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Synthesis, structures, and catalytic properties for ethylene polymerization of bridged $[\eta^5,\eta^1$-$C_5H_4CHPhArO]TiCl_2$ complexes

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Abstract

A number of bridged half-sandwich titanium complexes $[\eta^5:\eta^1$-2-C_5H_4CHPh-4-R^1-6-$R^2C_6H_2O]TiCl_2$ [R^1 = H (**5**), Me (**6**), ^tBu (**7,8**); R^2 = H (**6,7**), ^tBu (**5,8**)] were synthesized from the reaction of their corresponding trimethylsilyl substituted ligand precursors 2-$Me_3SiC_5H_4CHPh$-4-R^1-6-$R^2C_6H_2OSiMe_3$ [R^1 = H (**1**), Me (**2**), ^tBu (**3,4**); R^2 = H (**2,3**), ^tBu (**1,4**)] with $TiCl_4$ in hexane. All new complexes were characterized by ^1H and ^{13}C NMR spectroscopy. Molecular structures of complexes **5** and **8** were determined by single crystal X-ray diffraction analysis. Upon activation with $Al^iBu_3/Ph_3CB(C_6F_5)_4$, complexes **5–8** exhibit reasonable catalytic activity for ethylene polymerization and copolymerization with 1-hexene, producing polyethylene and poly(ethylene-co-1-hexene) with moderate molecular weights.
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1. Introduction

Since 1990s, the so-called constrained geometry metallocene catalysts (CGC) with the general formula of $[\eta^5:\eta^1$-$C_5Me_4(SiMe_2)N^tBu]TiCl_2$ (**I**) (see Chart 1) have been widely studied in academic [1] and industrial [2] institutions because of their high performance in catalyzing the copolymerization of different olefins. So far, various modifications on the chelating ligand have been conducted in order to improve the catalytic performance of the CGC catalysts and study the steric and electronic effects of the ligands on their catalytic properties. For example, a variety of CGC catalysts with ligands bearing different substituted cyclopentadienyl, indenyl and fluorenyl groups [3,4], different coordinating heteroatoms [5], and different linkages [6] have been synthesized and studied. In comparison with the

CGC catalysts of type **I**, the catalysts with a pendent oxygen donor on the cyclopentadienyl ring received relatively less attention and have not been studied systematically [1c]. We and other groups have developed a number of CGC catalysts of the type $[\eta^5:\eta^1$-C_5R_4–$ArO]TiCl_2$ (**II**) and found that these catalysts produce ethylene/α-olefin copolymers with relatively low molecular weights due probably to their ligands are not bulky enough [4c]. Similar catalysts with a formula of $[\eta^5:\eta^1$-C_5H_4–CR_2–$ArO]TiCl_2$ (**III**) were also synthesized, but no study on ethylene/α-olefin copolymerization has been reported [7]. Considering that the ligands of the complexes **III** have a longer linkage and thus are bulkier than those of the catalysts **II**, complexes **III** might be more suitable catalysts for producing ethylene/α-olefin copolymers with higher molecular weights. We have synthesized a number of new half-sandwich titanium complexes $[\eta^5:\eta^1$-2-C_5H_4CHPh-4-R^1-6-$R^2C_6H_2O]TiCl_2$ [R^1 = H (**5**), Me (**6**), ^tBu (**7,8**); R^2 = H (**6,7**), ^tBu (**5,8**)] from the reaction of their corresponding trimethylsilyl substituted ligand precursors 2-Me_3SiC_5-

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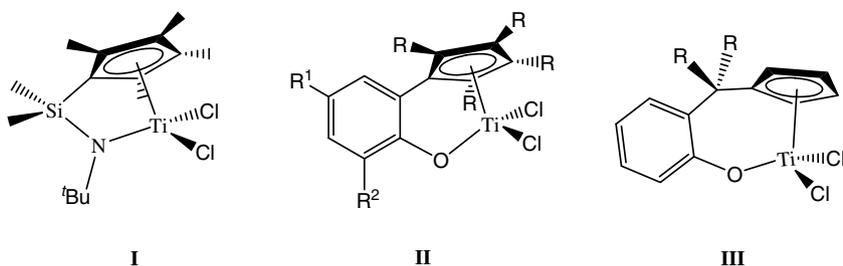
Chart 1.

$H_4CHPh-4-R^1-6-R^2C_6H_2OSiMe_3$ [R^1 = H (**1**), Me (**2**), ^tBu (**3,4**); R^2 = H (**2,3**), ^tBu (**1,4**)] with $TiCl_4$. In this paper, we report the synthesis and characterization of the new ligand precursors **1–4** and their titanium complexes **5–8**, as well as the catalytic performance of complexes **5–8** for ethylene polymerization and copolymerization with 1-hexene.

