Journal of Organometallic Chemistry 715 (2012) 119–128

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

2-Aldiminophenoxytitanium chloride complexes: Synthesis, characterization, and ethylene (co-)polymerization behavior

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ARTICLE INFO

Article history:
Received 25 February 2012
Received in revised form
23 May 2012
Accepted 31 May 2012

Keywords:
Bulky 2-aldiminophenoxylate
Trichlorotitanium complexes
Ethylene polymerization
Ethylene co-polymerization

ABSTRACT

A series of trichlorotitanium 2-aldiminophenoxylate complexes (**C1**–**C6**) was synthesized by the stoichiometric reaction of $TiCl_4(THF)_2$ with the potassium salts of 6-alkyl-2-aldiminophenolates derived from ligands (**L1**–**L6**) bearing a bulky benzhydryl substituent, whereas the bis(2-aldiminophenoxy) titanium dichloride (**C7**) was isolated in the reaction of a ligand **L6** with 0.5 equivalents of $TiCl_4(THF)_2$. All titanium complexes were characterized by $^1H/^{13}C$ NMR spectroscopy and elemental analysis. Single-crystal X-ray diffraction revealed distorted octahedron geometries around the titanium center for complexes **C2**, **C4** and **C7**. Upon activation with the co-catalyst MAO, all titanium pre-catalysts exhibited good to high activities (up to 1.3×10^6 g mol (Ti)$^{-1}$ h^{-1}) for ethylene polymerization at 70 °C, producing polyethylene products with high molecular weights. Furthermore, co-polymerization of ethylene with either α-olefins or norbornene was achieved with activities in the range of 10^5 g mol (Ti)$^{-1}$ h^{-1} by these titanium pre-catalysts along with good incorporation of co-monomer, typically 4.5 mol % for 1-hexene or 13.5 mol % for norbornene, respectively.

1. Introduction

Ziegler–Natta or metallocene-based systems are well established as commercial catalysts in ethylene polymerization [1–7], however early transition-metal complex pre-catalysts have received attention as attractive alternatives due to their high activity and controllability for α-olefin co-polymerization [8–10] along with potentially producing precise polymers [11–15] and advanced polymers [16–25]. The bis(iminophenoxy)titanium/zirconium pre-catalysts, namely FI catalysts, have been widely investigated in both ethylene polymerization and propylene syndiotactic polymerization [26–30]. Modification of these FI pre-catalysts has focused on improving their thermal stability and co-polymerization ability [31–38], with most examples focused on bis-ligated titanium complexes [39–46]. However, bis-ligated FI pre-catalysts were generally considered thermally unstable and possessed limited copolymerization ability compared with the PI pre-catalysts, the latter possessing more open space around the titanium center [31].

To enhance their co-polymerization behavior, mono-ligated trichlorotitanium pre-catalysts have been explored (shown in Scheme 1 and 2) [47–58]. The pre-catalyst **I** bearing a neutral pendent phosphine donor, namely $(L_{FI}\text{-}PPh_2)TiCl_3$ exhibited considerable activity in ethylene polymerization (up to 1.41 kg polymer/(mmol (Ti) h bar)) and co-polymerization with 1-hexene and NBE, providing high molecular weight (co)polymers (Mw 10^4–10^5 g/mol) with narrow PDI ($M_w/M_n = 2$–3). Presumably, the five-coordinated complex pre-catalyst is less sterically hindered, and consequently the co-monomer was more readily taken up [47]. The pre-catalyst **II** exhibited appreciable activity in both ethylene polymerization and co-polymerization [48], whereas the pre-catalysts **III** that possessed a 1-methyl-2-benzimidazolylmethyl group, produced an activity of 150 kg polymer/(mol (Ti) h bar) for ethylene polymerization only in the presence of $^iBu_3Al$/DMAO, but produced polyethylenes with large PDI values (~48) [49]. The tridentate titanium complex pre-catalyst **IV** exhibited a low activity for ethylene polymerization, and with a broad distribution of polyethylene molecular weights [50]. However, the tridentate phenoxy-imine ligated titanium complex pre-catalyst **V** was able to selectively trimerize ethylene in high

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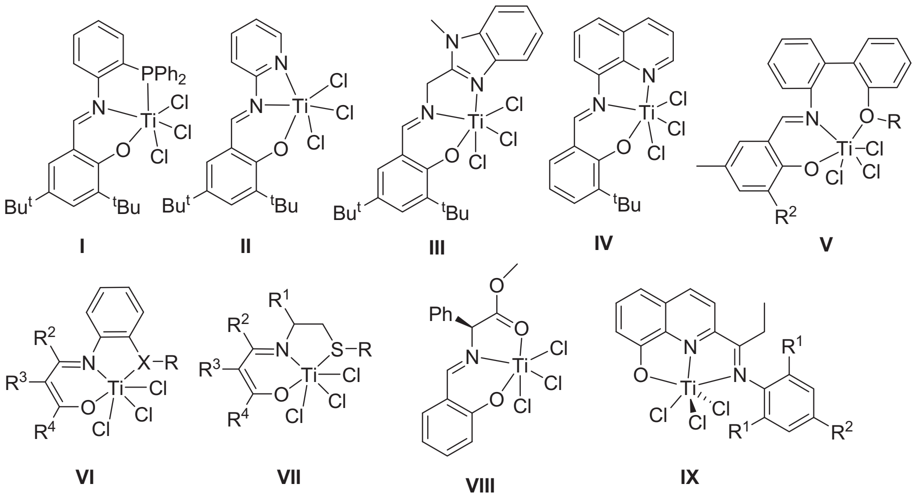
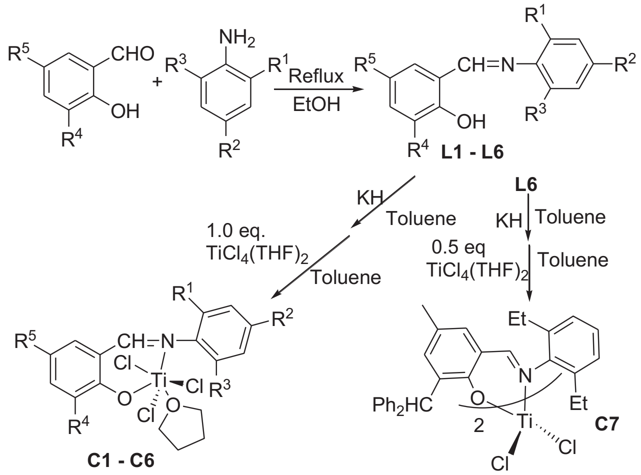
http://dx.doi.org/10.1016/j.jorganchem.2012.05.048



Scheme 1. Examples of mono-ligated trichlorotitanium pre-catalysts.

activity (up to 6.59 × 10^6 g/(g Ti h)) upon activation with MAO [51–54]. The modified pre-catalysts **VI** [55] and **VII** [56] were found to be capable of achieving high co-monomer incorporation during ethylene co-polymerization, which was probably due to the meridional arrangement of the ligands wrapped around the Ti center. Furthermore, the tridentate phenoxy-imine titanium complexes **VIII** [57], in which the carbonyl oxygen was bonded to the titanium, were reported without polymerization data. Attractively, modified tridentate trichlorotitanium complexes of the type **IX** exhibited good activity for both ethylene polymerization and co-polymerization [58].

Clearly, these mono-ligated trichlorotitanium pre-catalysts have not yet fulfilled the expected requirements of good catalytic activity, better co-polymerization ability, and thermal stability. To create more vacant space around the titanium center for improving the co-polymerization ability, bi-dentate mono-ligated trichlorotitanium complexes could be employed; a few examples of bi-dentate mono-ligated trichlorotitanium pre-catalysts [59–62] were reported and showed potential for considerable activity. Inspired by our recent successful synthesis of late-transition metal pre-catalysts employing ligands derived from benzhydryl-substituted anilines [63], we now deploy a number of benzhydryl-substituted anilines to react with salicylaldehydes to form corresponding bulky 2-aldiminophenolate derivatives. Further reaction of the potassium salts of 2-aldiminophenolates with titanium tetrachloride (THF complex) afforded trichlorotitanium 2-aldiminophenolates (**C1**–**C6**), and also an additional complex of bis(2-aldiminophenoxy)titanium dichloride (**C7**). When activated with methylaluminoxane (MAO), all titanium pre-catalysts exhibited high activities for ethylene polymerization at an optimized temperature at 70 °C, affording high molecular weight polyethylene products. Moreover, these titanium pre-catalysts also showed good co-polymerization of ethylene with either 1-hexene, or 1-octene, or norbornenes, illustrating a good incorporation of norbornene (up to 13.5%) in the resultant co-polymers. Herein, the synthesis and characterization of the trichlorotitanium 2-aldiminophenoxylates (**C1**–**C6**) and bis(2-aldiminophenoxy)titanium dichloride (**C7**) are reported, and their ethylene (co-)polymerization behavior has been investigated.



	R^1	R^2	R^3	R^4	R^5
L1, C1	$CHPh_2$	^{i}Pr	$CHPh_2$	^{t}Bu	^{t}Bu
L2, C2	$CHPh_2$	^{i}Pr	$CHPh_2$	^{t}Bu	Me
L3, C3	$CHPh_2$	Me	$CHPh_2$	^{t}Bu	Me
L4, C4	Me	$CHPh_2$	$CHPh_2$	^{t}Bu	Me
L5, C5	Me	Me	$CHPh_2$	^{t}Bu	Me
L6, C6	Et	H	Et	$CHPh_2$	Me

Scheme 2. Synthesis of ligands (**L1**–**L6**) and titanium complexes **C1**–**C7**.

