

Propylene polymerization to high molecular weight atactic polypropylene and copolymerization with 1-hexene using monocyclopentadienyl titanium catalysts†

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A number of cyclopentadienyltitanium aryloxy complexes, 1-Ar-2,3,4,5-Me₄-Cp(2,6-*i*-Pr₂C₆H₃O)TiCl₂ (Ar = 4-Me, SiPhenyl (**5**), 4-*i*-PrPhenyl (**6**), 4-MePhenyl (**7**), 3,5-(CF₃)₂Phenyl (**8**)) and (1-Ar-2,3,4,5-Me₄-CpTiCl₂)₂(OAr'O) (Ar' = 4,4'-(3,3',5,5'-*i*-Pr₄C₆H₂-C₆H₂), Ar = 4-SiMe₃Phenyl (**9**), 4-MePhenyl (**10**)) were synthesized from the reaction of a corresponding cyclopentadienyl titanium trichloride derivative with the lithium salt of a relevant phenol. The molecular structures of complexes **6**, **7** and **8** were determined by X-ray crystallography. Upon activation with *i*-Bu₃Al and Ph₃CB(C₆F₅)₄, all mononuclear complexes **5–8** exhibit good catalytic activities for propylene polymerization, whereas the binuclear complexes **9** and **10** show lower catalytic activities under the same polymerization conditions. ¹³C NMR, DSC and GPC analysis indicates the produced polymers are atactic polypropylene with relatively high molecular weight. It was found that the substituents on both the cyclopentadienyl and aryloxy ligands of these complexes show obvious influence on the molecular weight of the resultant polymers with complex **5** producing the highest molecular weight atactic polypropylene. Complexes **5**, **6** and **7** were also tested as catalysts for copolymerization of propylene with 1-hexene and copolymers with 1.2–10.1% comonomer incorporation were obtained in reasonable catalytic activity.

Introduction

Group 4 metallocene complexes have been an important and versatile class of olefin polymerization catalysts in the past decades, which exhibit unique characteristics in controlling over microstructure and molecular weight of polyolefins in a wide range.^{1–6} In particular, the stereoselective polymerization of propylene with metallocene catalysts has been intensively investigated.^{7–10} So far, the relationship between the nature of the catalyst system and the tacticity of the resulting polymer has been well established for metallocene catalyst systems, which offers a great opportunity for tailoring polyolefin materials.^{4,11–13} It has been known that C₂-symmetric ansa-metallocene catalysts^{5,14} produce isotactic polypropylene, C_s-symmetric ansa-metallocene catalysts¹⁵ afford syndiotactic polypropylene, C₁-symmetric ansa-metallocene catalysts¹⁶ provide isotactic or hemiisotactic polypropylene, and C_{2v}-symmetric and other achiral metallocene catalysts usually produce atactic polypropylene.¹⁷ To date, a large amount of studies have been devoted to the development of catalysts for isospecific and syndiospecific polymerization of propylene. However, only a limited number of works on the development of metallocene catalysts for producing high molecular weight