2. Results and discussion

2.1. Synthesis of ligand precursors and titanium complexes

The trimethylsilyl substituted ligand precursors **1–4** were synthesized (Scheme 1) by treatment of 6-plenylfulvene with the dilithium salt of corresponding phenol prepared in situ from the reaction of corresponding *o*-bromophenol with 2 equiv. *n*-BuLi in diethyl ether, followed by reaction with Me_3SiCl in diethyl ether [3c]. The yields of compounds **1–4** were found to be sensitive to the nature of the R^1 and R^2 groups on the phenol ring. It seems that stronger elec-

tron-donating ability of R^1 and R^2 groups leads to higher yields, which may be ascribed to the difference in the nucleophilicity of the dilithium salt of corresponding phenol [4c]. Compounds **1–4** were all characterized by ^1H NMR spectroscopy. Ligand precursors $2-C_5H_5CHPh-4-R^1-6-R^2C_6-H_2OH$ [R^1 = H, R^2 = ^tBu; R^1 = Me, R^2 = H; R^1 = ^tBu; R^2 = H, ^tBu] could also be synthesized from the reaction of 6-plenylfulvene with the dilithium salt of corresponding phenol by quenching the reaction before the addition of Me_3SiCl [4b]. Dilithium salts of these ligands could be obtained too before the reaction with Me_3SiCl. However, it was found that the trimethylsilyl substituted ligand precursors **1–4** are better starting materials for the synthesis of the titanium (IV) dichloride complexes **5–8**, and the ligand precursors $2-C_5H_5CHPh-4-R^1-6-R^2C_6H_2OH$ and their dilithium salts are not necessary to be isolated.

The titanium complexes **5–8** were synthesized in moderate yields by the TMSCl elimination reaction [8] of the trimethylsilyl substituted ligand precursors **1–4** with $TiCl_4$ in hexane. The yields of the complexes **5–8** were also found to

R_1 = H (**1**), Me (**2**), ^tBu (**3, 4**)
R_2 = H (**2, 3**), ^tBu (**1, 4**)

R_1 = H (**5**), Me (**6**), ^tBu (**7, 8**)
R_2 = H (**6, 7**), ^tBu (**5, 8**)
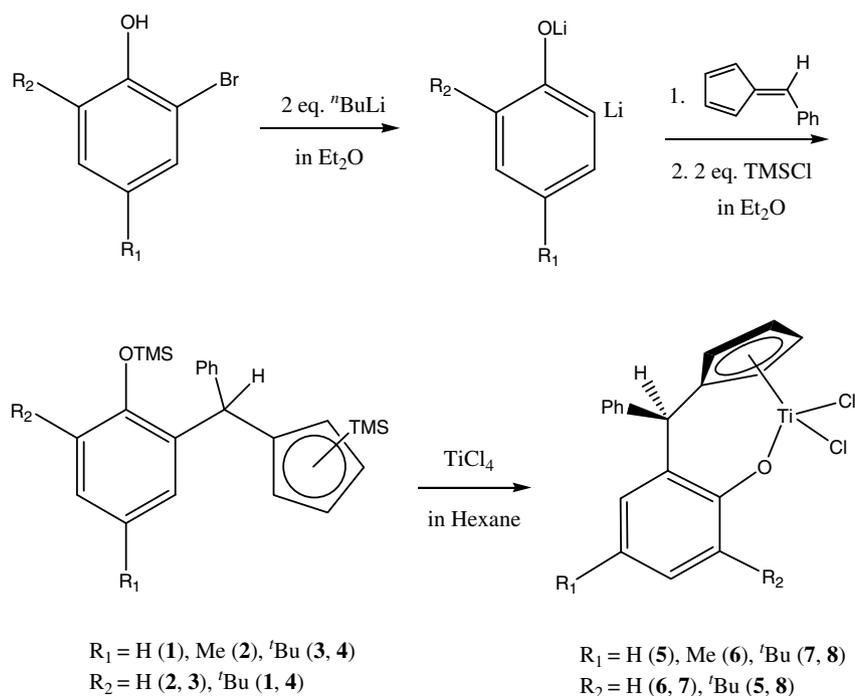
Scheme 1. Synthesis of compounds **1–4** and complexes **5–8**.

be sensitive to the R^1 and R^2 groups on the phenol ring of their ligands, and similar trend to that mentioned above for the synthesis of compounds **1**–**4** was observed. That is, stronger electron-donating ability of R^1 and R^2 groups results in higher yields due probably to stronger coordination ability of corresponding ligands and ligand precursors. The synthesis of these titanium complexes was also tried by the reaction of the dilithium salt of corresponding ligand with $TiCl_4$ [4c], from which complexes **5**–**8** were obtained in lower yields. All new Ti complexes **5**–**8** were characterized by means of ^1H and ^{13}C NMR spectroscopy and elemental analysis, and the structures of complexes **5** and **8** were determined by single crystal X-ray crystallography.

2.2. Crystal structures of 5 and 8

The molecular structures of complexes **5** and **8** were determined by single crystal X-ray diffraction analysis. The ORTEP drawings of the molecular structures of **5** and **8** are shown in Figs. 1 and 2, respectively. The selected bond lengths and angles are summarized in Table 1. Both complexes **5** and **8** adopt a pseudo-tetrahedral geometry with the sterically open feature in front of the central metal atom required for olefin copolymerization catalysts. The Cp (cent)–Ti–O angles for **5** and **8** are 111.6° and 109.5°, respectively, which are slightly bigger than the Cp(cent)–Ti–N angle in **I** (107.6°) [2a] and the Cp(cent)–Ti–O angle in **II** (106.8–107.3°) [4b]. The Cp(cent)–Ti distances of **5** (1.997 Å) and **8** (1.995 Å) are much shorter than that in **I** (2.340 Å) [2a] and **II** (2.335–2.348 Å) [4b]. The Ti–O bond lengths of 1.792(2) Å in **5** and 1.794(3) Å in **8** are slightly

Fig. 2. Structure of complex **8** (thermal ellipsoids are drawn at the 30% probability level).