2. Results and discussions

2.1. Synthesis and characterization of titanium complexes *C1*–*C7*

The 2-((arylimino)methyl)phenol ligands (**L1**–**L5**) were prepared by the condensation reaction of salicylaldehyde and benzhydryl-substituted anilines as our previous procedure [48,64]. However, the reaction of 2-hydroxy-3-benzhydrylbenzaldehyde with 2-benzhydrylanilines was not favorable, therefore the reaction of 2-hydroxy-3-benzhydrylbenzaldehyde with 2,6-diethylaniline was carried out to form the corresponding 2-(1-(2,6-diethylphenylimino)methyl)-3-benzhydryl phenol (**L6**). Treatment of the potassium salts of ligands (**L1**–**L5**) with either 0.5 or 1 equivalents of $TiCl_4(THF)_2$ afforded the same mono-ligated trichlorotitanium complexes (**L**$TiCl_3$(THF), **C1**–**C5**, Scheme 2) suggesting that the bulky ligands formed from 2-benzhydrylanilines prevented the formation of bis-ligated titanium complexes. In contrast, the reaction of the potassium salt of **L6** with 1 or 0.5 equivalents of $TiCl_4(THF)_2$ afforded two different complexes, *viz* the mono-ligated **L6**$TiCl_3$(THF) (**C6**) and the bis-ligated (**L6**)$_2$$TiCl_2$ (**C7**), respectively (Scheme 2). The difference in the reactivity of the set of ligands (**L1**–**L5**) and ligand **L6** indicated the influence of ligands' bulkiness (especially the location of the benzhydryl-substituent) on the coordination at the titanium center. These highly sensitive titanium complexes were fully characterized by $^{1}H/^{13}C$ NMR spectroscopy and by elemental analysis; complex **C6** was more sensitive than the analogs (**C1**–**C5**, **C7**). On comparing the ^{1}H NMR spectra with those of the corresponding ligands, the peak for the Ar–OH (12.9–13.2 ppm) of the 2-(2-pyridinyliminomethyl)-phenols disappeared in all the titanium complexes, indicating the formation of the Ti–O bond. The peak for the CH=N (7.23–8.27 ppm) in the ligands **L1**–**L6** shifted to lower field (7.31–8.22 ppm) in the corresponding titanium complexes **C1**–**C7**, illustrating the formation of a coordination bond between the N_{imine} and the Ti center. In the ^{13}C NMR spectra, the CH=N resonances in the complexes appeared at about 169–174 ppm and shifted downfield by 2.7–4.5 ppm compared with those of the corresponding ligands.

The structures of the representative complexes **C2**, **C4** and **C7** were confirmed by the single crystal X-ray diffraction, and the molecular structures are shown in Figs. 1–3, respectively. As is shown in Fig. 1, the titanium is coordinated with O_{phenol}, N_{imine}, O_{THF} and three chlorides to give a distorted octahedron geometry, for which the titanium is co-planar with the coordinated atoms of O1, O2, N1 and Cl1; the other two chlorines (Cl2 and Cl3) are located in *trans*-position with an angle Cl2–Ti1–Cl3 of 169.66(6)°. Within the framework of ligands, the two phenyl groups on both sides of the imine group are almost perpendicular, and the two chlorides Cl2 and Cl3 are located in *trans*-positions to each other, and the coordinative sphere is completed by a THF molecule. The Ti–Cl bond lengths are consistent with those previously reported [65–70].

As seen in Fig. 2, the distorted octahedron geometry around the Ti center in **C2** is repeated in complex **C4**, though slight differences are observed within the bond lengths Ti–O1, Ti–N_{imine} (1.817(4), 2.288(4) Å) in **C4** and (1.828(3), 2.185(4) Å) in **C2**. In contrast to **C2**, the THF molecule in **C4** is *trans* to a chloride (Cl3); the three chlorides adopt a *facial* arrangement. Moreover, the two phenyl rings are almost perpendicular in **C4**, similar to the situation observed for **C2**.

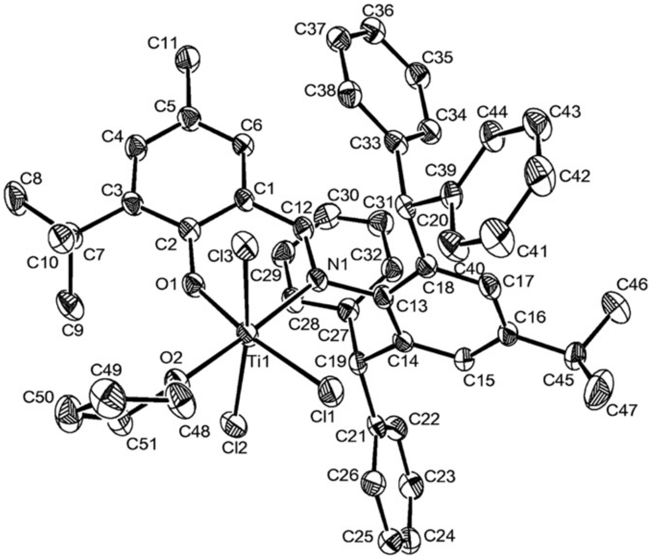


Fig. 1. ORTEP drawing of **C2** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond length (°) and selected bond angles (Å): Ti(1)–O(1) 1.828(3), Ti(1)–O(2) 2.100(4), Ti(1)–N(1) 2.185(4), Ti(1)–Cl(1) 2.3014(18), Ti(1)–Cl(2) 2.3309(18), Ti(1)–Cl(3) 2.3321(18), O(1)–Ti(1)–O(2) 97.24(15), O(1)–Ti(1)–N(1) 82.85(15), O(2)–Ti(1)–N(1) 176.15(15), O(1)–Ti(1)–Cl(1) 170.99(12), O(2)–Ti(1)–Cl(1) 91.77(11), N(1)–Ti(1)–Cl(1) 88.18(11), O(1)–Ti(1)–Cl(2) 89.42(12), O(2)–Ti(1)–Cl(2) 85.54(12), N(1)–Ti(1)–Cl(2) 98.31(12), Cl(1)–Ti(1)–Cl(2) 91.13(7), O(1)–Ti(1)–Cl(3) 89.54(12), O(2)–Ti(1)–Cl(3) 84.39(12), N(1)–Ti(1)–Cl(3) 91.77(11), Cl(1)–Ti(1)–Cl(3) 91.51(7), Cl(2)–Ti(1)–Cl(3) 169.66(6).

In Fig. 3, although complex **C7** also possesses a distorted octahedron geometry around the Ti center, because of the bis-ligated nature of complex **C7**, much longer bond lengths are present, for example Ti–O (1.864(3) and 1.884(3)). The *ortho*-benzhydryl at the phenol (within **L6**) probably caused the weakening of the Ti–O bond compared to those with an *ortho*-benzhydryl on the iminophenyl group (within **L1**–**L5**). This is also thought to be reason why the mono-ligated titanium complex **C6**, having more space at the metal, is more reactive than the other analogs **C1**–**C5**, and the stable bis-ligated complex **C7**.

2.2. Catalytic behavior toward ethylene (co-)polymerization

2.2.1. Ethylene polymerization

Various alkylaluminium reagents were screened for their suitability as co-catalysts in the catalytic system employing complex **C2**. Poor results were observed when using the trialkylaluminium reagents $AlEt_3$, $AlMe_3$ or $AlEt_2Cl$. Interestingly, ethylene polymerization was observed with an activity as high as 1.12×10^5 g mol^{-1} (Ti) h^{-1} when using methylaluminoxane (MAO) as co-catalyst and 0.76×10^5 g mol^{-1} (Ti) h^{-1} when using modified methylaluminoxane (MMAO) under 10 atm ethylene with 3000:1 M ratio of Al/Ti at 50 °C over 30 min. Considering the price advantage of MAO over MMAO, subsequent investigations of complex **C2** were carried out by employing MAO as co-catalyst, and the results are collected in Table 1.

2.2.1.1. Influence of the reaction parameters on the catalytic activities. Initially, the effect of temperature was investigated by employing the **C2**/MAO system with a 3000 ratio of Al/Ti over 30 min. Upon elevating the temperature from 20 °C to 50 °C, the catalytic activity gradually increased (runs 1–3, Table 1). When the temperature rose above 50 °C, the activity increased sharply and the highest activity of 6.06×10^5 g mol^{-1} (Ti) h^{-1} was achieved at 70 °C, followed by a rapid decrease in activity on further increasing the temperature until only trace polymer was observed at 90 °C (runs 4–7, Table 1), suggesting good thermal stability of the active species. The FI titanium complex pre-catalysts demonstrated an optimum activity of 3.8×10^6 g mol^{-1} (Ti) h^{-1} at 50 °C, but deactivation occurred on elevating the temperature [29,30]. Its analogs bearing the phenyl-substituent phenoxylimines showed a lower activity of 4.40×10^5 g mol (Ti)$^{-1}$ h^{-1} bar^{-1} at 60 °C (over 5 min at 1 bar) with a short lifetime. Other analogs bearing the isopropylbenzene imine exhibited a very low activity of 2×10^4 g mol (Ti)$^{-1}$ h^{-1} bar^{-1} at 60 °C over 35 min [71–73]. The current complex pre-catalysts showed reasonable thermal stability, which is comparable to the commercial metallocene catalytic system at around 75 °C [5,6,74–76]. The reason is likely associated with the bulkiness at the imine group, which plays a vital role in stabilizing the active species at high temperature.

The effect of the Al/Ti molar ratio on the catalytic behavior was also investigated. An increase of the Al/Ti molar ratio from 1000 to 4000 led to an increase of the activity for ethylene polymerization from 1.98×10^5 g mol^{-1} (Ti) h^{-1} to 12.26×10^5 g mol^{-1} (Ti) h^{-1} (runs 8–12, Table 1). However, a further increase of the Al/Ti ratio led to a dramatic decrease in catalytic activity and the amount of resultant polyethylene (runs 12–14, Table 1); meanwhile the molecular weights of the obtained polyethylenes decreased, which is possible due to enhanced chain transfer to aluminum for the termination [77,78]. Regarding the lifetime of the active species, the effect of time on the activity was also evaluated. On prolonging the reaction time, only a small decrease in the activity was observed over 30 min (run 17 *vs.* run 12, Table 1) suggesting that the active species could survive 30 min at this high temperature (70 °C).