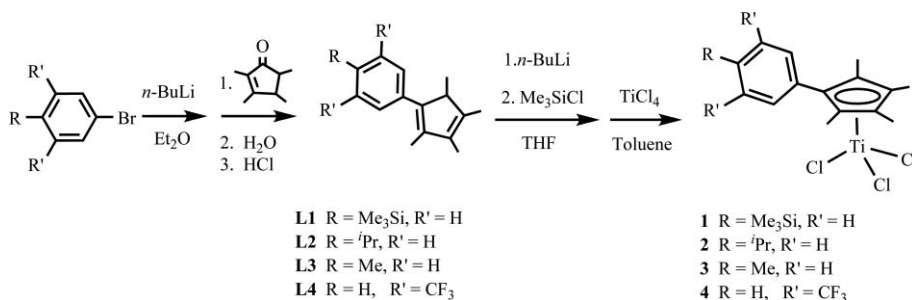
atactic polypropylene and polypropylene-co- α -olefins have been reported. High molecular weight atactic polypropylene and polypropylene-co- α -olefins have broad application prospects as adhesives, compatibilizers, and additives. Therefore, developing high performance catalyst systems capable of producing this type of polymers is of interest. Zirconocene-type complexes Cp₂ZrCl₂^{17b,18,19} and *meso*-Et(THID)₂ZrCl₂^{17c} (THID, namely tetrahydroindenyl) were studied as catalyst precursors in the polymerization of propylene, and atactic polypropylenes with low molecular weights were obtained. Similar complexes such as Et(Flu)₂ZrCl₂²⁰ and Me₂Si(Flu)₂ZrCl₂²¹ were found to produce high molecular weight atactic polypropylene ($M_w = 1\text{--}4 \times 10^5$). Et(Ind)₂ZrCl₂, Ph₂C(Flu)(Cp)ZrCl₂,²² Et(THID)₂ZrCl₂ and *i*-Pr(Flu)(Cp)ZrCl₂²³ have been studied as catalysts for the copolymerization of propylene with higher α -olefins to yield isotactic and syndiotactic propylene- α -olefin copolymers while Cp₂ZrCl₂²³ has been used as catalyst for producing atactic propylene-1-hexene copolymers. On the other hand, [Me₂Si(C₅Me₄)(NR)]TiCl₂/MAO (methylaluminoxane) systems²⁴ were reported to yield high molecular weight syndiotactic-enriched atactic polypropylene at relatively low polymerization temperatures (R = *i*-Bu, $M_w = 4 \times 10^5$ at 30 °C; R = adamantyl, $M_w = 5\text{--}7 \times 10^5$ at 40 °C; R = cyclododecyl, $M_w = 13\text{--}18 \times 10^5$ at 40 °C). A number of monocyclopentadienyltitanium(IV) trichlorides²⁵ and their derivatives^{26,27} were also reported to produce atactic polypropylene, but analogous monocyclopentadienylzirconium complexes²⁸ were found to promote atactic-specific oligomerization of propylene.

In recent years, Nomura's group has developed a type of non-bridged cyclopentadienyltitanium aryloxy complexes²⁹ as high performance catalysts for the copolymerization of ethylene with α -olefins to produce high molecular weight copolymers. On the

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Scheme 1 Synthetic procedure of complexes 1–4.

basis of knowledge on structure and property of metallocene catalysts, it could be expected that this type of catalyst might show good performance, too, for propylene polymerization to yield high molecular weight atactic polypropylene. However, one example has been reported for polymerization of propylene with this type of complexes, such as Cp*Ti(O-2,6-ⁱPrC₆H₃)Cl₂,^{29c} in the presence of MAO and these titanium catalysts containing aryloxy ligands have also been active for polymerization of 1-hexene in the presence of MAO or borate co-catalyst. No further studies for producing higher molecular weight atactic polypropylene with this type of catalysts have been reported so far. To develop new catalysts of the type for this purpose, we have synthesized a number of new non-bridged cyclopentadienyltitanium aryloxy complexes, 1-Ar-2,3,4,5-Me₄-Cp(2,6-ⁱPr₂C₆H₃O)TiCl₂ (Ar = 4-Me₃SiPhenyl (**5**), 4-ⁱPrPhenyl (**6**), 4-MePhenyl (**7**), 3,5-(CF₃)₂Phenyl (**8**)) and (1-Ar-2,3,4,5-Me₄-CpTiCl₂)₂(OAr'O) (Ar' = 4,4'-(3,3',5,5'-ⁱPr₄C₆H₂-C₆H₂), Ar = 4-SiMe₃Phenyl (**9**), 4-MePhenyl (**10**)), from their corresponding cyclopentadienyltitanium trichlorides, 1-Ar-2,3,4,5-Me₄-CpTiCl₃ (Ar = 4-Me₃SiPhenyl (**1**), 4-ⁱPrPhenyl (**2**), 4-MePhenyl (**3**), 3,5-(CF₃)₂Phenyl (**4**)), and studied their catalytic properties for propylene homopolymerization. By introducing a bulky aryl group (which can be easily introduced) into the Me₄Cp group, these catalysts have a more crowded coordination environment with the bulky aryl group in front of the metal center, which might slow down the rate of chain transfer through β-H elimination during the polymerization and therefore increase the molecular weight of the produced polymer. In addition, considering that complexes of this type are good catalysts for copolymerization of ethylene with α-olefins, we also briefly investigated the catalytic properties of complexes **5**, **6** and **7** for copolymerization of propylene with 1-hexene. The binuclear complexes **9** and **10** were synthesized mainly for examining the possible cooperative effect of the two metal centers. Herein we wish to report the synthesis and characterization of the new complexes **5–10**, their catalytic performance for propylene homopolymerization and copolymerization with 1-hexene, as well as the characterization of the resulting polypropylenes and propylene–1-hexene copolymers.