Table 1
Selected bond lengths and angles

Complex 5			
Ti(1)–O(1)	1.792(2)	Ti(1)–C(1)	2.322(4)
Ti(1)–C(2)	2.323(4)	Ti(1)–C(3)	2.341(4)
Ti(1)–C(4)	2.334(4)	Ti(1)–C(5)	2.314(5)
Ti(1)–Cl(1)	2.252(2)	Ti(1)–Cl(2)	2.2543(17)
O(1)–C(6)	1.371(4)	Cp(cent)–Ti(1)	1.997
C(1)–C(18)	1.522(5)	C(11)–C(18)	1.536(5)
O(1)–Ti(1)–Cl(1)	103.97(11)	O(1)–Ti(1)–Cl(2)	102.26(9)
Cl(1)–Ti(1)–Cl(2)	106.12(8)	Cp(cent)–Ti(1)–O(1)	111.6
Ti(1)–Cp(cent)–C(1)	89.3	Cp(cent)–C(1)–C(18)	179.2
C(1)–C(18)–C(11)	169.5	C(18)–C(11)–C(6)	123.5(3)
C(11)–C(6)–O(1)	118.7(3)	C(6)–O(1)–Ti(1)	148.2(2)
Complex 8			
Ti(1)–O(1)	1.794(3)	Ti(1)–C(1)	2.310(4)
Ti(1)–C(2)	2.306(4)	Ti(1)–C(3)	2.345(5)
Ti(1)–C(4)	2.346(5)	Ti(1)–C(5)	2.318(5)
Ti(1)–Cl(1)	2.2523(14)	Ti(1)–Cl(2)	2.2578(13)
O(1)–C(6)	1.384(4)	Cp(cent)–Ti(1)	1.995
C(1)–C(18)	1.501(5)	C(11)–C(18)	1.531(5)
O(1)–Ti(1)–Cl(1)	104.66(10)	O(1)–Ti(1)–Cl(2)	104.56(9)
Cl(1)–Ti(1)–Cl(2)	103.79(6)	Cp(cent)–Ti(1)–O(1)	109.5
Ti(1)–Cp(cent)–C(1)	88.5	Cp(cent)–C(1)–C(18)	177.7
C(1)–C(18)–C(11)	169.5	C(18)–C(11)–C(6)	122.6(4)
C(11)–C(6)–O(1)	119.0(4)	C(6)–O(1)–Ti(1)	147.1(3)

shorter than the Ti–O bonds in **II** [1.832(3)–1.837(2) Å] [4b], while the Ti–O–C angles of 148.2(2)° for **5** and 147.1(3)° for **8** are much larger than the Ti–O–C angle in **II** [128.34(18)–128.9(3)°] [4b]. These results indicate the Ti–O double-bond character in complexes **5**–**8** is stronger than that in complexes **II** [9,10]. In comparison to complexes **II**, the larger Cp(cent)–Ti–O and Ti–O–C angles in **5** and **8** make these complexes possessing less space in front of the central titanium atom and thus probably being better catalysts for producing polyolefins with higher molecular weights.

Fig. 1. Structure of complex **5** (thermal ellipsoids are drawn at the 30% probability level).

2.3. Ethylene polymerization studies

Complexes **5**–**8** were studied as ethylene polymerization catalysts and the results are summarized in Table 2. Upon activation with Al(^{i}Bu)$_3$ and Ph$_3$CB(C$_6$F$_5$)$_4$, complexes **5**–**8** all show good catalytic activity for ethylene polymerization and produce polyethylenes with moderate molecular weights and melting temperatures. In comparison to the polymers obtained with catalysts **II** [4], the molecular

weight of the polyethylenes formed by complexes **5**–**8** is obviously improved. The order of the catalytic activity for ethylene polymerization under similar conditions (see runs 1, 4, 7, and 12 in Table 2) is **8** > **5** > **7** > **6**, which could be attributed to the nature of the substituents on the phenoxy group in these complexes. It seems that the catalytic activity of these complexes is directly related to the electron-donating ability of both R^1 and R^2 groups [11]. By examining the structure and catalytic activity of **5** and **7**, it can also be seen that the steric effect of the R^2 group at the ortho position of the phenolate plays a role too in determining the order of their catalytic activity. For all complexes, the catalytic activity increases with the increase in Al/Ti ratio and reaches the highest values with the Al/Ti ratio of 150. Further increase in Al/Ti ratio results in a decrease in the catalytic activity. Similar results have been obtained with other metallocene catalyst systems [12]. The catalytic activity of these complexes is low at room temperature and increases with the polymerization temperature. Reasonable catalytic activity was obtained at temperatures higher than 70 °C, which reflects the nature of tight interaction between the catalyst cation and the cocatalyst anion in the constrained geometry catalyst systems [13]. The catalytic activity reaches the highest at 90 °C and begins to decrease with the further increase in temperature, which is ascribed to that the concentrations of ethylene and the active species would decrease at higher temperature [14]. The molecular weight of the obtained polyethylene is dependent on the structure of the catalyst and polymerization conditions as seen in Table 2. Catalysts **5** and **8** produce polyethylenes with relatively high molecular weights under similar conditions, due probably to that the ^{t}Bu group at the ortho position of the phenolate could slow down the chain transfer or chain termination reaction in some extent.