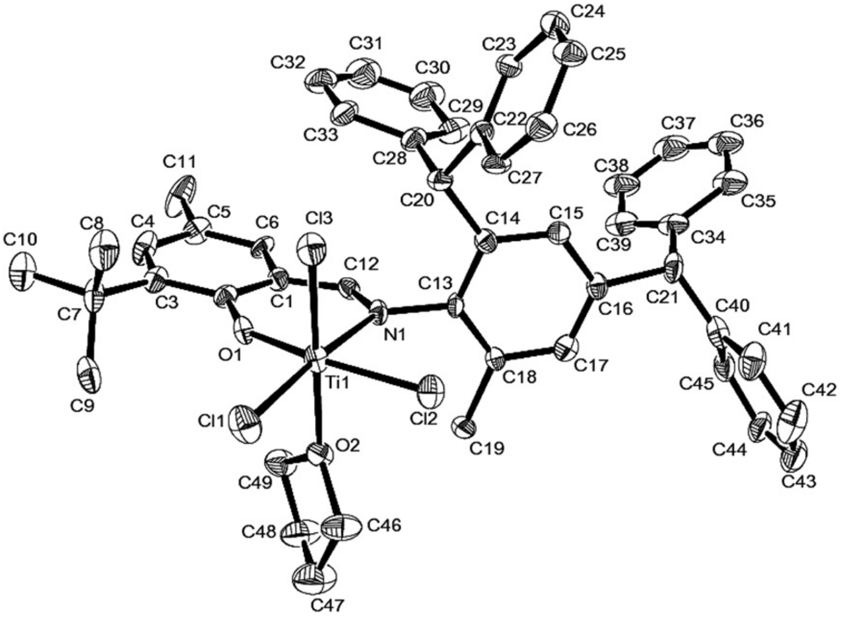


Fig. 2. ORTEP drawing of **C4** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond length (○) and selected bond angles (Å): Ti(1)–O(1) 1.817(4), Ti(1)–O(2) 2.129(4), Ti(1)–N(1) 2.288(4), Ti(1)–Cl(1) 2.2898(19), Ti(1)–Cl(3) 2.296(2), Ti(1)–Cl(2) 2.3057(19). O(1)–Ti(1)–O(2) 87.48(16), O(1)–Ti(1)–N(1) 79.96(16), O(2)–Ti(1)–N(1) 84.25(16), O(1)–Ti(1)–Cl(1) 97.42(13), O(2)–Ti(1)–Cl(1) 86.80(12), N(1)–Ti(1)–Cl(1) 170.77(13), O(1)–Ti(1)–Cl(3) 92.23(13), O(2)–Ti(1)–Cl(3) 179.71(12), N(1)–Ti(1)–Cl(3) 95.67(12), Cl(1)–Ti(1)–Cl(3) 93.27(8), O(1)–Ti(1)–Cl(2) 164.25(13), O(2)–Ti(1)–Cl(2) 86.73(11), N(1)–Ti(1)–Cl(2) 84.89(12), Cl(1)–Ti(1)–Cl(2) 96.86(8), Cl(3)–Ti(1)–Cl(2) 93.55(7).

2.2.1.2. Effect of the ligand environment on the catalytic behavior. By employing the optimized conditions of an Al/Ti molar ratio of 4000:1 at 70 °C over 30 min, all titanium complexes were investigated for ethylene polymerization; and the results are collected in Table 1. For the mono-ligated titanium complexes, catalytic activity decreased in the order: **C2** (R^1, R^3 = CHPh$_2$, R^2 = ^{i}Pr, R^4 = ^{t}Bu, R^5 = Me) > **C3** (R^1, R^3 = CHPh$_2$, R^2 = Me, R^4 = ^{t}Bu, R^5 = Me) > **C4** (R^2, R^3 = CHPh$_2$, R^1 = Me, R^4 = ^{t}Bu, R^5 = Me) > **C5** (R^1, R^2 = Me, R^3 = CHPh$_2$, R^4 = ^{t}Bu, R^5 = Me) > **C6** (R^1, R^3 = Me, R^2 = H, R^4 = CHPh$_2$, R^5 = Me), suggesting that more sterically bulky substituents on the benzene ring led to a more rigid environment around titanium, thereby providing better protection at the higher

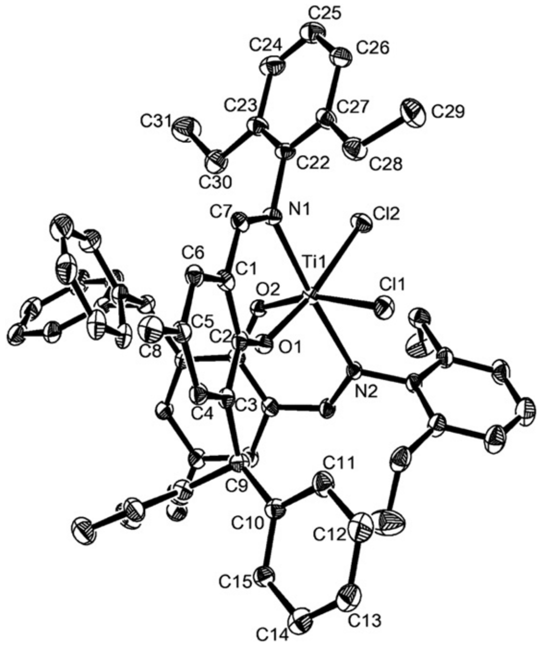


Fig. 3. ORTEP drawing of **C7** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond length (°) and selected bond angles (Å): Ti(1)–O(1) 1.864(3), Ti(1)–O(2) 1.884(3), Ti(1)–N(2) 2.212(4), Ti(1)–N(1) 2.222(4), Ti(1)–Cl(2) 2.2933(16), Ti(1)–Cl(1) 2.3458(16). O(1)–Ti(1)–O(2) 87.27(15), O(1)–Ti(1)–N(2) 98.20(15), O(2)–Ti(1)–N(2) 82.20(14), O(1)–Ti(1)–N(1) 83.30(15), O(2)–Ti(1)–N(1) 101.67(15), N(2)–Ti(1)–N(1) 175.94(15), O(1)–Ti(1)–Cl(2) 168.11(12), O(2)–Ti(1)–Cl(2) 96.63(11), N(2)–Ti(1)–Cl(2) 93.47(11), N(1)–Ti(1)–Cl(2) 84.91(11), O(1)–Ti(1)–Cl(1) 87.06(12), O(2)–Ti(1)–Cl(1) 165.17(11), N(2)–Ti(1)–Cl(1) 85.06(11), N(1)–Ti(1)–Cl(1) 91.26(12), Cl(2)–Ti(1)–Cl(1) 91.68(6).

Table 1
Ethylene polymerization results by **C1**–**C7**/MAO systems.[a]

Run	Cat.	Al/Ti	T/°C	t/min	Polymer (g)	Activity[b]	M_η[c]	T_m[d] (°C)
1[e]	**C2**	3000	20	30	0.109	0.44		134.4
2[e]	**C2**	3000	40	30	0.260	1.04	2.1	132.3
3[e]	**C2**	3000	50	30	0.279	1.12		135.2
4[e]	**C2**	3000	60	30	1.421	5.68	2.2	131.4
5[e]	**C2**	3000	70	30	1.515	6.06	4.0	128.7
6[e]	**C2**	3000	80	30	0.882	3.53	n.s	128.0
7[e]	**C2**	3000	90	30	Trace			
8[f]	**C2**	1000	70	30	0.247	1.98		131.7
9[f]	**C2**	2000	70	30	0.753	6.03	1.3	130.5
10[f]	**C2**	3000	70	30	0.781	6.24	15.9	133.5
11[f]	**C2**	3500	70	30	0.792	6.34	n.s	134.5
12[f]	**C2**	4000	70	30	1.532	12.26	4.4	133.0
13[f]	**C2**	4500	70	30	0.798	6.38	3.3	129.8
14[f]	**C2**	5000	70	30	0.484	4.30	3.1	134.9
15[f]	**C2**	4000	70	10	0.546	13.10		132.3
16[f]	**C2**	4000	70	20	1.062	12.74		132.5
17[f]	**C2**	4000	70	40	1.549	9.29		132.9
18[f]	**C1**	4000	70	30	1.073	8.58	3.0	131.1
19[f]	**C3**	4000	70	30	1.452	11.62	4.5	132.0
20[f]	**C4**	4000	70	30	1.259	10.07	4.7	131.3
21[f]	**C5**	4000	70	30	0.896	7.17	6.7	132.8
22[f]	**C6**	4000	70	30	0.532	4.26	8.9	133.1
23[f]	**C7**	4000	70	30	0.751	6.01	2.8	132.5

[a] Conditions: MAO as co-catalyst, 10 atm ethylene, toluene, total volume 100 mL.
[b] Activity: 10^5 g mol^{-1} h^{-1}.
[c] Determined by viscosity, 10^5 g mol^{-1}.
[d] Determined by DSC.
[e] 5.0 μmol cat.
[f] 25 μmol cat.

temperatures (runs 12, 18–22). The current complex pre-catalysts did not perform as well as the advanced FI pre-catalysts [26], but the activity (4.26–11.62 × 10^5 g mol^{-1} (Ti) h^{-1} at 70 °C) was generally considered better than those of analog titanium mono-salicy(aldiminato) complexes [72,73]. It is noteworthy that the sensitive complex **C6** had to be used fresh, and immediately recrystallized prior to catalytic screening. However, the molecular weight of the polymer produced by **C6** was much higher than that of **C1**–**C5**, suggesting that the larger distances between the substituents on the *ortho*-position of the phenol and titanium favored ethylene insertion and propagation. The bulky group at the *ortho*-position of the aniline is more efficient at protecting the active species than that at the *ortho*-position of the phenol for ethylene polymerization at high temperature. As expected, the bis-ligated titanium complex **C7** showed much lower activity than did the mono-ligated complexes **C1**–**C5** (run 22 *vs.* runs 12, 18–21), probably due to the crowded environment at the titanium center in **C7**. However, the complex **C7** showed higher activity than its mono-ligated analog **C6**, which was quite unstable during the catalysis.

2.2.2. Co-polymerization of ethylene/1-octene

The co-polymerization of ethylene with 1-octene by complexes **C1**–**C7** was also investigated with the Al/Ti molar ratio of 4000 at 70 °C under 10 atm ethylene and the results are tabulated in Table 2. The results showed that all catalysts exhibited moderate activities toward ethylene/1-octene co-polymerization. Compared with the results for ethylene homo-polymerization (Table 1), generally the activities were lower; the reason is probably that the bulky environment around the active species precludes the insertion of the co-monomer.

Initially, the effect of the 1-octene concentration on the catalytic behavior was investigated. An increase of 1-octene concentration from 0.3 mol/L to 1.0 mol/L resulted in a slightly lower T_m value for the resultant co-polymer (runs 1–3, Table 2), which is consistent with previous results [50,57,79–84]. However, due to the low incorporation of 1-octene, there were no significant differences in T_m values of the resultant copolymer. The highest activity for co-polymerization by **C2** was achieved with 1-octene at 0.5 M. The ligand environment also had a big effect on the catalytic behavior and activities decreased in the order: **C2** > **C3** > **C4** > **C1** > **C5** > **C7**, which is the same as that for the ethylene polymerization, suggesting that bulkier and stronger donor substituents on the *ortho*-position of the arylimine are favorable for the stability of the active species at high temperature. The order of the molecular weights of the polymers produced was **C4** > **C3** > **C2** > **C1**, indicating that the bulkier substituent on the *ortho* position of the arylimine resulted in slower chain insertion and propagation in the co-polymerization of ethylene with 1-octene. The T_m values of the ethylene/1-octene co-polymers produced by **C1**–**C5**, and **C7** were in the range 122.2–126.4 °C (runs 2, 4–8, Table 2), lower than those for the polyethylenes (131–135 °C), which was consistent with the incorporation of 1-octene. The ^{13}C NMR (see Fig. 4) analysis of the co-polymers (run 5, Table 2) revealed a 1-octene incorporation rate of about 2.7 mol % [85].