Results and discussion

Synthesis of the free ligands L1–L4

The free ligands 1-aryl-2,3,4,5-tetramethylcyclopentadiene **L1–L4** were synthesized using a modified literature procedure as shown in Scheme 1.^{30,31} The reaction of 2,3,4,5-tetramethyl-2-cyclopentenone with the corresponding aryllithium salt in

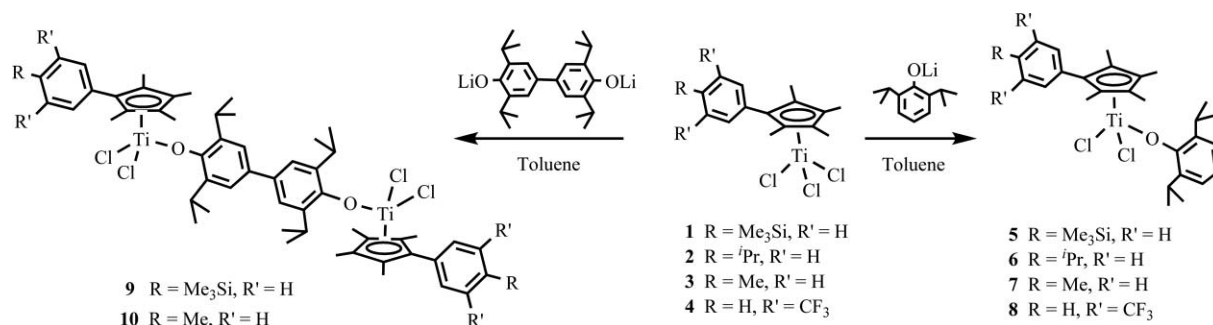
Et₂O, followed by treatment of the reaction mixture with concentrated HCl at room temperature, gives the free ligands **L1–L4** in high yields, respectively. The aryllithium salts were obtained by treating 1-bromo-4-trimethylsilylbenzene, 1-bromo-4-isopropylbenzene, 1-bromo-4-methylbenzene, or 1-bromo-3,5-bis(trifluoromethyl)benzene with 1 equiv. of *n*-BuLi at low temperature. The synthetic reaction was also tried in THF, which gave the products in lower yields. The free ligands **L1–L4** were all characterized by elemental analyses and ¹H NMR spectroscopy. ¹H NMR analysis indicates that the freshly prepared compounds **L1–L4** exist mainly in the form of one isomer, not as a mixture of three isomers as observed in the *N,N*-dimethylaminophenyltetramethylcyclopentadiene³² and tetramethylcyclopentadienyl-phenol³³ ligand systems.

Synthesis of complexes 1–4

Complexes **1–4** were synthesized in similar way to the published procedure^{34,35} in high yields as red or orange solids (Scheme 1). Deprotonation of the free ligands **L1–L4** with *n*-butyl lithium in THF, followed by the reaction with chlorotrimethylsilane, gives the trimethylsilyl substituted derivatives of **L1–L4**, respectively. The subsequent reactions of these trimethylsilyl substituted derivatives with TiCl₄ in toluene produce the corresponding complexes **1–4**. These complexes are well soluble in methylene chloride, diethyl ether, toluene and benzene, while slightly soluble in *n*-hexane and *n*-pentane. Complexes **1–4** were found to be relatively stable to air and moisture in the solid state, while readily decomposed in solution when exposed to air. These titanium complexes were all characterized by ¹H and ¹³C NMR spectroscopy along with elemental analyses. The chemical shifts observed for the protons of the CpCH₃ moiety in complexes **1–4** (*ca.* 2.00–2.47 ppm) are significantly downfield shifted in comparison with the corresponding signals of their free Cp ligands. The ¹³C NMR spectra show that complexes **1–4** have similar resonance signals for the methyl carbons on the Cp ligands (two characteristic signals at *ca.* 14.0–15.5 ppm for the four methyl carbons). The NMR spectral features of complexes **1–4** indicate that these molecules are symmetric in solution.