Table 2
Summary of ethylene polymerization catalyzed by **5**–**8**/Al^{i}Bu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4^a$

No.	Catalyst	Al:Ti	T (°C)	Yield (g)	Activity[b] $\times 10^6$	Mη[c] $\times 10^{-3}$	T_m (°C)[d]
1	**5**	120	90	2.82	2.82	137	138.9
2	**5**	150	90	3.06	3.06	126	138.8
3	**5**	180	90	2.14	2.14	111	138.6
4	**6**	120	90	1.68	1.68	79	137.6
5	**6**	150	90	1.93	1.93	66	137.3
6	**6**	180	90	1.27	1.27	55	136.6
7	**7**	120	90	2.2	2.2	106	138.5
8	**7**	150	90	2.52	2.52	93	138.1
9	**7**	180	90	2.04	2.04	79	137.9
10	**7**	150	70	1.96	1.96	143	139.2
11	**7**	150	110	1.42	1.42	61	137.2
12	**8**	120	90	3.39	3.39	172	139.3
13	**8**	150	90	3.54	3.54	156	139.6
14	**8**	180	90	3.19	3.19	141	139.1
15	**8**	150	70	3.04	3.04	216	140.6
16	**8**	150	110	2.89	2.89	102	138.5

[a] Polymerization conditions: solvent 60 ml of toluene, catalyst 2×10^{-6} mol, B/Ti ratio 1.5, time 30 min, ethylene pressure 6 bar.
[b] g PE(mol Ti)$^{-1}$ h^{-1}.
[c] Measured in decahydronaphthalene at 135 °C.
[d] Determined by DSC at a heating rate of 10 °C min^{-1} and the data from second scan are used.

Table 3
Summary of ethylene copolymerization with 1-hexene catalyzed by **5**–**8**/Al^{i}Bu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4^a$

No.	Catalyst	1-Hexene (mol/l)	Yield (g)	Activity[b] $\times 10^6$	1-Hexene content[c] (%)	Mη[d] $\times 10^{-3}$	T_m (°C)[e]
1	**5**	0.2	0.76	4.57	7.88	91	122.3
2	**5**	0.5	0.71	4.23	16.03	57	111.5
3	**5**	0.8	0.61	3.67	24.32	8.9	107.3
4	**6**	0.2	0.56	3.34	8.53	83	120.6
5	**6**	0.5	0.50	3.00	17.57	36	110.0
6	**6**	0.8	0.40	2.40	25.11	7.9	107.1
7	**7**	0.2	0.70	4.19	7.96	89	121.9
8	**7**	0.5	0.63	3.80	16.39	43	110.7
9	**7**	0.8	0.55	3.29	24.03	8.8	107.3
10	**8**	0.2	0.80	4.79	7.10	97	122.8
11	**8**	0.35	0.77	4.63	11.93	85	117.3
12	**8**	0.5	0.76	4.53	15.69	66	112.1
13	**8**	0.65	0.71	4.24	19.49	42	110.6
14	**8**	0.8	0.65	3.89	23.68	9.8	107.6

[a] Polymerization conditions: solvent 60 ml of toluene, temperature 90 °C, catalyst 2×10^{-6} mol, B/Ti ratio 1.5, Al/Ti ratio 150, time 10 min, ethylene pressure 6 bar.
[b] g polymer (mol Ti)$^{-1}$ h^{-1}.
[c] Calculated by ^{13}C NMR spectra.
[d] Measured in xylene at 105 °C.
[e] Determined by DSC at a heating rate of 10 °C min^{-1} and the data from second scan are used.

2.4. Copolymerization of ethylene with 1-hexene

Complexes **5–8** were also tested for copolymerization of ethylene with 1-hexene, and the results are summarized in Table 3. It can be seen that the copolymerization catalytic activity of these catalysts changes in the same order as that observed in the ethylene homopolymerization under similar conditions. ^{13}C NMR analysis of the obtained copolymers indicates reasonable incorporation of 1-hexene into the polymer chains for all catalyst systems. As expected, the 1-hexene content of the copolymers produced by **5–8** is comparable to that of copolymers formed by catalysts **II**, while the molecular weight of the copolymers resulted from **5–8** is obviously improved in comparison to that of the latter copolymers under similar conditions [4c]. However, both the 1-hexene content and the molecular weight of the copolymers produced by **5–8** are lower than those of copolymers from related non-bridged $C_5R_5TiCl_2(OAr)$ catalyst systems [15]. As can be seen from Table 3, the molecular weight of the obtained copolymers is sensitive to the microstructure of the catalyst and polymerization conditions. The melting temperature and molecular weight of the copolymers are also dependent on the 1-hexene content [16] and decrease as the 1-hexene content increases (see runs 10–14 in Table 3). The ethylene and 1-hexene reactivity ratios (r_E and r_H are the reactivity ratios of ethylene and

1-hexene, respectively) were calculated from Finemane–Ross plots [17] as shown in Fig. 3. The value of reactivity ratio products $r_E r_H$ is close to 1, which demonstrates that the ethylene/1-hexene copolymerization proceeds in a random manner. Table 4 summarizes selected triad sequence distributions (monomer sequences) and dyads in the resultant copolymers estimated by ^{13}C NMR spectra. The results suggest that the monomer sequence distributions in the copolymers produced by **5–8** are basically independent on the substituents R^1 and R^2 in their ligands [16].

