2.46 to 3.45, Figure 3) was observed on increasing the molar ratio of Al/Ti.
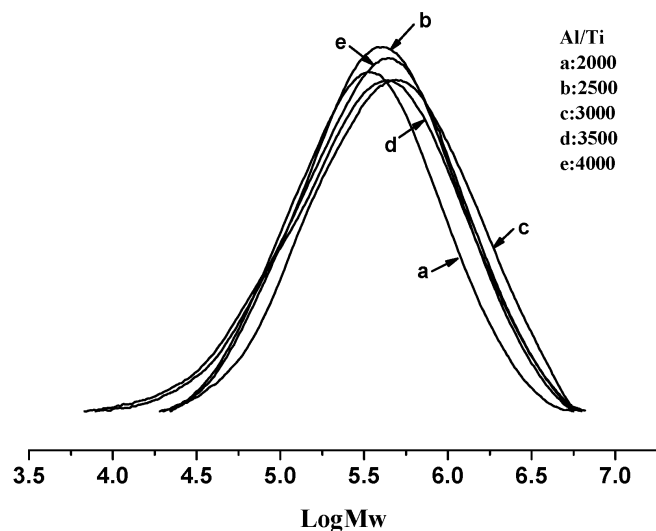
Fig. 3 GPC profiles of PEs obtained from Run 1-5 in Table 2.

The reaction temperature significantly affects the ethylene polymerization performance using Al/Ti 3000 from 20 °C to 60 °C (runs 3, and 6-9 in Table 2, Figure 4), revealing the optimum temperature as 40 °C; the higher reaction temperature, the lower the molecular weight of the polyethylene (8.34×10^5 g·mol^{-1} to 4.35×10^5 g·mol^{-1}). These are considered to result from faster chain termination occurring at higher temperature.
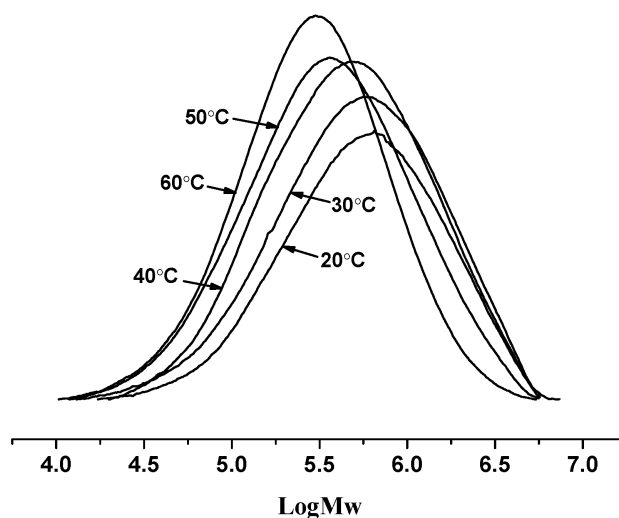

Fig. 4 GPC profiles of PEs obtained from Run 3 and 6-8 in Table 2.

Concerning the lifetime of the active species, the catalytic polymerization was conducted over different reaction times, namely 5 min, 10 min and 30 min (Run 3, 10 and 11, Table 2). Obviously, more polyethylene of higher molecular weight was observed on prolonging the reaction time, however, the activities gradually decreased.

These observations were consistent to previously reported results.[17]

Employing the optimum conditions of Al/Ti ratio 3000 at 40°, all complexes **C1-C5** were investigated for ethylene polymerization (Table 3), which indicated the best performance was for complex **C2** with an activity of 4.8×10^5 g·mol^{-1}(Ti)·h^{-1}. In comparison with the catalytic results obtained for the titanium 2-iminoquinolin-8-olates,[13,14,15] especially the half-titanocene 2-iminoquinolin-8-olates,[13,14,15b] for the current complex pre-catalysts, the presence of the additional *t*-butyl group did not have a positive influence. On the base of a MANCC simulation study,[18] in principle, the better catalytic activities were observed for the early-transition metal complex pre-catalysts with electron-donation substituents[18a] and for the late-transition metal complex pre-catalysts with the electron-withdrawing substituents;[18b-d] however, the turnover point of net charge was observed to affect their catalytic activities. As the η^5-C$_5$H$_5$ is a strong electron-donating substituent, there is no requirement for a substituent with electron-donation features. Better solubility of complexes was possibly achieved through the additional *t*-butyl substituent, though the combined effect did not enhance the catalytic activities of their complexes because the net charge effect is considered to be dominant.