2.2.3. Co-polymerization of ethylene/1-hexene

The co-polymerization behavior of ethylene with 1-hexene using the catalysts herein was also investigated and the results are collected in Table 3. The co-polymerization results for ethylene/1-hexene (Table 3) were similar to those for ethylene/1-octene (Table 2) and the catalysts exhibited moderate activity. The newly purified complex **C6** was screened, however, complex **C6** exhibited much lower activity for the co-polymerization of ethylene/1-hexene than did **C1**–**C5** at 70 °C (run 1–7, Table 3); besides stability, the steric bulk close to the Ti–O bond was thought to play an important role, inhibiting the insertion of monomer and co-monomer. The molecular weights of the resultant co-polymers decreased in the order **C4** > **C3** > **C2** > **C1**, which was the same as the results observed for 1-octene. All the resultant co-polymers also exhibited lower T_m values than did polyethylene, consistent with incorporation of 1-hexene. In Fig. 5, the ^{13}C NMR spectrum of the ethylene/1-hexene co-polymer (run 8, Table 3) indicated the resultant polymer contained a 4.5 mol % incorporation of 1-hexene [85], which was higher than that observed for 1-octene.

2.2.4. Co-polymerization of ethylene/norbornene

Co-polymers of ethylene with cyclo-olefins are known to be amorphous materials with a promising combination of high transparency in the UV–Vis region along with humidity and heat-resistance (called COC), all of which is attractive to industry [86–88]. Herein, the catalysts were also tested for the co-polymerization of ethylene with norbornene. As is shown in Table 4, both the co-monomer concentration and the ligand environment had a large effect on the catalytic activities. On increasing the co-monomer concentration, the catalytic activities increased initially and then decreased rapidly, which was consistent with previous systems reported in the literature [84]; the best activity was achieved at 1.8 mol/L concentration. The catalytic activities decreased in the order: **C2** > **C3** > **C4** > **C5** > **C1**, suggesting that the substituents on the imino-phenyl group had a strong influence on the reactivity of their complexes. The bis-ligated complex **C7** showed the lowest activity, with the highest T_m value of the resultant co-polymer, and, as expected, also exhibited the lowest incorporation of norbornene. The M_η produced by **C5** was higher than that observed for **C1**–**C4**, probably due to the smaller steric

Table 2
Co-polymerization of ethylene with 1-octene by **C1**–**C5**, **C7**/MAO.[a]

Run	Cat.	1-Octene[b]	Polymer (g)	Activity[c]	M_η[d]	T_m[e] (°C)
1	**C2**	0.3	0.065	0.52	n.d	123.0
2	**C2**	0.5	0.584	4.67	4.4	122.7
3	**C2**	1.0	0.204	1.63	n.d	122.1
4	**C1**	0.5	0.210	1.68	2.6	125.5
5	**C3**	0.5	0.378	3.01	7.7	122.2
6	**C4**	0.5	0.256	2.06	9.1	126.0
7	**C5**	0.5	0.172	1.38	n.d	126.4
8	**C7**	0.5	0.144	1.16	n.s	126.2

[a] Conditions: 2.5 μmol of cat., MAO, Al/Ti = 4000, 70 °C, 10 atm, 30 min, toluene, total volume 100 mL, 30 min.
[b] Mol L^{-1}.
[c] Activity: 10^5 g mol^{-1} (Ti) h^{-1}.
[d] Determined by viscosity, 10^5 g mol^{-1}.
[e] Determined by DSC.

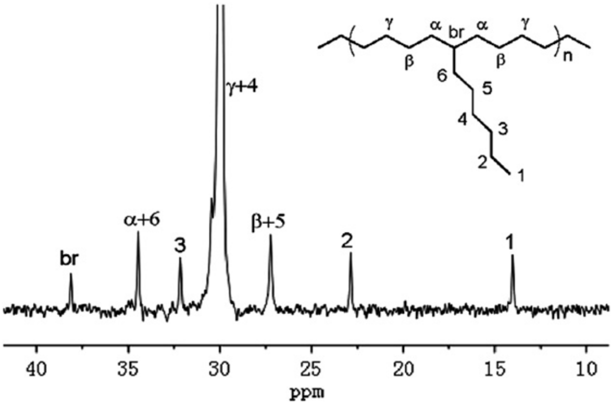


Fig. 4. ^{13}C NMR spectrum of ethylene/1-octene co-polymer.

Table 3
Co-polymerization of ethylene with 1-hexene by **C1**–**C7**/MAO.[a]

Run	Complex	1-Hexene[b]	Polymer (g)	Activity[c]	M_η[d]	T_m[e] (°C)
1	**C1**	0.5	0.283	2.27	1.2	125.5
2	**C2**	0.5	0.641	5.16	4.0	125.2
3	**C2**	1.0	0.285	2.28	n.d	124.7
4	**C3**	0.5	0.434	3.47	5.1	125.0
5	**C4**	0.5	0.403	3.22	5.6	124.8
6	**C5**	0.5	0.189	1.52	n.d	124.6
7	**C6**	0.5	0.151	1.21	n.d	124.1
8	**C7**	0.5	0.187	1.50	4.2	123.6

[a] Conditions: 2.5 μmol Ti, 10 atm, 70 °C, 30 min, Al/Ti = 4000, toluene, total volume 100 mL.
[b] Mol L^{-1}.
[c] Activity: 10^5 g mol^{-1} (Ti) h^{-1}.
[d] Determined by viscosity, 10^5 g mol^{-1}.
[e] Determined by DSC.

hindrance associated with **C5**, which favored the consecutive coordination and insertion of ethylene or co-monomer. As seen from the results, **C7** produced the co-polymer with the lowest molecular weight.

In order to evaluate the incorporation rate of the norbornene, the ^{13}C NMR spectrum (Fig. 6) of the ethylene/norbornene co-polymer (run 8, Table 4) was measured and the analysis indicated that the resultant polymer possessed a 13.5 mol % incorporation of norbornene [89–92].

3. Conclusion

A series of 2-aldiminophenoxylate titanium complexes containing the bulky $CHPh_2$ group were prepared and fully characterized. When the $-CHPh_2$ substituent was at the *ortho*-position of the arylimine, the reaction of the potassium salt of the corresponding ligands (**L1**–**L5**) with $TiCl_4(THF)_2$ at different ratios (2:1 or 1:1) gave mono-ligated trichlorotitanium complexes [$\mathbf{L}TiCl_3(THF)$]. Whereas, when this bulky group was located at the *ortho*-position of the aryloxo moiety, the reaction afforded both the mono-ligated complex **C6** [$\mathbf{L6}TiCl_3(THF)$] and the bis-ligated complex **C7** [$(\mathbf{L6})_2TiCl_2$]. In the presence of MAO, good activities were achieved for ethylene homo-polymerization and co-polymerization of ethylene with 1-hexene/1-octene/norbornene at 70 °C, which was much higher than the optimized temperature for FI catalysts (50 °C), and the incorporation rate for norbornene reached 13.5 mol %. The bulky ligands enhanced the stability of their mono-ligated titanium complexes, which provides an attractive strategy for designing pre-catalysts for ethylene both homo-polymerization and co-polymerization.

Table 4
Co-polymerization of ethylene with norbornene by **C1**–**C5**, **C7**/MAO.[a]

Run	Cat.	Norbornene[b]	Polymer(g)	Activity[c]	M_η[d]	T_m[e] (°C)
1	**C2**	0.5	0.232	1.86	7.0	128.3
2	**C2**	1.0	0.239	1.91	n.d	131.1
3	**C2**	1.8	0.559	4.47	2.1	129.2
4	**C2**	3.0	0.031	0.25	n.d	128.3
5	**C1**	1.8	0.219	1.75	1.9	130.2
6	**C3**	1.8	0.368	2.94	2.8	129.7
7	**C4**	1.8	0.298	2.38	3.2	130.1
8	**C5**	1.8	0.245	1.96	4.5	123.2
9	**C7**	1.8	0.202	1.62	2.1	132.4

[a] Conditions: 2.5 μmol of cat., MAO, 10 atm, 70 °C, 30 min, Al/Ti = 4000, toluene, total volume 100 mL.
[b] Mol L^{-1}.
[c] Activity: 10^5 g mol^{-1} (Ti) h^{-1}.
[d] Determined by viscosity, 10^5 g mol^{-1}.
[e] Determined by DSC.

4. Experimental section

4.1. General procedure

All manipulations of air and/or moisture-sensitive compounds were carried out under nitrogen atmosphere in a glove-box or using standard Schlenk techniques. Methylaluminoxane (MAO, 1.46 M in toluene) was purchased from Albemarle. Potassium hydride (KH) was washed with *n*-hexane before use to remove contained mineral oil. Toluene, *n*-hexane and *n*-heptane were refluxed in the presence of sodium and benzophenone, then freshly distilled under nitrogen atmosphere before to use. Dichloromethane (CH_2Cl_2), 1-hexene and 1-octene were dried over calcium hydride. Elemental analysis was performed on a Flash EA 1112 microanalyzer. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard at 25 °C. ^{13}C NMR spectra of the polymers was recorded on a Bruker DMX-300 MHz instrument at 110 °C in deuterated 1,2-dichlorobenzene with TMS as an internal standard. 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. In the trial of measuring the molecular weights of obtained polymers by GPC, the GPC curves could be not repeated, even for one same sample, with indicating portions of ultra-high molecular weights. Therefore the molecular weights of resultant polymers were measured by viscosity method. Viscosity measurements [η] were carried out in decalin at 130 °C using an Ubbelohde viscometer and molecular weight was calculated by the $M_\eta = 5.37 \times 10^4[\eta]^{1.37}$.

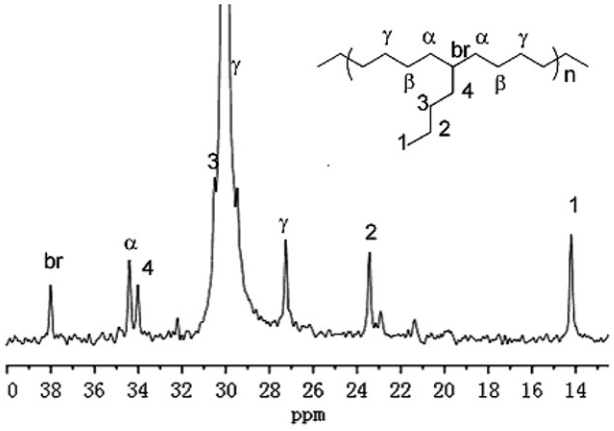


Fig. 5. ^{13}C NMR spectrum of ethylene/1-hexene co-polymer.