3. Experimental

3.1. General details

All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture using standard Schlenk techniques [18]. Ether and toluene were refluxed over sodium benzophenone ketyl under nitrogen and distilled before use. CH_2Cl_2 and n-hexane were refluxed over CaH_2 and distilled under nitrogen before use [19]. Polymerization grade ethylene was further purified by passage through columns of 5 Å molecular sieves and MnO. $Al(^iBu)_3$, ^nBuLi, and $TiCl_4$ were purchased from Aldrich. 2-bromothenol [9], 6-plenylfulvene [20] and $Ph_3CB(C_6H_5)_4$ [21] were prepared according to literature procedures. NMR spectra were recorded on a Varian Mercury-300 or a Varian Utility-400 NMR spectrometer.

3.2. Preparation of $2\text{-}Me_3SiC_5H_4CHPh\text{-}6\text{-}^tBuC_6H_3OSiMe_3$ (**1**)

A solution of 2-bromo-2-*tert*-butylphenol (1.63 g, 7.13 mmol) in Et_2O (20 ml) was added dropwise to a solution of ^nBuLi (14.3 mmol) in Et_2O (10 ml) at $-15\,°C$. The mixture was slowly warmed to room temperature and stirred for 6 h. To this solution was slowly added 6-phenylfulvene (1.10 g, 7.13 mmol) in Et_2O (10 ml) at $-15\,°C$ over 1 h. The resulting solution was then allowed to warm to room temperature and stirred overnight. The solvent was removed in vacuo, and 20 ml hexane was added. The supernatant solution was decanted and the residue was suspended with an additional 20 ml of Et_2O. A solution of Me_3SiCl (1.85 ml, 14.5 mmol) in Et_2O (10 ml) was added
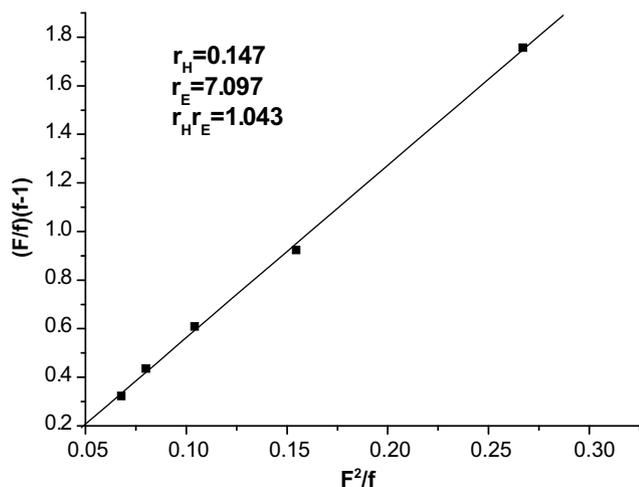
Fig. 3. Finemane–Ross plot for ethylene/1-hexene copolymerization.

Table 4
Selected monomer sequence distribution data for some poly(ethylene-co-1-hexene) samples[a]

Run	Catalyst	1-Hexene[b] (mol%)	Triads sequence distribtuion[c]						Dyads (%)[d]		
			EEE	HEE + EEH	HEH	EHE	HHE + EHH	HHH	EE	EH + HE	HH
3	**5**	24.32	44.04	25.91	5.73	15.36	8.09	0.87	56.99	38.09	4.92
6	**6**	25.11	45.53	24.95	4.41	16.57	7.42	1.12	58.01	37.17	4.83
9	**7**	24.03	47.92	23.56	4.49	15.29	8.05	0.69	59.70	35.59	4.72
14	**8**	23.68	46.60	24.27	5.44	14.71	8.23	0.74	58.73	36.41	4.85

[a] Detailed polymerization conditions see Table 3.
[b] 1-Hexene content in copolymer determined by ^{13}C NMR spectra.
[c] Calculated by ^{13}C NMR spectra.
[d] [EE] = [EEE] + 1/2[EEH + HEE], [EH] = [HEH] + [EHE] + 1/2{[EEH + HEE] + [HHE + EHH]}, [HH] = [HHH] + 1/2[HHE + EHH].

to the suspension at 0 °C. The resulting mixture was slowly warmed to room temperature and stirred over night. The reaction mixture was then filtered and concentrated by evaporation. Pure product (1.29 g, 40.3%) was obtained by column chromatography over silica (hexane/ethyl acetate, 10:1) as yellow oil. Anal. Calc. for $C_{28}H_{40}OSi_2$ (448.79): C, 74.94; H, 8.98. Found: C, 74.89; H, 8.95%. ^{1}H NMR (CDCl$_3$, 300 MHz; 298 K): δ 6.90–7.36 (m, 8H, PhH), 6.33–6.50 (m, 3H, CpH), 5.49–5.52 (s, 1H, PhCH), 3.29–3.32 (1H, m, CpH), 1.40 (s, 9H, ^tBu), 0.13 (s, 9H, OSiMe_3), 0.02–0.06 (s, 9H, CpSiMe_3).