Table 3 Ethylene polymerization by **C1-C5**/**MMAO** systems*^{a}*

Run	Cat.	Polym(g)	Act*^{b}*	M_w*^{c,d}*	M_w/M_n*^{d}*	T_m*^{e}*(°C)
1	C1	0.79	3.16	6.61	2.70	134.5
2	C2	1.20	4.80	6.70	2.75	135.1
3	C3	0.92	3.68	7.17	2.77	134.1
4	C4	0.70	2.80	6.47	3.02	134.5
5	C5	0.90	3.60	8.13	2.42	134.6

^{a} Condition: 5 *u*mol Ti, Al/Ti =3000:1, toluene (total volume 100 mL), 30 min, 40 °C, 10 atm. *^{b}* Activity: 10^5 g·mol^{-1}(Ti)·h^{-1}. *^{c}* 10^5 g·mol^{-1}. *^{d}* Determined by GPC. *^{e}* Determined by DSC.

Concerning the correlations between the nature of the various ligands and the catalytic activities of their half-titanocence complexes, the catalytic activities were

observed in the order **C2** > **C3** > **C5** > **C1** > **C4**, indicating the combined effects of the electronic and steric influences of the alkyl-substituents with better results for the ethyl-substituted derivatives (**C2** and **C5**). In cases having a *para*-methyl substituent, the catalytic activities of their complex pre-catalysts were negatively affected as the results showed in the order **C1** > **C4**, and **C2** > **C5**; these was consistent to the observations for their half-titanocence complex analogs.[14,15b] In general, these complex pre-catalysts produced polyethylene of similar molecular weight, molecular weight distribution (PDI) and also melting points T_m; the high T_m values indicated the linearity of obtained polyethylene.

The co-polymerization of ethylene with either 1-hexene or 1-octene. The half-titanocene pre-catalysts are capable of co-polymerization,[4,5] and here, the scope of the co-polymerization of ethylene with 1-hexene or 1-octene was conducted with the complexes **C1** to **C5** (Table 4). Similar to observations in the literature[10d,11b] and their analogue pre-catalysts,[13,14] the co-monomer had a negative effect on the catalytic activity on increasing the concentration of 1-hexene (Runs 1 – 3 in Table 4). Effective co-polymerization was reflected in the lower melting points of the resultant polyethylene. The activity trend was similar to the ethylene polymerization, *ie* **C2** > **C3** > **C1** > **C5** > **C4**.

Table 4 Co-polymerization by **C1–C5/ MMAO**[a]

Run	Complexes	Monomer	Polymer(g)	Act[b]	M_w[c,d]	M_w/M_n[d]	T_m[e](°C)
1	C3[f]	2 ml	0.33	1.30	7.17	2.74	123.6
2	C3[f]	4 ml	0.22	0.88	6.03	2.57	120.1
3	C3[f]	6 ml	0.18	0.72	8.10	2.36	121.4
4	C1[f]	2 ml	0.27	1.08	6.57	2.68	128.0
5	C2[f]	2 ml	0.40	1.60	6.74	2.74	124.5
6	C4[f]	2 ml	0.14	0.55	5.89	2.55	125.5
7	C5[f]	2 ml	0.24	0.96	6.42	2.69	125.0
8	C1[g]	2 ml	0.24	0.95	5.56	2.45	126.7
9	C2[g]	2 ml	0.41	1.64	6.89	2.50	126.4

10	C3[g]	2 ml	0.32	1.29	7.96	2.40	126.5
11	C4[g]	2 ml	0.18	0.73	8.31	1.45	127.5
12	C5[g]	2 ml	0.22	0.87	8.66	1.86	126.9

[a] Condition: 5 umol Ti, Al/Ti =1500:1, toluene (total volume 100 mL), 30 min, 20 °C, 10 atm. [b] Activity: 10^5 g·mol^{-1}(Ti)·h^{-1}, [c] 10^5 g·mol^{-1}. [d] Determined by GPC. [e] Determined by DSC. [f] 1-hexene. [g] 1-octene.