Synthesis of complexes 5–10

Complexes **5–8** were synthesized in relatively high yields (75–80%) by reactions of 2,6-ⁱPr₂C₆H₃OLi (Scheme 2) with the cyclopentadienyltitanium trichloride derivatives **1–4**, respectively. These reactions were usually carried out in toluene at 80 °C for 12 h to make the reaction go to completion. The synthetic reaction

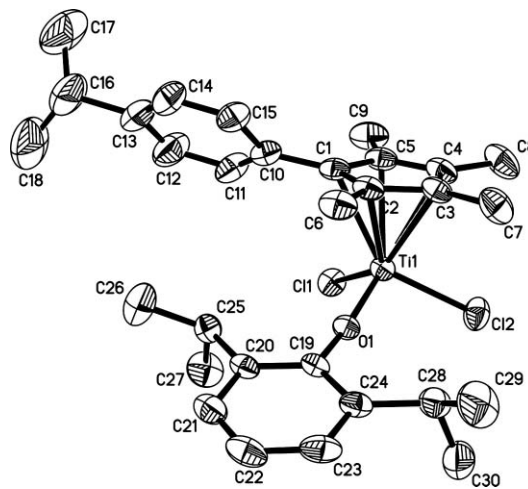
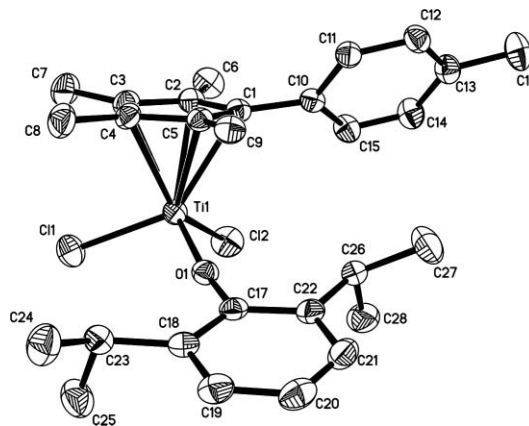


Scheme 2 Synthetic procedure of complexes 5–10.

was also tested in Et₂O and THF, from which the desired product was obtained in lower isolated yields. The binuclear titanium complexes **9** and **10** were obtained by a similar procedure (Scheme 2) from the reactions of 4,4'-(3,3',5,5'-*i*Pr₄C₆H₂–C₆H₂)O₂Li₂ with the cyclopentadienylnitrogen trichloride derivatives **1** and **3**, respectively. The isolated yields for complexes **9** and **10** (~70%) are lower than those for complexes **5–8**, which is understandable since any undesired reaction or decomposition happening on one side of either the dilithium salt of the biphenol ligand or the formed binuclear complex will cause the loss of the whole binuclear complex molecule and thus lead to lower yields. Complexes **5–10** are quite soluble in methylene chloride, toluene, benzene, and diethyl ether, but less soluble in *n*-pentane and *n*-hexane. These complexes were found to be more air and moisture sensitive in solution than complexes **1–4** and the recrystallization of these complexes must be handled very carefully to avoid the formation of oxo-bridged complexes. Complexes **5–10** were all characterized by elemental analyses, ¹H and ¹³C NMR spectroscopy and satisfactory analytic results were obtained. The ¹H NMR signals for the CpCH₃ protons in complexes **5–10** shift slightly to higher field compared to the corresponding signals in complexes **1–4**, and the ¹³C NMR signals for the CpCH₃ carbons in complexes **5–10** shift about 1.0–1.6 ppm to higher field compared to the corresponding signals in complexes **1–4**. The ¹³C NMR spectra of complexes **5–10** all show a down-field resonance about 160 ppm, which can be assigned to the carbon adjacent to the oxygen atom in the aryloxy ligand.

Crystal structures of complexes 6, 7 and 8

Molecular structures of complexes **6**, **7** and **8** were determined by single-crystal X-ray diffraction analysis. The ORTEP drawings of molecule structures are shown in Fig. 1, 2 and 3, respectively. The selected bond lengths and angles were summarized in Table 1. The X-ray crystal structural analysis reveals complexes **6**, **7** and **8** all adopt a distorted tetrahedral geometry in the solid state with their two bulky aryl groups folded on one side of their central titanium atom due to the packing force. The Ti–O distances of complexes **6** (1.773(2) Å), **7** (1.784(2) Å) and **8** (1.779(3) Å) are in the range of 1.772–1.820 Å reported for their analogues.^{29c,36} The average Ti–Cl distances in complexes **6** (2.268(1) Å), **7** (2.268(1) Å) and **8** (2.267(1) Å) are also in the range of observed values (2.250–2.305 Å) for known dichloro titanium complexes.^{36,37} The Cp(cent)–Ti–O angles are 127.1(3)° for **6**, 119.0(1)° for **7** and 124.2(3)° for **8**, which are related to the sterically open degree in front of the titanium atom in these complexes, and might influence the