3.3. Preparation of 2-Me₃SiC₅H₄CHPh-4-MeC₆H₃OSiMe₃ (2)

Compound **2** was synthesized using a procedure identical to that for **1** with 2-bromo-4-metylphenol (1.78 g, 9.53 mmol) as starting material. Pure product (1.65 g, 33.5%) was obtained as yellow oil. Anal. Calc. for $C_{25}H_{34}OSi_2$ (406.71): C, 73.83; H, 8.43. Found: C, 73.79; H, 8.46%. ^{1}H NMR (CDCl$_3$, 300 MHz; 298 K): δ 6.92–7.30 (m, 8H, PhH), 6.36–6.47 (m, 3H, CpH), 5.48–5.55 (s, 1H, PhCH), 3.26–3.31 (1H, m, CpH), 2.26 (s, 9H, PhMe), 0.15 (s, 9H, OSiMe_3), 0.01–0.07 (s, 9H, CpSiMe_3).

3.4. Preparation of 2-Me₃SiC₅H₄CHPh-4-ᵗBuC₆H₃OSiMe₃ (3)

Compound **3** was synthesized using a procedure identical to that for **1** with 2-bromo-4-*tert*-butylphenol (2.24 g, 9.76 mmol) as starting material. Pure product (2.14 g, 39.3%) was obtained as yellow oil. Anal. Calc. for $C_{28}H_{40}OSi_2$ (448.79): C, 74.94; H, 8.98. Found: C, 74.89; H, 8.94%. ^{1}H NMR (CDCl$_3$, 300 MHz; 298 K): δ 6.91–7.40 (m, 8H, PhH), 6.38–6.54 (m, 3H, CpH), 5.54–5.56 (s, 1H, PhCH), 3.24–3.30 (1H, m, CpH), 1.27 (s, 9H, ^tBu), 0.15 (s, 9H, OSiMe_3), 0.01–0.05 (s, 9H, CpSiMe_3).

3.5. Preparation of 2-Me₃SiC₅H₄CHPh-4-ᵗBu-6-ᵗBuC₆H₂OSiMe₃ (4)

Compound **4** was synthesized using a procedure identical to that for **1** with 2-bromo-4, 6-di-*tert*-butylphenol (2.53 g, 8.86 mmol) as starting material. Pure product (2.25 g, 48.0%) was obtained as yellow oil. Anal. Calc. for $C_{32}H_{48}OSi_2$ (504.89): C, 76.12, H, 9.58. Found: C, 76.22, H, 9.61%. ^{1}H NMR (CDCl$_3$, 300 MHz; 298 K): δ 6.98–7.34 (m, 7H, Ph), δ 6.32–6.45 (m, 3H, CpH), δ 5.43–5.48 (s, 1H, Ph–CH), δ 2.92–3.01 (1H, m, CpH), δ 1.30 (s, 9H, o-^tBu), δ 1.23 (s, 9H, p-^tBu), δ 0.27 (s, 9H, O–Si–Me_3), δ 0.10–0.11 (s, 9H, Cp–Si–Me_3).

3.6. Preparation of [η⁵:η¹-2-C₅H₄CHPh-6-ᵗBuC₆H₃O]-TiCl₂ (5)

A solution of **1** (1.21 g, 2.70 mmol) in hexane (20 ml) was added dropwise to a solution of TiCl$_4$ (0.3 ml,

2.73 mmol) in hexane (30 ml) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The precipitate was filtered off, and the solvent was removed to leave brown oil. Recrystallization from CH$_2$Cl$_2$/hexane (1:2) gave pure **5** as yellow crystals (0.55 g, 48.4%). Anal. Calc. for $C_{22}H_{21}Cl_2OTi$ (420.17): C, 62.89; H, 5.04. Found: C, 62.78; H, 5.09%. ^{1}H NMR (CDCl$_3$, 300 MHz; 298 K): δ 6.86–7.34 (m, 8H, PhH), 6.06–6.07 (m, 2H, CpH), 5.91–5.92 (m, 2H, CpH), 5.44 (s, 1H, PhCH), 1.48 (s, 9H, ^tBu). 13C NMR (CDCl$_3$, 75.4 MHz; 298 K): δ 160.5, 149.2, 140.4, 137.4, 130.5, 129.9, 129.5, 128.5, 128.5, 126.0, 123.9, 121.5, 120.9, 120.4, 116.8, 39.7, 31.8, 24.9 ppm.

3.7. Preparation of [η⁵:η¹-2-C₅H₄CHPh-4-MeC₆H₃O]-TiCl₂ (6)

Complex **6** was synthesized in the same progress as **5** with **2** (1.07 g, 2.63 mmol) as starting material. Pure product was obtained as yellow crystals (0.31 g, 31.3%). Anal. Calc. for $C_{19}H_{15}Cl_2OTi$ (378.09): C, 60.36; H, 4.00. Found: C, 60.25; H, 4.03%. ^{1}H NMR (CDCl$_3$, 300 MHz; 298 K): δ 6.80–7.35 (m, 8H, PhH), 6.02–6.03 (m, 2H, CpH), 5.87–5.88 (m, 2H, CpH), 5.38 (s, 1H, PhCH), 2.26 (s, 9H, Me). ^{13}C NMR (CDCl$_3$, 75.4 MHz; 298 K): δ 160.3, 148.1, 139.6, 136.3, 134.9, 131.6, 130.7, 129.1, 128.7, 127.8, 123.1, 120.8, 120.1, 119.5, 114.3, 46.9 ppm.