To confirm the incorporation of 1-hexene or 1-octene in the resultant polymers, ^{13}C NMR measurements of representative samples were carried out; the selected samples are the polymers obtained from the co-polymerization of ethylene with 1-hexene (Run 2, Table 4) and 1-octene (Run 10, Table 4) by the **C3/MMAO** system. Interpreted using the calculation method reported in the literature,[19] 1-hexene was incorporated in 3.2 mol% (Figure 5), meanwhile the 1-octene was incorporated in about 1.8 mol% (Fig. 6). Similar results were observed for the half-titanocene 2-iminoquinolin-8-olates.[13]
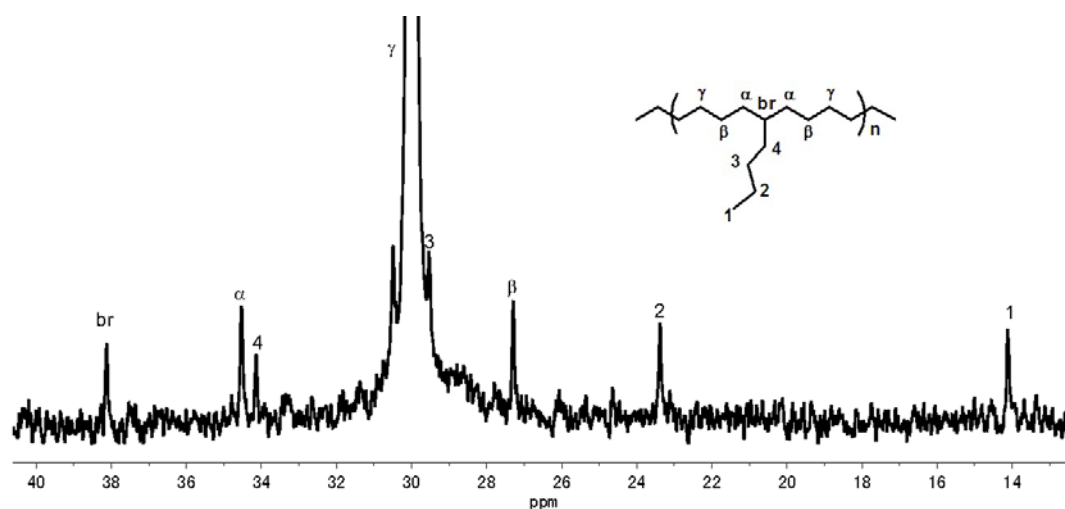

Fig. 5 ^{13}C NMR spectrum of ethylene/1-hexene co-polymer by the **C3/MMAO** system (Run 2, Table 4).
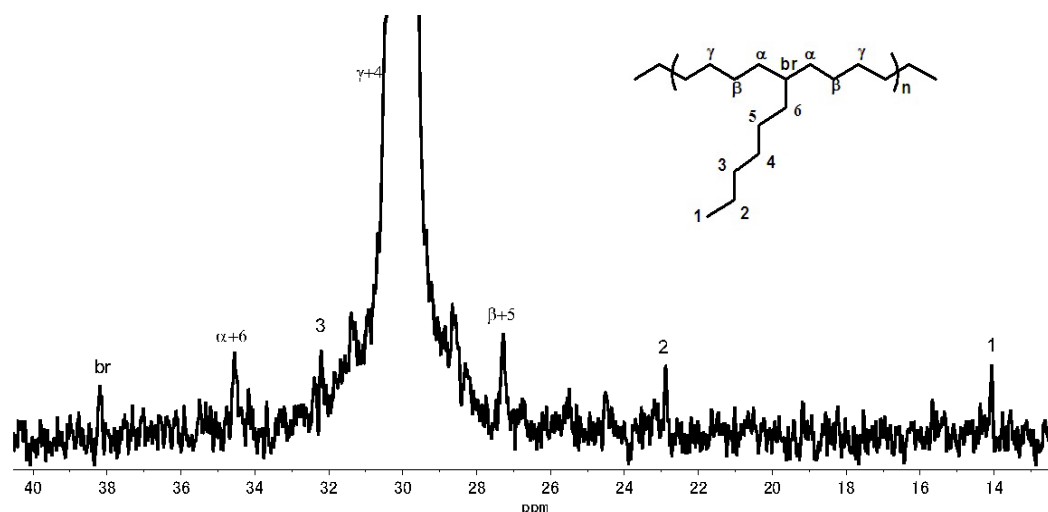
Fig. 6 ^{13}C NMR spectrum of ethylene/1-octene co-polymer by the **C3/MMAO** system (Run 10, Table 4).

2.3.2 Polymerization and co-polymerization results by MAO systems

As well as the catalytic systems with MMAO, the catalytic system with **C3**/MAO was also explored for the optimizing conditions for ethylene polymerization, and results are summarized in Table 5. Varying the Al/Ti ratio from 500 to 2500 (Runs 1-5 in Table 5) at 20 °C, the best activity was observed at 3.76 × 10^5 g·mol^{-1}(Ti)·h^{-1} with Al/Ti 1500. On increasing the reaction temperature (Runs 3, and 6-8 in Table 5), the catalytic activities decreased, and the polyethylene possessed lower molecular weights. In general, the same tendency of catalytic performances was illustrated as the above catalytic system when activated by MMAO, but the catalytic system using MAO produced polyethylene of higher molecular weight.