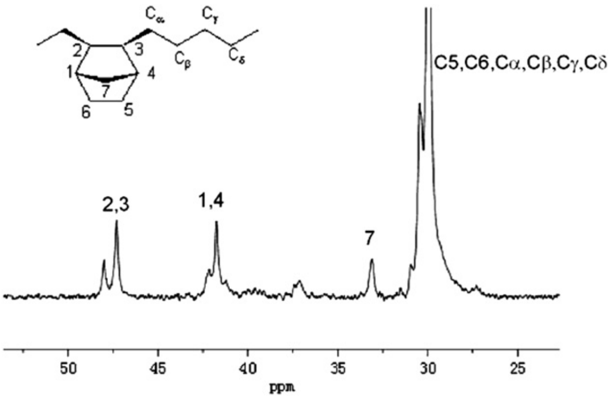


Fig. 6. ^{13}C NMR spectrum of ethylene/norbornene co-polymer.

4.2. Synthesis of ligand ***L1***–***L6***

4.2.1. 2-((2,6-Dibenzhydryl-4-isopropylphenylimino)methyl)-4,6-di-tert-butylphenol (***L1***)

A mixture of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (2.34 g, 10.0 mmol), 2,6-dibenzhydryl-4-isopropylbenzenamine (4.77 g, 10.0 mmol) and a catalytic amount of *p*-toluenesulfonic acid (0.30 g) in 100 mL ethanol was refluxed for 12 h. The solution was then cooled to room temperature, 2-((2,6-dibenzhydryl-4-isopropylphenylimino)methyl)-4,6-di-*tert*-butylphenol (**L1**) was obtained as a yellow solid (4.98 g, 72.8%). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 12.94 (s, 1H, OH), 7.33 (s, 1H, C*H*=N), 7.26–7.12 (m, 12H, Ph–H), 7.03–7.01 (m, 8H, Ph–H), 6.89 (s, 1H, Ph–H), 6.71 (s, 2H, Ph–H), 6.12 (d, 1H, *J* = 2.04, Ph–H), 5.47 (s, 2H, C*H*Ph$_2$), 2.69 (m, 1H, C*H*(CH$_3$)$_2$), 1.46 (s, 9H, *t*-Bu–H), 1.22 (s, 9H, *t*-Bu–H), 1.04 (d, 6H, *J* = 6.88, CH(C*H*$_3$)$_2$–H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ 170.1 (CH=N), 158.0, 146.4, 144.4, 143.8, 139.8, 136.4, 135.0, 129.8, 128.3, 127.5, 127.2, 126.4, 126.2, 117.6, 52.6, 35.2, 34.1, 33.7, 31.6, 29.6, 24.1. IR (KBr, cm^{-1}): 3661.2 (O–H) (w), 3059, 2956, 2164, 1629 (CN=N) (m), 1593, 1443, 1359, 1251, 1163, 1118, 1027, 878, 845, 772, 737. Mp: 182 °C. Anal. Calcd. For C$_{50}$H$_{53}$NO: C, 87.80; H, 7.81; N, 2.05. Found: C, 87.98; H, 7.91; N, 2.11%.

4.2.2. 2-((2,6-Dibenzhydryl-4-isopropylphenylimino)methyl)-6-tert-butyl-4-methylphenol (***L2***)

Using the same procedure as for **L1**, 2-((2,6-dibenzhydryl-4-isopropylphenylimino)methyl)-6-*tert*-butyl-4-methylphenol (**L2**) was obtained as an orange yellow solid in 63.9% yield (4.10 g). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 12.94 (s, 1H, O*H*–H), 7.23–7.12 (m, 14H, Ph–H), 7.04–7.02 (m, 8H, Ph–H), 6.73 (s, 2H, Ph–H), 6.08 (s, 1H, Ph–H), 5.49 (s, 2H, C*H*Ph$_2$–H), 2.71 (m, 1H, C*H*(CH$_3$)$_2$–H), 2.18 (s, 3H, PhC*H*$_3$–H), 1.45 (s, 9H, *t*-Bu–H), 1.06 (d, 6H, *J* = 6.88, CH(C*H*$_3$)$_2$–H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ 169.3 (CH=N), 158.3, 146.3, 144.5, 143.7, 137.0, 134.8, 131.3, 130.4, 129.8, 128.3, 126.5, 126.4, 126.3, 118.0, 52.5, 34.9, 33.7, 29.6, 24.1, 20.7. IR (KBr, cm^{-1}): 3662 (O–H) (w), 3057, 3026, 2954, 2168, 1621 (CH=N) (w), 1592, 1432, 1388, 1266, 1207, 1157, 1127, 1029, 867, 772, 743, 699. Mp: 178 °C. Anal. Calcd. For C$_{47}$H$_{47}$NO: C, 87.94; H, 7.38; N, 2.18. Found: C, 87.78; H, 7.46; N, 2.25%.

4.2.3. 2-((2,6-Dibenzhydryl-4-methylphenylimino)methyl)-6-tert-butyl-4-methylphenol (***L3***)

Using the same procedure as for **L1**, 2-((2,6-dibenzhydryl-4-methylphenylimino)methyl)-6-*tert*-butyl-4-methylphenol (**L3**) was obtained as an orange/yellow solid in 70.2% yield (4.31 g). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ: 12.94 (s, 1H, O*H*–H), 7.29 (s, 1H, C*H*=N–H), 7.27–7.25 (m, 2H, Ph–H), 7.23–7.13 (m, 7H, Ph–H), 7.10–7.08 (m, 5H, Ph–H), 7.03–6.99 (m, 6H, Ph–H), 6.66 (s, 2H, Ph–H), 6.38 (s, 1H, Ph–H), 6.06 (s, 1H, Ph–H), 5.47 (s, 2H, C*H*Ph$_2$–H), 2.17 (s, 3H, C*H*$_3$–H), 2.16 (s, 3H, C*H*$_3$–H), 1.44 (s, 9H, *t*-Bu–H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ 169.4 (CH=N), 158.2, 146.1, 143.6, 142.9, 137.0, 135.0, 131.3, 130.4, 129.8, 128.3, 126.7, 126.4, 126.3, 118.0, 52.4, 34.8, 29.6, 21.5, 20.7. IR (KBr, cm^{-1}): 3662 (O–H) (w), 3026, 2960, 1619 (CH=N) (s), 1591, 1440, 1321, 1234, 1203, 1161, 1123, 1030, 983, 864, 743, 697. Mp: 156 °C. Anal. Calcd. For C$_{45}$H$_{43}$NO: C, 88.05; H, 7.06; N, 2.28. Found: C, 88.22; H, 7.18; N, 2.23%.

4.2.4. 2-((2,4-Dibenzhydryl-6-methylphenylimino)methyl)-6-tert-butyl-4-methylphenol (***L4***)

Using the same procedure as for **L1**, 2-((2,4-dibenzhydryl-6-methylphenylimino)methyl)-6-*tert*-butyl-4-methylphenol (**L4**) was obtained as an orange/yellow solid in 74.3% yield (4.56 g). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 13.14 (s, 1H, O*H*–H), 7.73 (s, 1H, C*H*=N), 7.25–7.22 (d, 4H, *J* = 7.47, Ph–H), 7.19–7.13 (m, 9H, Ph–H), 7.04 (d, 4H, *J* = 7.24, Ph–H), 6.95 (d, 4H, *J* = 6.51, Ph–H), 6.88 (s, 1H, Ph–H), 6.61 (s, 1H, Ph–H), 6.55 (s, 1H, Ph–H), 5.52 (s, 1H, C*H*Ph$_2$–H), 5.39 (s, 1H, C*H*Ph$_2$–H), 2.24 (s, 3H, C*H*$_3$–H), 2.09 (s, 3H, C*H*$_3$–H), 1.45 (s, 9H, *t*-Bu–H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): 168.4 (CH=N), 158.4, 146.6, 144.2, 143.5, 139.9, 137.4, 135.3, 131.5, 130.4, 130.0, 129.6, 129.4, 128.4, 128.3, 126.8, 126.3, 126.2, 118.2, 56.4, 52.3, 34.9, 29.5, 20.8, 18.8. IR (KBr, cm^{-1}): 3662 (O–H) (w), 3022, 2961, 2029, 1619 (CH=N) (s), 1592, 1440, 1388, 1319, 1263, 1204, 1163, 1128, 1076, 1028, 983, 863, 743, 696. Mp: 176 °C. Anal. Calcd. For C$_{45}$H$_{43}$NO: C, 88.05; H, 7.06; N, 2.28. Found: C, 88.25, H, 7.17; N, 2.16%.

4.2.5. 2-((2-Benzhydryl-4,6-dimethylphenylimino)methyl)-6-tert-butyl-4-methylphenol (***L5***)

Using the same procedure as for **L1**, 2-((2-benzhydryl-4,6-dimethylphenylimino)methyl)-6-*tert*-butyl-4-methylphenol (**L5**) was obtained as an orange/yellow solid in 62.5% yield (2.89 g). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 13.20 (s, 1H, O*H*–H), 7.70 (s, 1H, C*H*=N), 7.26–7.15 (m, 7H, Ph–H), 7.09–7.04 (m, 4H, Ph–H), 6.97 (s, 1H, Ph–H), 6.62 (s, 1H, Ph–H), 6.56 (s, 1H, Ph–H), 5.55 (s, 1H, C*H*Ph$_2$–H), 2.25 (s, 3H, C*H*$_3$–H), 2.24 (s, 3H, C*H*$_3$–H), 2.14 (s, 3H, C*H*$_3$–H), 1.46 (s, 9H, *t*-Bu–H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ 168.4 (CH=N), 158.3, 146.0, 143.5, 137.3, 135.2, 133.8, 131.3, 130.3, 129.8, 129.7, 128.6, 128.3, 128.0, 126.7, 126.2, 118.2, 52.2, 34.8, 29.5, 21.1, 20.6, 18.5. IR (KBr, cm^{-1}): 3662 (O–H) (m), 3061, 2954, 2908, 2167, 1758, 1620 (CH=N) (s), 1581, 1476, 1431, 1389, 1358, 1320, 1262, 1234, 1199, 1158, 1132, 1031, 978, 860, 819, 775, 744, 697. Mp: 145 °C. Anal. Calcd. For C$_{33}$H$_{35}$NO: C, 85.86; H, 7.64; N, 3.03. Found: C, 85.92; H, 7.66; N, 2.96%.