3.8. Preparation of [η⁵:η¹-2-C₅H₄CHPh-4-ᵗBuC₆H₃O]TiCl₂ (7)

Complex **7** was synthesized in the same progress as **5** with **3** (1.49 g, 3.32 mmol) as starting material. Pure product was obtained as yellow crystals (0.57 g, 40.6%). Anal. Calc. for $C_{22}H_{21}Cl_2OTi$ (420.17): C, 62.89; H, 5.04. Found: C, 62.78; H, 5.01%. ^{1}H NMR (CDCl$_3$, 300 MHz; 298 K): δ 6.82–7.36 (m, 8H, PhH), 6.04–6.05 (m, 2H, CpH), 5.87–5.88 (m, 2H, CpH), 5.41 (s, 1H, PhCH), 1.23 (s, 9H, ^tBu). ^{13}C NMR (CDCl$_3$, 75.4 MHz; 298 K): δ 160.7, 148.2, 139.7, 136.6, 129.7, 129.0, 128.7, 127.6, 127.7, 125.1, 123.0, 120.8, 120.1, 119.6, 113.9, 47.2, 34.5, 31.3 ppm.

3.9. [η⁵:η¹-2-C₅H₄CHPh-4-ᵗBu-6-ᵗBuC₆H₂O]TiCl₂ (8)

Complex **8** was synthesized in the same progress as **5** with **4** (1.31 g, 2.59 mmol) as starting material. Pure product was obtained as yellow crystals (0.69 g, 55.7%). Anal. Calc. for $C_{26}H_{29}Cl_2OTi$ (420.17): C, 65.57; H, 6.14. Found: C, 65.51; H, 6.16%. ^{1}H NMR (CDCl$_3$, 300 MHz; 298 K): δ 6.86–7.36 (m, 7H, PhH), 6.05–6.06 (m, 2H, CpH), 5.84–5.85 (m, 2H, CpH), 5.44 (s, 1H, PhCH), 1.50 (s, 9H, o-^tBu), 1.24 (s, 9H, p-^tBu). ^{13}C NMR (CDCl$_3$, 75.4 MHz; 298 K): δ 159.9, 147.3, 140.2, 135.0, 134.5, 130.8, 129.0, 128.6, 127.5, 126.3, 123.1, 122.9, 120.6, 119.7, 119.3, 47.7, 35.2, 34.6, 31.3, 30.2 ppm.

Table 5
Crystal data and structural refinement details for complexes **5** and **8**

Complex	5	8
Molecular formula	C$_{22}$H$_{22}$Cl$_2$OTi	C$_{26}$H$_{30}$Cl$_2$OTi
Molecular weight	421.20	477.30
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pbcn*
a (Å)	9.652(9)	17.513(2)
b (Å)	9.716(8)	12.1321(14)
c (Å)	13.125(10)	23.578(3)
α (°)	97.44(2)	90
β (°)	108.35(2)	90
γ (°)	112.463(17)	90
V (Å^3)	1034.9(15)	5009.7(11)
Z	2	8
Density (g cm^{-3})	1.352	1.266
$F(000)$	436	2000
Absorption coefficient (mm^{-1})	0.679	0.569
Scan type	ω–2θ	ω–2θ
Collected range (°)	$3.42 \leqslant 2\theta \leqslant 46.50$	$3.46 \leqslant 2\theta \leqslant 56.78$
Number of reflections	2204	34,800
Number of independent reflections	2197	6261
R_{int}	0.0327	0.2683
Number of data/restraints/parameters	2197/0/238	6261/0/315
R	0.0373	0.0528
R_w	0.1047	0.0717
Goodness-of-fit	1.043	0.841
Largest difference in peak and hole (e Å^{-3})	0.390–0.139	0.293–0.284

3.10. X-ray structure determinations of 5 and 8

Single crystals of **5** and **8** suitable for X-ray structural analysis were obtained from the mixture of CH$_2$Cl$_2$/hexane (v/v = 1:2). Details of the crystal data, data collections, and structure refinements are summarized in Table 5. Both structures were solved by direct methods [22] and refined by full matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealized positions. All calculations were performed using the SHELXTL [23] crystallographic software packages.

3.11. Polymerization reactions

A dry 250 ml steel autoclave was charged with 80 ml of toluene, thermostated at the desired temperature, and saturated with ethylene (1.0 bar). The polymerization reaction was started by injection of a mixture of Al(^{i}Bu)$_3$ and a catalyst in toluene (10 ml) and a solution of Ph$_3$CB(C$_6$F$_5$)$_4$ in toluene (10 ml) at the same time. The vessel was repressurized to the needed pressure with ethylene immediately, and the pressure was maintained by continuously feeding ethylene. After 30 min, the polymerization was quenched with acidified methanol [HCl (3 M)/methanol 1:1]. The polymer was collected by filtration, washed with water and methanol, and dried at 60 °C in vacuo to a constant weight. For copolymerization experiments, appropriate amounts of 1-hexene were added into the system.