Table 5 Ethylene polymerization results by **C3**/**MAO** systems^a

Run	Al/Ti	T/°C	t(min)	Polym(g)	Act^b	M_w^{c,d}	M_w/M_n^{d}	T_m^{e}(°C)
1	500	20	30	Trace	-	-	-	-
2	1000	20	30	0.59	2.36	8.65	2.29	132.4
3	1500	20	30	0.94	3.76	10.83	2.27	132.1
4	2000	20	30	0.84	3.36	11.82	2.01	131.8
5	2500	20	30	0.65	2.60	10.63	2.18	129.9

6	1500	30	30	0.76	3.06	8.43	2.49	131.2
7	1500	40	30	0.50	2.00	8.36	2.42	132. 4
8	1500	50	30	0.38	1.52	6.94	2.97	132.3

[a] Conditions: 5 $u$mol complex **C3**, toluene (total volume 100 mL), 10 atm. [b] Activity: 10^5 g·mol^{-1}(Ti)·h^{-1}, [c] 10^5 g·mol^{-1}. [d] Determined by GPC. [e] Determined by DSC.

Employing the optimized polymerization conditions, results for all complexes **C1-C5** are tabulated in Table 6. On comparison with the systems activated by the co-catalyst MMAO, the same order of catalytic activities was observed here with MAO, *ie* **C2** > **C3** > **C1** > **C5** > **C4**. The narrow values of PDI from 2.05 to 2.53 illustrated a controlled active species had formed.

Table 6 Ethylene polymerization results by **C1-C5**/**MAO** systems[a]

Run	Cat.	Polym(g)	Act[b]	$M_w{}^{c,d}$	$M_w/M_n{}^d$	$T_m{}^e$(°C)
1	C1	0.59	2.36	8.49	2.53	133.4
2	C2	1.05	4.20	10.78	2.05	133.2
3	C3	0.94	3.76	10.83	2.27	132.1
4	C4	0.38	1.52	8.20	2.48	133.6
5	C5	0.58	2.32	10.07	2.14	133.2

[a] Conditions: 5 $u$mol complex, Al/Ti =1500:1, toluene (total volume 100 mL), 30 min,20 °C, 10 atm. [b] Activity: 10^5 g·mol^{-1}(Ti)·h^{-1}, [c] 10^5 g·mol^{-1}. [d] Determined by GPC. [e] Determined by DSC.

Co-polymerization of ethylene with 1-hexene or 1-octene. Subsequently, co-polymerization using MAO was conducted with all half-titanocene complexes (Table 7). In comparison with data in Table 5, the data (numbers) were slightly lower in Table 7, but the same trends for catalytic activities and molecular weights were observed.

Table 7 Co-polymerization by **C1–C5/MAO** [a]

Run	Complexes	Monomer	Polymer(g)	Act[b]	$M_w{}^{c,d}$	$M_w/M_n{}^d$	$T_m{}^e$(°C)

1	C3^f	2 ml	0.175	0.700	8.00	3.26	123.1
2	C3^f	4 ml	0.103	0.412	6.06	6.86	121.5
3	C3^f	6 ml	0.075	0.300	4.48	6.49	120.6
4	C1^f	2 ml	0.145	0.580	7.34	6.10	122.6
5	C2^f	2 ml	0.217	0.868	7.28	2.92	122.2
6	C4^f	2 ml	0.114	0.456	5.34	2.73	123.6
7	C5^f	2 ml	0.168	0.672	6.03	1.85	122.5
8	C1^g	2 ml	0.150	0.600	6.38	2.57	124.2
9	C2^g	2 ml	0.214	0.856	3.77	2.20	122.9
10	C3^g	2 ml	0.195	0.780	7.43	2.75	123.5
11	C4^g	2 ml	0.124	0.496	8.73	2.59	123.1
12	C5^g	2 ml	0.174	0.696	8.08	2.63	123.2

^{a} Conditions: 5 $u$mol complex, Al/Ti =1500:1, toluene (total volume 100 mL), 30 min, 20 °C, 10 atm. ^{b} Activity: 10^5 g·mol^{-1}(Ti)·h^{-1}, ^{c} 10^5 g·mol^{-1}. ^{d} Determined by GPC. ^{e} Determined by DSC. ^{f} 1-hexene was added. ^{g} 1-octene was added.