Fig. 1 Structure of complex **6** (Thermal ellipsoids are drawn at the 30% probability level). Hydrogen atoms are omitted for clarity.Fig. 2 Structure of complex **7** (Thermal ellipsoids are drawn at the 30% probability level). Hydrogen atoms are omitted for clarity.

catalytic performance of these complexes. The Ti–O–C angles for complexes **6** (168.4(2)°), **7** (166.77(14)°) and **8** (170.2(3)°), together with the corresponding Ti–O distances, suggest that the Ti–O bond in these complexes may be additionally stabilized by partial π -donation from the oxygen atom of the aryloxy ligand. Other key bond lengths and angles listed in Table 1 are comparable with those values previously reported for similar titanium complexes.³⁸ The dihedral angle between the Cp ring and the adjacent phenyl ring in complex **8** (58.7(1)°) is larger than the ones in **6** (43.7(2)°)

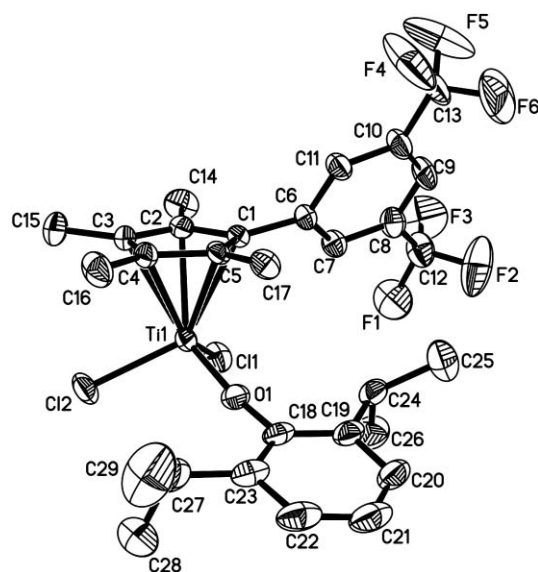
Table 1 Selected bond lengths and angles for complexes **6**, **7** and **8**

Complex 6			
Ti(1)–C(1)	2.359(3)	Ti(1)–O(1)–C(19)	168.4(2)
Ti(1)–C(2)	2.342(3)	O(1)–Ti(1)–Cl(1)	102.97(8)
Ti(1)–C(3)	2.351(3)	O(1)–Ti(1)–Cl(2)	102.54(8)
Ti(1)–C(4)	2.401(3)	Cl(2)–Ti(1)–Cl(1)	100.88(5)
Ti(1)–C(5)	2.402(3)	O(1)–Ti(1)–C(1)	106.10(11)
Ti(1)–Cl(1)	2.2719(12)	O(1)–Ti(1)–C(2)	88.77(11)
Ti(1)–Cl(2)	2.2643(13)	O(1)–Ti(1)–C(3)	107.52(12)
Ti(1)–O(1)	1.773(2)	O(1)–Ti(1)–C(4)	142.07(12)
Ti(1)–Cp(cent)	2.086(1)	O(1)–Ti(1)–C(5)	141.38(12)
Complex 7			
Ti(1)–C(1)	2.383(2)	Ti(1)–O(1)–C(17)	166.77(14)
Ti(1)–C(2)	2.419(2)	O(1)–Ti(1)–Cl(1)	102.77(5)
Ti(1)–C(3)	2.392(2)	O(1)–Ti(1)–Cl(2)	103.91(6)
Ti(1)–C(4)	2.337(2)	Cl(2)–Ti(1)–Cl(1)	100.31(3)
Ti(1)–C(5)	2.355(2)	O(1)–Ti(1)–C(1)	105.83(7)
Ti(1)–Cl(1)	2.2774(8)	O(1)–Ti(1)–C(2)	140.51(7)
Ti(1)–Cl(2)	2.2600(8)	O(1)–Ti(1)–C(3)	141.28(8)
Ti(1)–O(1)	1.7839(16)	O(1)–Ti(1)–C(4)	106.40(8)
Ti(1)–Cp(cent)	2.049(11)	O(1)–Ti(1)–C(5)	88.08(7)
Complex 8			
Ti(1)–C(1)	2.351(4)	Ti(1)–O(1)–C(17)	170.2(3)
Ti(1)–C(2)	2.405(4)	O(1)–Ti(1)–Cl(1)	103.39(12)
Ti(1)–C(3)	2.396(4)	O(1)–Ti(1)–Cl(2)	102.90(12)
Ti(1)–C(4)	2.352(4)	Cl(2)–Ti(1)–Cl(1)	100.39(5)
Ti(1)–C(5)	2.349(4)	O(1)–Ti(1)–C(1)	106.05(14)
Ti(1)–Cl(1)	2.2685(14)	O(1)–Ti(1)–C(2)	141.07(14)
Ti(1)–Cl(2)	2.2657(12)	O(1)–Ti(1)–C(3)	141.79(16)
Ti(1)–O(1)	1.776(3)	O(1)–Ti(1)–C(4)	107.13(16)
Ti(1)–Cp(cent)	2.084(1)	O(1)–Ti(1)–C(5)	88.40(14)