4.2.6. 2-((2,6-Diethylphenylimino)methyl)-6-benzhydryl-4-methylphenol (***L6***)

Using the same procedure as for **L1**, 2-((2,6-diethylphenylimino)methyl)-6-benzhydryl-4-methylphenol (**L6**) was obtained as an orange/yellow solid in 63.2% yield (2.74 g). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 13.09 (s, 1H, O*H*), 8.27 (s, 1H, C*H*=N), 7.32–7.29 (m, 1H, Ph–H), 7.25 (d, 3H, *J* = 3.58, Ph–H), 7.22–7.19 (d, 4H, *J* = 3.58, Ph–H), 7.11–7.09 (m, 3H, Ph–H), 7.02 (d, 3H, *J* = 1.23, Ph–H), 6.86 (s, 1H, Ph–H), 6.07 (s, 1H, C*H*Ph$_2$–H), 2.51 (m, 4H, C*H*$_2$CH$_3$–H), 2.23 (s, 3H, C*H*$_3$–H), 1.13 (t, 6H, *J* = 7.52, CH$_2$C*H*$_3$–H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ 166.2 (CH=N), 156.3, 143.1, 134.4, 133.9, 131.5, 130.2, 129.0, 127.8, 126.9, 125.9, 125.7, 124.7, 48.4, 24.3, 20.1, 14.4. IR (KBr, cm^{-1}): 3662 (O–H) (m), 2963, 2925, 2870, 1620 (CH=N) (s), 1583, 1494, 1447, 1261, 1185, 1158, 1077, 1030, 988, 865, 797, 728, 699. Mp: 176 °C. Anal. Calcd. For C$_{31}$H$_{31}$NO: C, 85.87; H, 7.21; N, 3.23. Found: C, 85.62; H, 7.35; N, 3.36%.

4.3. Synthesis of trichlorotitanium 2-aldiminophenoxylates ***C1***–***C6***

4.3.1. Trichlorotitanium 2-((2,6-dibenzhydryl-4-isopropylphenylimino)methyl)-4,6-di-tert-butyl-phenoxylate THF adduct, ***L1***TiCl$_3$(THF) (***C1***)

To a stirred solution of 2-((2,6-dibenzhydryl-4-isopropylphenylimino)methyl)-4,6-di-*tert*-butylphenol (**L1**) (0.684 g, 1.00 mmol) in dried toluene (30 mL), KH (0.040 g, 1.00 mmol) was added at −78 °C. The mixture was stirred for additional 3 h, then TiCl$_4$(THF)$_2$ (0.334 g, 1.00 mmol) was added to the mixture solution at −78 °C, and the resultant mixture was allowed to warm to room temperature and stirred for additional 24 h. The residue, obtained by removing the solvent under vacuum, was extracted with CH$_2$Cl$_2$ (3 × 20 mL) and the combined filtrates were concentrated in vacuum to 20 mL. The solution was recrystallized at −20 °C to afford brown crystals of trichlorotitanium 2-((2,6-dibenzhydryl-4-isopropylphenylimino)methyl)-4,6-di-*tert*-butylphenoxylate (**C1**) (0.611 g, 67.2%). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 7.58 (s, 1H, C*H*=N), 7.28–7.14 (m, 10H, Ph–H), 6.95–6.94 (m, 7H, Ph–H), 6.87–6.85 (m, 4H, Ph–H), 6.69 (s, 2H, Ph–H), 6.28 (s, 1H, Ph–H), 5.72 (s, 2H, C*H*Ph$_2$–H), 4.52 (m, 4H, THF), 2.72 (m, 1H, CH(C*H*$_3$)$_2$), 1.93 (m, 4H, THF), 1.56 (s, 9H, *t*-Bu–H), 1.19 (s, 9H, *t*-Bu–H), 1.05 (d, 6H, J = 6.88, CH(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): 173.5 (CH=N), 160.6, 147.4, 145.5, 142.5, 136.4, 132.8, 129.9, 129.8, 128.4, 128.3, 126.8, 126.6, 126.5, 123.8, 52.9, 35.3, 34.4, 33.7, 31.1, 30.0, 29.7, 25.4, 23.9. Anal. Calcd. For $C_{54}H_{60}Cl_3NO_2Ti$: C, 71.33; H, 6.65; N, 1.54. Found: C, 71.42; H, 6.59; N, 1.58%.

*4.3.2. Trichlorotitanium 2-((2,6-dibenzhydryl-4-isopropylphenylimino)methyl)-6-tert-butyl-4-methyl-phenoxylate THF adduct, **L2**TiCl$_3$(THF) (**C2**)*

Using the same procedure as for **C1**, trichlorotitanium 2-((2,6-dibenzhydryl-4-isopropylphenylimino)methyl)-6-*tert*-butyl-4-methylphenoxylate (**C2**) was isolated as a red solid (0.683 g, 77.6%). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 7.47 (s, 1H, C*H*=N), 7.29–7.19 (m, 9H, Ph–H), 6.98–6.66 (s, 14H, Ph–H), 6.15 (s, 1H, Ph–H), 6.05 (s, 2H, C*H*Ph$_2$–H), 4.24 (m, 4H, THF), 2.71 (m, 1H, C*H*Me$_2$), 2.14 (s, 3H, CH$_3$–H), 1.90 (m, 4H, THF), 1.51 (s, 9H, *t*-Bu–H), 1.04 (d, 6H, J = 5.16, C*H*(CH$_3$)$_2$–H), ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): 172.7 (CH=N), 160.1, 146.9, 143.7, 143.5, 137.7, 136.0, 135.3, 133.5, 130.0, 129.9, 128.3, 128.1, 127.0, 126.3, 53.6, 51.2, 35.0, 33.6, 30.1, 25.6, 24.0, 20.7. Anal. Calcd. For $C_{51}H_{54}Cl_3NO_2Ti$: C, 70.63; H, 6.28; N, 1.62. Found: C, 70.75; H, 6.33; N, 1.68%.

*4.3.3. Trichlorotitanium 2-((2,6-dibenzhydryl-4-methylphenylimino)methyl)-6-tert-butyl-4-methyl-phenoxylate THF adduct, **L3**TiCl$_3$(THF) (**C3**)*

Using the same procedure as for **C1**, trichlorotitanium 2-((2,6-dibenzhydryl-4-methylphenylimino)methyl)-6-*tert*-butyl-4-methylphenoxylate (**C3**) was isolated as a brown solid (0.538 g, 64.1%). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 7.31 (s, 1H, C*H*=N), 7.30–7.16 (m, 7H, Ph–H), 7.05 (d, 4H, J = 6.72, Ph–H), 7.00–6.94 (m, 4H, Ph–H), 6.88–6.87 (d, 4H, J = 5.70, Ph–H), 6.65 (s, 2H, Ph–H), 6.56 (s, 1H, Ph–H), 6.19 (s, 1H, Ph–H), 6.07 (s, 1H, Ph–H), 5.94 (s, 2H, C*H*Ph$_2$–H), 4.50 (m, 4H, THF), 2.18 (s, 3H, C*H*$_3$–H), 2.15 (s, 3H, C*H*$_3$–H), 2.02 (m, 4H, THF), 1.54 (s, 9H, *t*-Bu–H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): 172.9 (CH=N), 160.5, 143.0, 140.4, 133.0, 130.4, 130.0, 129.8, 129.5, 129.2, 129.1, 128.4, 128.2, 127.7, 126.4, 51.4, 35.0, 30.0, 25.7, 21.7, 21.6, 20.8. Anal. Calcd. For $C_{49}H_{50}Cl_3NO_2Ti$: C, 70.13; H, 6.01; N, 1.67; Found: C, 70.25; H, 5.92; N, 1.62%.

*4.3.4. Trichlorotitanium 2-((2,4-dibenzhydryl-6-methylphenylimino)methyl)-6-tert-butyl-4-methyl-phenoxylate THF adduct, **L4**TiCl$_3$(THF) (**C4**)*

Using the same procedure as for **C1**, trichlorotitanium 2-((2,4-dibenzhydryl-6-methylphenylimino)methyl)-6-*tert*-butyl-4-methylphenoxylate (**C4**) was isolated as a brown solid (0.621 g, 74.0%). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 7.29 (s, 1H, C*H*=N), 7.28–7.17 (m, 6H, Ph–H), 7.12–7.10 (m, 4H, Ph–H), 7.07–7.01 (m, 8H, Ph–H), 6.89 (s, 1H, Ph–H), 6.84 (d, 2H, J = 7.27, Ph–H), 6.59 (s, 1H, Ph–H), 6.19 (s, 2H, Ph–H), 5.41 (s, 1H, C*H*Ph$_2$–H), 5.30 (s, 1H, C*H*Ph$_2$–H), 4.26 (m, 4H, THF), 2.27 (s, 3H, C*H*$_3$–H), 2.12 (s, 3H, C*H*$_3$–H), 1.89 (m, 4H, THF), 1.55 (s, 9H, *t*-Bu–H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): 171.4 (CH=N), 160.2, 143.9, 143.7, 143.6, 143.2, 142.0, 137.9, 136.7, 135.4, 133.5, 133.0, 129.6, 129.3, 129.1, 128.4, 128.3, 127.9, 126.3, 126.0, 125.3, 56.2, 50.9, 35.0, 30.1, 25.2, 21.5, 20.8, 19.0. Anal. Calcd. For $C_{49}H_{50}Cl_3NO_2Ti$: C, 70.13; H, 6.01; N, 1.67. Found: C, 70.28; H, 6.13; N, 1.59%.

*4.3.5. Trichlorotitanium 2-((2-benzhydryl-4,6-dimethylphenylimino)methyl)-6-tert-butyl-4-methyl-phenoxylate THF adduct, **L5**TiCl$_3$(THF) (**C5**)*

Using the same procedure as for **C1**, trichlorotitanium 2-((2-benzhydryl-4,6-dimethylphenylimino)methyl)-6-*tert*-butyl-4-methylphenoxylate (**C5**) was isolated as a brown solid (0.432 g, 62.9%). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 7.34 (s, 1H, C*H*=N), 7.24–7.00 (m, 10H, Ph–H), 6.96–6.94 (m, 4H, Ph–H), 5.79 (s, 1H, C*H*Ph$_2$–H), 4.05 (m, 4H, THF), 2.24 (s, 6H, C*H*$_3$–H), 2.11 (s, 3H, C*H*$_3$–H), 1.90 (m, 4H, THF), 1.52 (s, 9H, *t*-Bu–H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): 171.8 (CH=N), 160.2, 143.2, 137.3, 136.8, 135.9, 135.5, 132.1, 129.9, 129.8, 129.3, 129.0, 128.4, 128.2, 128.1, 126.3, 125.3, 52.0, 34.9, 29.6, 25.2, 21.2, 20.7, 18.7, 18.0. Anal. Calcd. For $C_{37}H_{42}Cl_3NO_2Ti$: C, 64.69; H, 6.16; N, 2.04. Found: C, 64.83; H, 6.24; N, 2.11%.