3. Conclusion

A series of half-titanocene 5-t-butyl-2-(1-(arylimino)methyl)quinolin-8-olate chlorides **C1**-**C5** was synthesized and fully characterized. Upon activation with either MMAO or MAO, all half-titanocene complexes exhibited good catalytic activities toward ethylene polymerization as well as co-polymerization with 1-hexene or 1-octene. In comparison with the analogs half-titanocene 2-(1-(arylimino)methyl)quinolin-8-olate chlorides,[13] in the current system of complexes, the result of bearing an additional t-butyl substituent was detrimental to their catalytic activities. Within the current system, the complexes bearing an additional methyl-substituent caused lower activity such that **C1** > **C4** and **C2** > **C5**. All catalytic systems produced polyethylene with relatively narrow polydispersity, indicating a controlled active species had formed. Moreover, the high T_m values for all the resultant polyethylene confirmed their highly linear nature; the slightly lower T_m values for all the co-polymers indicated effective co-polymerization had been

achieved.

4. Experimental

General procedures

All manipulations of air and/or moisture-sensitive compounds were performed under nitrogen atmosphere in a glove-box or using standard Schlenk techniques. Methylaluminoxane (MAO, 1.46 M in toluene) was purchased from Albemarle. Modified methylaluminoxane (MMAO, 1.93 M in heptane) was purchased from Akzo Nobel Corp. Potassium hydride (KH), purchased from Beijing Regent Chemicals, was washed with hexane before use to remove contained mineral oil. Toluene, *n*-hexane were refluxed over sodium and benzophenone, distilled, and then stored over activated molecular sieves (4 Å) for 24 h under nitrogen atmosphere. 1-Hexene and 1-octene were refluxed over calcium hydride, distilled, and then stored over activated molecular sieves (4 Å) for 24 h in a glove-box prior to use. $CDCl_3$ was dried over activated 4 Å molecular sieves. IR spectra were recorded on a Perkin Elmer FT-IR 2000 spectrometer in the range of 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. Assignments are based on COSY, HSQC and HMBC experiments. DSC trace and melting points of polyethylene were obtained from the second scanning run on a Perkin-Elmer DSC-7 at a heating rate of 10 °C·min^{-1}. ^{13}C NMR spectra of the polymers were recorded on a Bruker DMX-300 MHz instrument at 130 °C in deuterated 1,2-dichlorobenzene with TMS as an internal standard. Molecular weights (*Mw*) and molecular weight distribution of polyethylenes were determined by a PL-GPC220 at 150 °C, with 1,2,4-trichlorobenzene as the solvent.

Synthesis of 5-*t*-butyl-2-(1-(2,6-dimethylphenylimino)methyl)quinolin-8-ol (L1)

A solution of 2,6-dimethylbenzenamine (0.96 g, 7.9 mmol) and 5-*t*-butyl-8-hydroxyquinoline-2-carbaldehyde (1.5 g, 6.6 mmol) and a catalytic

amount of *p*-toluenesulfonic acid in toluene (100 mL) was refluxed for 12 h, then the solvent was evaporated at reduced pressure. The product, 5-*t*-butyl-2-((2,6-dimethylphenylimino)methyl)quinolin-8-ol (**L1**), was purified by alumina column chromatography ($V_{petroleum\ ether}$: $V_{ethyl\ acetate}$ = 20 : 1), and was a yellow powder, which was collected in 28.6 % (0.62 g) yield. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 8.91 (d , *J* = 8.8 Hz, 1H), 8.47 (s, 1H), 8.42 (d, *J* = 8.8 Hz, 1H), 8.36 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.01 (t, *J* = 7.6Hz, 1H), 2.20 (s, 6H), 1.60 (s, 9H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ 163.2, 151.0, 150.7, 150.4, 139.0, 137.0, 136.1, 128.2, 127.6, 126.8, 126.0, 124.3, 117.1, 109.3, 35.6, 32.0, 18.4. IR (cm^{-1}): 3393 (m), 2956 (m), 2872 (w), 1635 (s), 1568 (w), 1508 (m), 1470 (s), 1396 (w), 1359 (m), 1321 (m), 1242 (s), 1189 (m), 1072 (m), 975 (m), 924 (m), 836 (m), 771 (s), 724 (m). Mp: 109 °C. Anal. Calcd. For C$_{22}$H$_{24}$N$_2$O (332.44): C, 79.48; H, 7.28; N, 8.43. Found: C, 79.06; H, 7.29; N, 8.39 %.