4. Supplementary material

CCDC 669008 and 669007 contain the supplementary crystallographic data for **5** and **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data are available free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033: e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] (a) H.G. Alt, Alexander Reb, W. Milius, A. Weis, J. Organomet. Chem. 628 (2001) 169–182;
(b) F. Amor, J. Okuda, J. Organomet. Chem. 520 (1996) 245–248;
(c) K. Kunz, G. Erker, G. Kehr, R. Fröhlich, H. Jacobsen, H. Berke, O. Blacque, J. Am. Chem. Soc. 124 (2002) 3316–3326.
[2] (a) J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nickas, R.K. Rosen, G.W. Knight, S.Y. Lai, Eur. Pat. Appl. EP 416815 A2, 1991 (Dow);
(b) J.A.M. Canich, Eur. Pat. Appl. EP 420436 Al, 1991 (Exxon);
(c) J.A.M. Canich, US Patent 5,026,798, 1991 (Exxon);
(d) J.A.M. Canich, PCT Int. Appl. WO 96/00244, 1996 (Exxon).
[3] (a) J. Okuda, F.J. Schattenmann, S. Wocadlo, W. Massa, Organometallics 14 (1996) 789–795;
(b) L.J. Irwin, J.H. Reibenspies, S.A. Miller, J. Am. Chem. Soc. 126 (2004) 16716–16717;
(c) A. Rau, S. Schmitz, G. Luft, J. Organomet. Chem. 608 (2000) 71–75.
[4] (a) Y.X. Chen, C.L. Stern, S.T. Yang, T.J. Marks, J. Am. Chem. Soc. 118 (1996) 12451–12452;
(b) Y. Zhang, Y. Mu, C. Lü, G. Li, J. Xu, Y. Zhang, D. Zhu, S. Feng, Organometallics 23 (2004) 540–546;
(c) Y. Zhang, J. Wang, Y. Mu, Z. Shi, C. Lü, Y. Zhang, L. Qiao, S. Feng, Organometallics 22 (2003) 3877–3883.
[5] (a) S.J. Brown, X.L. Gao, D.G. Harrison, L. Koch, R.E.v.H. Spence, G.P.A. Yap, Organometallics 17 (1998) 5445–5447;
(b) A.J. Ashe, X.G. Fang, J.W. Kampf, Organometallics 18 (1999) 1363–1365.
[6] H. Braunschweig, F.M. Breitling, C.V. Koblinski, A.J.P. White, D.J. Williams, Dalton Trans. (2004) 938–943.
[7] (a) Y. Qian, J. Huang, J. Yang, A.S.C. Chan, W. Chen, X. Chen, L. Guisheng, X. Jin, Q. Yang, J. Organomet. Chem. 547 (1997) 263–279;
(b) Y. Qian, J. Hang, Chinese J. Chem. 19 (2001) 1009–1022;
(c) J. Wang, Y. Mu, W. Pu, Y. Zhang, G. Yang, J. Liu, Chem. Res. Chinese Univ. 17 (2001) 115–116;
(d) K. Yamamoto, H. Johoji, H. Hozumi, (Sumitomo) US Patent 6,121,401, 2000.
[8] T.E. Ready, J.C.W. Chien, M.D. Rausch, J. Organomet. Chem. 519 (1996) 21–28.
[9] Y.X. Chen, P.F. Fu, C.L. Stern, T.J. Marks, Organometallics 16 (1997) 5958–5963.
[10] B. Cetinkaya, P.B. Hitchcock, M.F. Lappert, S. Torroni, J.L. Atwood, W.E. Hunter, M.J. Zaworotko, J. Organomet. Chem. 188 (1980) C31–C35.
[11] P.C. Möhring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1–29.
[12] M. Bochmann, M.J. Sarsfield, Organometallics 17 (1998) 5908–5912.

[13] G.M. Diamond, R.F. Jordan, J.L. Petersen, J. Am. Chem. Soc. 118 (1996) 8024–8033.

[14] A.M. Martins, M.M. Marques, J.R. Ascenso, A.R. Dias, M.T. Duarte, A.C. Fernandes, S. Fernandes, M.J. Ferreira, I. Matos, M.C. Oliveira, S.S. Rodrigues, C. Wilson, J. Organomet. Chem. 690 (2005) 874–884.

[15] (a) K. Nomura, A. Tanaka, S. Katao, J. Mol. Catal. A 254 (2006) 197–205;
(b) K. Nomura, K. Oya, T. Komatsu, Y. Imanishi, Macromolecules 33 (2000) 3187–3189.

[16] K. Nomura, K. Fujita, M. Fujiki, J. Mol. Catal. A 220 (2004) 133–144.

[17] M. Fineman, S.D. Ross, J. Polym. Sci. 5 (1950) 259–262.

[18] D.F. Shriver, The Manipulation of Air-Sensitive Compounds, McGraw-Hill, New York, 1969.

[19] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, Pergamon, New York, 1980.

[20] K.J. Stone, R.D. Little, J. Org. Chem. 49 (1984) 1849–1853.

[21] (a) A.G. Massey, A.J. Park, J. Organomet. Chem. 2 (1964) 245–250;
(b) A.G. Massey, A.J. Park, J. Organomet. Chem. 5 (1966) 218–225.

[22] SHELXTL; PC Siemens Analytical X-ray Instruments, Madison, WI, 1993.

[23] G.M. Sheldrick, SHELXTL Structure Determination Programs, Version 5.0, PC Siemens Analytical Systems, Madison, WI, 1994.