*4.3.6. Trichlorotitanium 2-((2,6-diethylphenylimino)methyl)-6-benzhydryl-4-methylphenoxylate THF adduct, **L6**TiCl$_3$(THF) (**C6**)*

To a 30 mL toluene solution of 2-((2,6-diethylphenylimino)methyl)-6-benzhydryl-4-methylphenol (1.00 mmol of **L6**), (0.040 g, 1.00 mmol) KH was added at −20 °C. The mixture was stirred for additional 4 h, then 0.334 g (1.0 mmol) TiCl$_4$(THF)$_2$ was added at −78 °C, and the resultant mixture was slowly warmed up to room temperature and stirred for additional 12 h. After solvent evaporation, the residue was extracted with CH$_2$Cl$_2$ (3 × 20 mL), and the filtrate was combined and concentrated to about 20 mL. The concentrated solution was covered with *n*-heptane and left for three days to obtain brown crystals of trichlorotitanium 2-((2,6-diethylphenylimino)methyl)-6-benzhydryl-4-methylphenoxylate (**C6**) (0.493 g, 73.3%). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 8.22 (s, 1H, C*H*=N), 7.29 (m, 4H, Ar–H), 7.24 (m, 7H, Ar–H), 7.16 (m, 4H, Ar–H), 6.12 (s, 1H, C*H*Ph$_2$–H), 3.86 (m, 4H, THF–O(C*H*$_2$)$_2$–H), 2.61 (s, 3H, C*H*$_3$–H), 2.22 (s, 4H, C*H*$_2$CH$_3$–H), 1.84 (m, 4H, THF–O(CH$_2$C*H*$_2$)$_2$–H), 1.03 (s, 6H, CH$_2$C*H*$_3$–H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): 168.9 (CH=N), 158.8, 139.9, 135.7, 134.0, 130.4, 129.1, 129.0, 128.5, 128.0, 127.3, 126.2, 125.6, 122.6, 47.3, 25.5, 20.6, 15.5. Anal. Calcd. For $C_{35}H_{38}Cl_3NO_2Ti$: C, 63.80; H, 5.81; N, 2.13. Found: C, 64.02; H, 5.95; N, 2.14%.

*4.3.7. Bis(2-((2,6-diethylphenylimino)methyl)-6-benzhydryl-4-methylphenoxy)titanium dichloride, (**L6**)$_2$TiCl$_2$ (**C7**)*

To a 30 mL toluene solution of 2-((2,6-diethylphenylimino)methyl)-6-benzhydryl-4-methylphenol (**L6**), 0.040 g (1.00 mmol) KH was added at −20 °C. The mixture was stirred for additional 4 h, then 0.167 g (0.50 mmol) TiCl$_4$(THF)$_2$ was added at −78 °C, and the resultant mixture was slowly warmed up to room temperature and stirred for additional 12 h. After solvent evaporation, the residue was extracted with CH$_2$Cl$_2$ (3 × 20 mL), and the filtrate was combined and concentrated into about 20 mL. The concentrated solution was covered with *n*-heptane and kept for three days to obtain brown crystals of bis(2-((2,6-diethylphenylimino)methyl)-6-benzhydryl-4-methylphenoxy)titanium dichloride (**C7**) (0.642 g, 65.2%). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): 8.13 (s, 2H, C*H*=N), 7.14–6.90 (m, 30H; Ph–H), 5.91 (s, 2H, C*H*Ph$_2$–H), 2.78 (s, 6H; C*H*$_3$), 2.24 (s, 8H; C*H*$_2$CH$_3$), 1.03 (s, 12H, CH$_2$C*H*$_3$). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): 169.2 (CH=N), 159.7, 139.7, 136.7, 133.9, 130.4, 129.3, 129.1, 128.3, 128.1, 127.1, 126.1, 125.4, 122.6, 47.7, 25.2, 20.8, 15.2. Anal. Calcd. For $C_{62}H_{60}Cl_2N_2O_2Ti$: C, 75.68; H, 6.15; N, 2.85. Found: C, 75.80; H, 6.01; N, 2.72%.

4.4. Procedure for ethylene polymerization and co-polymerization

A stainless steel autoclave (250 mL) equipped with a mechanical stirrer and a temperature controller was heated in vacuum at 120 °C and recharged with ethylene three times, then cooled to room temperature under ethylene atmosphere. A toluene solution of the titanium pre-catalyst (with co-monomer) was transferred into the reactor. After the desired reaction temperature was reached and the required amount of co-catalyst (with total 100 mL volume maintained through adding toluene) was added, the autoclave was immediately pressurized to 10 atm. The ethylene

Table 5
Crystal refinement of **C2**, **C4** and **C7**.

	C2	**C4**	**C7**
Empirical formula	$C_{51}H_{54}Cl_3NO_2Ti$	$C_{49}H_{49}Cl_3NO_2Ti$	$C_{62}H_{60}Cl_2N_2O_2Ti$
Formula weight	867.20	838.14	983.92
Crystal color	Red	Red	Red
Temperature (K)	173(2)	173(2)	293(2) K
Wavelength (Å)	0.71073	0.71073	0.71073 A
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P2(1)/c	P2
a (Å)	10.857(2)	15.291(3)	11.165(2)
b (Å)	15.604(3)	14.971(3)	22.239(4)
c (Å)	15.689(3)	24.297(5)	22.190(4)
α (°)	69.83(3)	90	90
β (°)	80.60(3)	105.34(3)	93.08(3)
γ (°)	85.88(3)	90	90
Volume ($Å^3$)	2461.1(9)	5363.8(19)	5501.6(19)
Z	2	4	4
Dcalc(Mg m^{-3})	1.170	1.038	1.188
μ (mm^{-1})	0.374	0.341	0.296
F(000)	912	1756	2072
Crystal size (mm)	0.29 × 0.20 × 0.12	0.37 × 0.16 × 0.13	0.51 × 0.39 × 0.35
θ range (°)	1.39–25.37	1.38–25.32	1.30–25.35
Limiting indices	$-10 \le h \le 13$ $-18 \le k \le 18$ $-18 \le k \le 18$	$-18 \le h \le 18$ $-17 \le k \le 18$ $-27 \le k \le 29$	$-13 \le h \le 13$ $-24 \le k \le 26$ $-26 \le k \le 20$
No. of rflns collected	18,848	36,971	38,215
No. of unique rflns	8906	9764	10,067
Rint	0.0552	0.1017	0.0754
Completeness to θ (%)	98.7%	99.8%	99.9%
Goodness-of-fit on F^2	1.096	1.072	1.193
Final R indices $[I > 2\sigma](I)]$	$R1 = 0.0921$,w$R2 = 0.2436$	$R1 = 0.1049$,w$R2 = 0.2657$	$R1 = 0.0990$,w$R2 = 0.2529$
R indices (all data)	$R1 = 0.1191$,wR2 = 0.2666	$R1 = 0.1484$,w$R2 = 0.2925$	$R1 = 0.1154$,w$R2 = 0.2646$
Largest diff peak, hole (e $Å^{-3}$)	0.581, −0.648	0.579, −0.422	0.540, −0.730

pressure was kept constant during the reaction through feeding ethylene. At the end of the reaction time, the polymerization reaction was stopped and the autoclave was placed in a water-ice bath for an hour when 10% HCl-acidic ethanol was added. The solid polyolefin was washed with ethanol and water several times and then dried in vacuum to constant weight.

4.5. X-ray structure determination

Crystals of **C2**, **C4** and **C7** suitable for single-crystal X-ray analysis were obtained by laying n-heptane onto toluene solution of **C2**, **C4** and **C7**, respectively. Single-crystal X-ray diffraction for **C2**, **C4** and **C7** were performed on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ 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 are solved by direct methods and refined by full-matrix least-squares on $F2$. All non-hydrogen atoms are refined anisotropically. Structure solution and refinement are performed by using the SHELXL-97 package [93]. Crystal data and processing parameters for **C2**, **C4** and **C7** are summarized in Table 5.

Acknowledgments

This work was supported by National Natural Science Foundation of China (No. 20904059) and the MOST 863 program No. 2009AA034601. The EPSRC are thanked for the award of a travel grant (to CR).

Appendix A. Supplementary material

CCDC 859463(**C2**), 850462(**C4**) and 859461(**C7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, G. Moraglio, J. Am. Chem. Soc. 77 (1955) 1708–1710.
[2] K. Ziegler, E. Holzkamp, H. Breil, H. Martin, Angew. Chem. 67 (1955) 541–547.
[3] G. Natta, J. Polym. Sci. 16 (1955) 143–154.
[4] K. Ziegler, H.G. Gellert, K. Zosel, W. Lehmkuhl, W. Pfohl, Angew. Chem. 67 (1955). 424–424.
[5] H. Sinn, W. Kaminsky, H.-J. Vollmer, R. Woldt, Angew. Chem. Int. Ed. Engl. 19 (1980) 390–392.
[6] H.G. Alt, A. Köppl, Chem. Rev. 100 (2000) 1205–1221.
[7] W. Kaminsky, Macromol. Chem. Phys. 197 (1996) 3907–3945.
[8] E.Y. Tshuva, I. Goldberg, M. Kol, J. Am. Chem. Soc. 122 (2000) 10706–10707.
[9] E.Y. Tshuva, I. Goldberg, M. Kol, H. Weitman, Z. Goldchmidt, Chem. Commun. (2001) 2120–2121.
[10] J.D. Scollard, D.H. McConville, J. Am. Chem. Soc. 118 (1996) 10008–10009.
[11] D.J. Arriola, E.M. Carnahan, P.D. Hustad, R.L. Kuhlman, T.T. Wenzel, Science 312 (2006) 714–719.
[12] F. Alfano, H.W. Boone, V. Busico, R. Cipullo, J.C. Stevens, Macromolecules 40 (2007) 7736–7738.
[13] M.V. Meurs, G.J.P. Britovsek, V.C. Gibson, S.A. Cohen, J. Am. Chem. Soc. 127 (2005) 9913–9923.
[14] F. Alfano, H.W. Boone, V. Busico, R. Cipullo, J.C. Stevens, Macromolecules 40 (2007) 7061–7064.
[15] C. Capacchione, A. Proto, H. Ebeling, R. Mülhaupt, T.P. Spaniol, K. Möller, J. Okuda, J. Am. Chem. Soc. 125 (2003) 4964–4965.
[16] D. Herskovicskorine, M.S. Eisen, J. Organomet. Chem. 503 (1995) 307–314.
[17] V. Volkis, M. Shmulinson, C. Averbuj, A. Lisovskii, F.T. Edelmann, M.S. Eisen, Organometallics 17 (1998) 3155–3157.
[18] H.C.S. Clark, G.N. Cloke, P.B. Hitchcock, J.B. Love, A.P. Wainwright, J. Organomet. Chem. 501 (1995) 333–340.
[19] J.D. Scollard, D.H. McConville, N.C. Payne, J.J. Vittal, Macromolecules 29 (1996) 5241–5243.
[20] A.D. Horton, J. de With, A.J. van der Linden, H. van de Weg, Organometallics 15 (1996) 2672–2674.
[21] T.H. Warren, R.R. Schrock, W.M. Davis, Organometallics 17 (1998) 308–319.
[22] R. Baumann, W.M. Davis, R.R. Schrock, J. Am. Chem. Soc. 119 (1997) 3830–3831.
[23] V.C. Gibson, B.S. Kimberley, A.J.P. White, D.J. Williams, P. Howard, Chem. Commun. (1998) 313–328.