5-*t*-butyl-2-(1-(2,6-diethylphenylimino)methyl)quinolin-8-ol (L2)

Using the same procedure as for **L1**, but 2,6-dimethylbenzenamine was used instead of 2,6-diethylbenzenamine. The 5-*t*-butyl-2-(1-(2,6-diethyl-phenylimino)methyl)quinolin-8-ol was obtained as a yellow solid in 42.0 % (0.99 g) yield. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 8.91 (d , *J* = 9.2 Hz, 1H), 8.46 (s, 1H), 8.40 (d, *J* = 9.2 Hz, 1H), 8.34 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.15-7.06 (m , 4H), 2.57-2.52 (m, 4H), 1.60 (s, 9H), 1.16 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ 162.8, 151.0, 150.6, 149.7, 139.1, 137.0, 136.1, 132.8, 127.6, 126.5, 126.1, 124.5, 117.2, 109.3, 35.6, 32.0, 24.8, 14.7. IR (cm^{-1}): 3380 (m), 2965 (m), 2872 (w), 1633 (s), 1568 (w), 1510 (m), 1453 (s), 1397 (w), 1361 (m), 1324 (m), 1244 (s), 1184 (s), 1098 (w), 974 (m), 926 (w), 854 (m), 827 (s), 778 (m), 744 (w). Mp: 139 °C. Anal. Calcd. For C$_{24}$H$_{28}$N$_2$O (360.49): C, 79.96; H, 7.83; N, 7.77. Found: C, 79.90; H, 7.92; N, 7.89 %.

5-*t*-butyl-2-(1-(2,6-diisopropylphenylimino)methyl)quinolin-8-ol (L3)

Similarly, the 5-*t*-butyl-2-(1-(2,6-diisopropyl-phenylimino)-methyl)quinolin-8-ol was obtained as a yellow solid in 34.3 % (0.87 g) yield. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 8.92 (d , J = 9.2 Hz, 1H), 8.44 (s, 1H), 8.40 (d, J = 8.8 Hz, 1H), 8.39 (s, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.22-7.12 (m, 4H), 3.03-2.97 (m, 2H), 1.60 (s, 9H), 1.20 (d ,J = 6.8 Hz, 12H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ 162.8, 151.0, 150.6, 148.5, 139.1, 137.2, 137.0, 136.2, 127.6, 126.1, 124.7, 123.3, 117.3, 117.1, 109.3, 35.6, 32.1, 28.1, 23.5. IR (cm^{-1}): 3378 (m), 2961 (m), 2871 (w), 1633 (s), 1569 (w), 1508 (m), 1469 (s), 1434 (w), 1360 (m), 1320 (m), 1244 (s), 1181 (m), 1112 (m), 1070 (w), 975 (m), 850 (s), 825 (s), 772 (s), 743 (m), 721 (m). Mp: 178 °C. Anal. Calcd. For C$_{26}$H$_{32}$N$_2$O (388.55): C, 80.37; H, 8.30; N, 7.21. Found: C, 80.43; H, 8.17; N, 7.48 %.

Synthesis of 5-*t*-butyl-2-(1-(2,4,6-trimethylphenylimino)methyl)-quinolin-8-ol (L4)

Similarly, 5-*t*-butyl-2-(1-(2,4,6-trimethylphenylimino)methyl)quinolin-8-ol was obtained as a yellow solid in 16.3 % (0.37 g) yield. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 8.90 (d , J = 8.8 Hz, 1H), 8.47 (s, 1H), 8.42 (d, J = 8.8 Hz, 1H), 8.38 (s, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.13 (d, J = 8.0 Hz, 1H), 6.94 (s, 2H), 2.32 (s, 3H), 2.19 (s, 6H), 1.61 (s, 9H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ 163.3, 151.0, 150.8, 147.9, 139.1, 137.0, 136.1, 133.7, 128.9, 127.6, 126.9, 126.0, 117.2, 109.2, 35.6, 32.0, 20.9, 18.4. IR (cm^{-1}): 3403 (m), 2952 (m), 1633 (m), 1569 (m), 1508 (m), 1471 (s), 1400 (w), 1359 (m), 1323 (m), 1271(m), 1241 (s), 1182 (w), 1142 (w), 1077 (m), 1033 (m), 972 (m), 837 (s), 745 (w), 720 (s), 655 (m). Mp: 158 °C. Anal. Calcd. For C$_{23}$H$_{26}$N$_2$O (346.47): C, 79.73; H, 7.56; N, 8.09. Found: C, 79.49; H, 7.57; N, 7.97 %.

5-*t*-butyl-2-(1-(2,6-diethyl-4-methylphenylimino)methyl)quinolin-8-ol (L5)

Similarly, 5-*t*-butyl-2-(1-(2,6-diethyl-4-methylphenylimino)methyl)quinolin-8-ol was obtained as a yellow solid in 19.1 % (0.48 g) yield. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 8.90 (d , J = 9.2 Hz, 1H), 8.46 (s, 1H), 8.39 (d, J = 9.2 Hz, 1H), 8.36 (s, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.13 (d, J = 7.6 Hz, 1H), 6.95 (s, 2H), 2.52 (m, 4H), 2.35 (s, 3H),

1.60 (s, 9H), 1.16 (t, J = 7.6 Hz, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ 162.7, 150.9, 150.7, 147.2, 139.0, 136.9, 136.0, 133.8, 132.8, 127.5, 127.1, 125.9, 117.1, 109.2, 35.5, 32.0, 24.7, 21.0, 14.8. IR (cm^{-1}): 3387 (m), 2965 (m), 2874 (w), 1632 (s), 1566 (m), 1510 (m), 1459 (s), 1399 (w), 1361 (m), 1322 (m), 1275(w), 1245 (s), 1201 (w), 1140 (w), 1073 (m), 974 (m), 884 (m), 850 (s), 825 (s), 756 (w), 720 (m). Mp: 161 °C. Anal. Calcd. For C$_{25}$H$_{30}$N$_2$O (374.52): C, 80.17; H, 8.07; N, 7.48. Found: C, 79.71; H, 8.12; N, 7.29 %.

Synthesis of Titanium(IV) Complexes (C1–C5)

(η^5-Cyclopentadienyl)dichlorotitanium

5-t-butyl-2-(1-(2,6-dimethyl-phenylimino)methyl)quinolin-8-olate (C1)

To a 30 ml toluene solution of 0.332 g (1.00 mmol) 5-t-butyl-2-((2,6-dimethylphenylimino)methyl)quinolin-8-ol, 0.040g (1.00 mmol) KH was added at -78 °C. The mixture was stirred for additional 4 h, and then 0.220 g (1.00 mmol) CpTiCl$_3$ was added at -78 °C. The resulting suspension was warmed to room temperature and kept stirring for additional 12 h. and the solvent was removed under vacuum. The residue was extracted in 20 mL of toluene to remove KCl salt. Removal of volatiles under vacuum left a brown powder. Recrystallization of the product from toluene/hexane afforded **C1** in 89.4 % (0.46 g) yield. ^{1}H NMR (400 MHz, CDCl$_3$, ppm: δ 9.03 (d, J = 8.8 Hz, 1H), 8.44 (s, 1H), 7.84 (d, J = 8.8 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.21 (s, 3H), 6.90 (d, J = 8.4 Hz, 1H), 6.79 (s, 5H), 2.46 (s, 6H), 1.59 (s, 9H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 167.1, 166.0, 151.8, 140.6, 139.9, 137.3, 137.1, 130.2, 130.0, 128.8, 127.3, 124.6, 120.4, 110.7, 35.7, 31.8, 20.3.

(η^5-Cyclopentadienyl)dichlorotitanium

5-t-butyl-2-(1-(2,6-diethyl-phenylimino)methyl)quinolin-8-olate (C2)

The synthesis of **C2** was carried out by the same procedure as that of **C1**. **C2** was prepared by using **L2** instead of **L1** and brown crystals were obtained in 74.6 % (0.41g) yield. ^{1}H NMR 400 MHz, CDCl$_3$, ppm): δ 9.03 (d, J = 8.8 Hz, 1H), 8.43 (s,

1H), 7.84 (d, J = 8.8 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.33-7.28 (m, 3H), 6.90 (d, J = 8.4 Hz, 1H), 6.78 (s, 5H), 3.08-3.03 (m, 2H), 2.84-2.80 (m, 2H), 1.59 (s, 9H), 1.15 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 166.8, 166.0, 150.7, 140.7, 139.8, 137.3, 137.1, 136.0, 130.1, 128.8, 127.8, 127.3, 124.6, 120.4, 110.7, 35.7, 31.8, 25.0, 15.8.

(η^5-Cyclopentadienyl)dichlorotitanium

5-t-butyl-2-(1-(2,6-diisopropyl-phenylimino)methyl)quinolin-8-olate (C3)

The synthesis of **C3** was carried out by the same procedure as that of **C1**. **C3** was prepared by using **L3** instead of **L1** and brown crystals were obtained in 86.1 % (0.49g) yield. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 9.02 (d, J = 8.8 Hz, 1H), 8.37 (s, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.38-7.32 (m, 3H), 7.01 (d, J = 8.4 Hz, 1H), 6.80 (s, 5H), 3.72-3.66 (m, 2H), 1.59 (s, 9H), 1.41 (d, J = 6.4 Hz, 6H), 1.01 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 166.3, 166.0, 149.5, 140.8, 139.9, 137.3, 137.0, 130.1, 128.8, 128.1, 124.6, 123.3, 120.5, 119.1, 110.7, 35.7, 31.9, 27.6, 26.0, 23.2.