[24] A. Vanderlinden, C.J. Schaverien, N. Meijboom, C. Ganter, A.G. Orpen, J. Am. Chem. Soc. 117 (1995) 3008–3021.
[25] S. Fokken, T.P. Spaniol, H.C. Kang, W. Massa, J. Okuda, Organometallics 15 (1996) 5069–5072.
[26] H. Makio, N. Kashiwa, T. Fujita, Adv. Synth. Catal. 344 (2002) 477–493.
[27] T. Matsugi, T. Fujita, Chem. Soc. Rev. 37 (2008) 1264–1277.
[28] H. Makio, H. Terao, A. Iwashita, T. Fujita, Chem. Rev. 111 (2011) 2363–2449.
[29] S. Matsui, T. Fujita, Catal. Today 66 (2001) 63–73.
[30] N. Matsukawa, S. Matsui, M. Mitani, J. Saito, K. Tsuru, N. Kashiwa, T. Fujita, J. Mol. Catal. A: Chem. 169 (2001) 99–104.
[31] R. Furuyama, M. Mitani, J. Mohri, R. Mori, T. Nakano, H. Tanaka, T. Fujita, Macromolecules 38 (2005) 1546–1552.
[32] L. Matilainen, M. Klinga, M. Leskelä, J. Chem. Soc. Dalton Trans. (1996) 219–225.
[33] P. Sobota, K. Przybylak, J. Utko, L.B. Jerzykiewicz, A.J.L. Pombeiro, M.F.C. Guedes da Silva, K. Szczegot, Chem. Eur. J. 7 (2001) 951–958.
[34] O. Motta, C. Capacchione, A. Proto, D. Acierno, Polymer 43 (2002) 5847–5854.
[35] C. Capacchione, P. Neri, A. Proto, Inorg. Chem. Commun. 6 (2003) 339–342.
[36] V. Reimer, T.P. Spaniol, J. Okuda, H. Ebeling, A. Tuchbreiter, R.T. Mulhaup, Inorg. Chim. Acta 345 (2003) 221–227.
[37] R.J. Long, V.G. Gibson, A.J.P. White, Organometallics 27 (2008) 235–245.
[38] Y. Suzuki, Y. Inoue, H. Tanaka, T. Fujita, Macromol. Rapid Commun. 25 (2004) 493–497.
[39] Y. Yoshida, S. Matsui, Y. Takagi, M. Mitani, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, Organometallics 20 (2001) 4793–4799.
[40] Y. Yoshida, S. Matsui, T. Fujita, J. Organomet. Chem. 690 (2005) 4382–4397.
[41] X.-F. Li, K. Dai, W.-P. Ye, L. Pan, Y.-S. Li., Organometallics 23 (2004) 1223–1230.
[42] J. Liu, S. Liu, L. Pan, Y. Li, Adv. Synth. Catal. 351 (2009) 1505–1511.
[43] W.-P. Ye, X.-C. Shi, B.-X. Li, J.-Y. Liu, Y.-S. Li, Y.-X. Cheng, N.-H. Hu, Dalton Trans. 39 (2010) 9000–9007.
[44] L.M. Broomfield, Y. Sarazin, J.A. Wright, D.L. Hughes, W. Clegg, R.W. Harrington, M. Bochmann, J. Organomet. Chem. 692 (2007) 4603–4611.
[45] A. Pärssinen, T. Luhtanen, T. Pakkanen, M. Leskelä, Timo. Repo, Eur. J. Inorg. Chem. (2010) 266–274.
[46] M. Lamberti, M. Mazzeo, C. Pellecchia, Dalton Trans. (2009) 8831–8837.
[47] W.-Q. Hu, X.-L. Sun, C. Wang, Y. Gao, Y. Tang, L.-P. Shi, W. Xia, J. Sun, H.-L. Dai, X.-Q. Li, X.-L. Yao, X.-R. Wang, Organometallics 23 (2004) 1684–1688.
[48] Y. Wang, W. Zhang, W. Huang, L. Wang, C. Redshaw, W.-H. Sun, Polymer 52 (2011) 3732–3737.
[49] R. Cariou, V.C. Gibson, A.K. Tomov, A.J.P. White, J. Organomet. Chem. 694 (2009) 703–716.
[50] G. Paolucci, A. Zanella, L. Sperni, V. Bertolasi, M. Mazzeo, C. Pellecchia, J. Mol. Catal. A: Chem. 258 (2006) 275–283.
[51] M. Lamberti, M. Bortoluzzi, G. Paolucci, C. Pellecchia, J. Mol. Catal. A: Chem. 351 (2011) 112–119.
[52] Y. Suzuki, S. Kinoshita, A. Shibahara, S. Ishii, K. Kawamura, Y. Inoue, T. Fujita, Organometallics 29 (2010) 2394–2396.
[53] P.J.W. Deckers, B. Hessen, J.H. Teuben, Organometallics 21 (2002) 5122–5135.
[54] S. Kinoshita, K. Kawamura, T. Fujita, Chem. Asian J. 6 (2011) 284–290.
[55] X.-H. Yang, Z. Wang, X.-L. Sun, Y. Tang, Dalton Trans. (2009) 8945–8954.
[56] D. Zhang, G.-X. Jin, Appl. Catal. A 262 (2004) 85–91.
[57] J. Müller, G. Kehr, R. Fröhlich, G. Erker, Eur. J. Inorg. Chem. (2005) 2836–2841.
[58] W. Huang, W. Zhang, S. Liu, T. Liang, W.-H. Sun, J. Polym. Sci. A: Polym. Chem. 49 (2011) 1887–1894.
[59] J.C. Flores, J.C.W. Chien, M.D. Rausch, Organometallics 14 (1995) 2106–2108.
[60] Y.-Y. Long, L.-P. Ye, T. Ping, Y.-S. Li, Dalton Trans. 40 (2011) 1610–1618.
[61] D.A. Pennington, S.J. Coles, M.B. Hursthouse, M. Bochmann, S.J. Lancaster, Chem. Commun. (2005) 3150–3152.
[62] M. Talja, M. Klinga, M. Polamo, E. Aitola, M. Leskela, Inorg. Chim. Acta 358 (2005) 1061–1067.
[63] J. Yu, H. Liu, W. Zhang, X. Hao, W.-H. Sun, Chem. Commun. 47 (2011) 3257–3259.
[64] H. Yang, W.-H. Sun, Z. Li, L. Wang, Synth. Commun. 32 (2002) 2395–2402.
[65] A. Senier, F.G. Shepheard, J. Chem. Soc. Dalton Trans. 95 (1909) 441–449.
[66] H.W. Grimmel, A. Guenther, J.F. Morgan, J. Am. Chem. Soc. 68 (1946) 539–545.
[67] D.J. Barnes, R.L. Chapman, R.S. Vagg, E.C. Watton, J. Chem. Eng. Data 23 (1978) 349–350.
[68] O. Belda, N.-F. Kaiser, U. Bremberg, M. Larhed, A. Hallberg, C. Moberg, J. Org. Chem. 65 (2000) 5868–5870.
[69] P.-M. Chan, W.-Y. Yu, C.-M. Che, K.-K. Cheung, Dalton Trans. 79 (1998) 3183–3190.
[70] D.A. Conlon, N. Yasuda, Adv. Synth. Catal. 343 (2001) 137–138.
[71] D. Owiny, S. Parkin, F.T. Ladipo, J. Organomet. Chem. 678 (2003) 134–141.
[72] D.A. Pennington, D.L. Hughes, M. Bochmann, S.J. Lancaster, Dalton Trans. (2003) 3480–3482.
[73] Dale A. Pennington, W. Clegg, Simon J. Coles, R.W. Harrington, M.B. Hursthouse, D.L. Hughes, M.E. Light, M. Schormann, M. Bochmann, S.J. Lancaster, Dalton Trans. (2005) 561–571.
[74] A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587–2598.
[75] H.H. Brintzinger, D. Fischer, R. Mulhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143–1170.
[76] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. 38 (1999) 428–447.
[77] S. Koltzenburg, J. Mol. Catal. A: Chem. 116 (1997) 355–363.
[78] E.Y.X. Chen, T.J. Marks, Chem. Rev. 100 (2000) 1391–1434.
[79] W. Zuo, S. Zhang, S. Liu, X. Liu, W.-H. Sun, J. Polym. Sci. A: Polym. Chem. 46 (2008) 3396–3410.
[80] W. Zuo, M. Zhang, W.-H. Sun, J. Polym. Sci. A: Polym. Chem. 47 (2009) 357–372.
[81] S. Liu, J. Yi, W. Zuo, K. Wang, D. Wang, W.-H. Sun, J. Polym. Sci. A: Polym. Chem. 47 (2009) 3154–3169.
[82] W.-H. Sun, S. Liu, W. Zhang, Y. Zeng, T. Liang, Organometallics 29 (2010) 732–741.
[83] S. Liu, W.-H. Sun, Y. Zeng, D. Wang, W. Zhang, Y. Li, Organometallics 29 (2010) 2459–2464.
[84] W. Zuo, W.-H. Sun, S. Zhang, P. Hao, A. Shiga, J. Polym. Sci. A: Polym. Chem. 45 (2007) 3415–3420.
[85] M.R. Seger, G.E. Maciel, Anal. Chem. 76 (2004) 5734–5747.
[86] G. Nicoler, P.A. Kohl, S.A.B. Allen, S. Jayaramam, R. Shick, J. Polym. Sci. B: Polym. Phys. 37 (1999) 3003–3010.
[87] S. Ahmed, S.A. Bidstrup, P. Kohl, P. Ludovice, Macromol. Symp. 133 (1998) 1–10.
[88] T.-Y. Bo, Y.Y. Do, Macromol. Res. 15 (2007) 185–190.
[89] R.A. Wendt, R. Mynott, K. Hauschild, D. Ruchatz, G. Fink, Macromol. Chem. Phys. 200 (1999) 1340–1350.
[90] D. Ruchatz, G. Fink, Macromolecules 31 (1998) 4674–4680.
[91] A. Provasoli, D.R. Ferro, I. Tritto, L. Boggioni, Macromolecules 32 (1999) 6697–6706.
[92] I. Tritto, C. Marestin, L. Boggioni, L. Zetta, A. Provasoli, D.R. Ferro, Macromolecules 33 (2000) 8931–8944.
[93] G.M. Sheldrick, SHELXTL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.