(η^5-Cyclopentadienyl)dichlorotitanium

5-t-butyl-2-(1-(2,4,6-trimethyl-phenylimino)methyl)quinolin-8-olate (C4)

The synthesis of **C4** was carried out by the same procedure as that of **C1**. **C4** was prepared by using **L4** instead of **L1** and brown crystals were obtained in 90.9 % (0.48g) yield. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 9.02 (d, J = 8.8 Hz, 1H), 8.42 (s, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.01 (s, 2H), 6.89 (d, J = 8.4 Hz, 1H), 6.80 (s, 5H), 2.42 (s, 6H), 2.36 (s, 3H), 1.58 (s, 9H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 167.2, 166.0, 149.7, 140.6, 140.0, 137.2, 137.1, 136.8, 130.1,1 29.7, 129.6, 128.8, 124.6, 120.3, 110.7, 35.7, 31.8, 20.7, 20.2.

(η^5-Cyclopentadienyl)dichlorotitanium

5-t-butyl-2-(1-(2,6-diethyl-4-methyl-pheny-limino)-methyl)quinolin-8-olate (C5)

The synthesis of **C5** was carried out by the same procedure as that of **C1**. **C5** was

prepared by using **L5** instead of **L1** and brown crystals were obtained in 66.7 % (0.37g) yield. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 9.02 (d, J = 8.8 Hz, 1H), 8.40 (s, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.06 (s, 3H), 6.90 (d, J = 8.4 Hz, 1H), 6.79 (s, 5H) , 3.06-3.00 (m, 2H), 2.77-2.72 (m, 2H), 2.40 (s, 3H), 1.60 (s, 9H), 1.13 (t, J = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 167.0, 166.0, 148.6, 140.7, 139.8, 137.3, 137.0, 135.8, 130.1, 128.8, 127.9, 127.6, 124.7, 120.3, 110.7, 35.7, 31.8, 24.9, 21.0, 15.9.

Table 8 Crystallographic data and refinement details for complexes **C1** and **C2**

	C1	**C2**
Empirical formula	C$_{27}$H$_{36}$Cl$_2$N$_2$OTi	C$_{29}$H$_{32}$Cl$_2$N$_2$OTi
Formula weight	523.38	543.37
Crystal color	black	black
Temperature (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P 21/C	P2(1)/n
a (Å)	14.671(3)	14.544(3)
b (Å)	13.072(3)	12.517(3)
C (Å)	14.980(7)	14.676(3)
α (°)	90	90
β (°)	119.7	96.54(3)
γ (°)	90	90
Volume (Å^3)	2495.5(14)	2654.4(9)
Z	4	4
D calcd (mg m^{-3})	1.393	1.360
μ (mm^{-1})	0.580	0.549
F (000)	1104	1136
Crystal size (mm)	0.30 × 0.28 × 0.18	0.25 × 0.24 × 0.19

θ range (°)	2.21 - 27.48	1.87 - 25.00
Limiting indices	$-19 \le h \le 18,$	$-17 \le h \le 17,$
	$-16 \le k \le 16,$	$-14 \le k \le 14,$
	$-19 \le l \le 19$	$-17 \le l \le 17$
No. of rflns collected	16180	15674
No. of unique rflns	5684	4644
R_{int}	0.0875	0.0460
Completeness to θ (%)	99.3 ($\theta = 27.48$)	99.5 ($\theta = 25.00$)
Goodness-of-fit on F^2	1.020	1.262
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0827,	R1 = 0.0563,
	wR2 = 0.1621	wR2 = 0.1794
R indices (all data)	R1 = 0.0944,	R1 = 0.0734,
	wR2 = 0.1685	wR2 = 0.2271

X-Ray structure determinations

Crystals of **C1** and **C2** suitable for single-crystal X-ray analysis were obtained by laying *n*-hexane on the toluene solutions. Single-crystal X-ray diffraction for **C1** and **C2** were performed on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 173(2) K. Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Structure solution and refinement were performed by using the SHELXL-97 package.[20] Crystal data collection and refinement details are given in Table 8.

Procedures for ethylene polymerization and co-polymerization

A 500-mL autoclave stainless steel reactor equipped with a mechanical stirrer and a

temperature controller was heated under vacuum at 80 °C. It was allowed to cool to the desired reaction temperature under an ethylene atmosphere and then charged with toluene (with co-monomer), the desired amount of co-catalyst (MAO or MMAO) and a toluene solution of the pre-catalyst (the total volume was 100 mL). Next, the autoclave was immediately pressurized to 10 atm of ethylene pressure and it should be kept constant during the reaction time by feeding the reactor with ethylene. After a period of desired reaction time, the polymerization reaction was quenched by addition of a solution of ethanol containing HCl. The precipitated polymer was washed with ethanol several times and dried in vacuum.

Acknowledgements

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