and **7** (49.6(1)°), which should result from the integrated steric interaction among the two bulky aryl groups and the Me₄Cp ring in these complexes.

Propylene polymerization studies

Propylene polymerization using complexes **5–10** as pre-catalysts under different conditions was studied, and the results are summa-

**Fig. 3** Structure of complex **8** (Thermal ellipsoids are drawn at the 30% probability level). Hydrogen atoms are omitted for clarity.

rized in Table 2. Upon activation with Al(^{*i*}Bu)₃ and Ph₃CB(C₆F₅)₄, complexes **5–10** all exhibit moderate catalytic activity (1156–3436 kg PP (mol Ti)^{–1} h^{–1}) for propylene polymerization. Under similar conditions, the catalytic activity increases in the order of **10** < **9** < **8** < **7** < **6** < **5**, which indicates that the catalytic activity of these complexes is notably affected by the nature of the substituents on both the cyclopentadienyl and aryloxy ligands, and increases with the increase in the electron-donating ability of the aryl group on the Cp ring although the variation in the catalytic activity is not very significant. It is well known for group 4 metallocene catalysts that electron-donating substituents on the ligands would stabilize the catalytically active cationic species formed during the polymerization and therefore improve the catalytic activity.³⁹ The observed weak electronic effect may be due to that the considered electron-donating or -withdrawing substituents (Me, F₃C, ^{*i*}Pr, Me₃Si) on the aryl group are too far away from the metal center. In comparison with complex **7**, the

Table 2 Summary of propylene polymerization catalyzed by complexes **5–10** activated with Al(^{*i*}Bu)₃ and Ph₃CB(C₆F₅)₄^a

Run	Catalyst	Al : Ti	<i>T</i> /°C	Yield/g	Activity ^b	<i>M</i> _w ^c × 10 ^{–4}	<i>M</i> _w / <i>M</i> _n ^c	<i>M</i> _η ^d × 10 ^{–4}	<i>T</i> _g /°C ^e
1	5	100	70	5.76	2304	29.5	2.58	28.3	–3.7
2	5	200	70	8.32	3328	23.8	3.06	22.7	–4.6
3	5	300	70	7.38	2952			20.1	
4	5	500	70	3.22	1288			16.5	
5	5	200	50	4.80	1920			30.6	
6	5	200	60	6.53	2612			26.7	
7	5	200	80	8.59	3436			19.8	
8	6	100	70	5.40	2160			21.6	
9	6	200	70	7.21	2884	19.8	2.31	17.5	–6.5
10	7	100	70	4.35	1740			20.4	
11	7	200	70	6.50	2600	18.1	3.27	17.2	–6.9
12	8	100	70	3.92	1568			22.1	
13	8	200	70	6.17	2468	20.0	2.30	18.3	–5.5
14	9	200	70	3.16	1264	23.3	3.14	22.6	–4.9
15	10	200	70	2.89	1156	18.9	2.91	18.6	–5.6

^a Polymerization conditions: toluene solution, catalyst 5.0 μmol (2.5 μmol for **9** and **10**), B/Ti ratio 1.25, time 30 min, propylene pressure 5 bar.

^b Polymerization activity: kg PP (mol Ti)^{–1} h^{–1}. ^c Measured by GPC analysis. ^d Intrinsic viscosity measured at 135 °C in THN. ^e Measured by DSC.

catalyst activity of complex **8** doesn't decrease very much, which may suggest that, except the electronic effect, the steric effect of the ligand on the catalytic activity also works by affecting the interaction between the catalytically active cationic species and the anionic co-catalyst. Similar results have been previously reported by Waymouth *et al.* for $(2\text{-Ar-Ind})_2\text{ZrCl}_2/\text{MAO}$ catalyst systems.⁴⁰ The mononuclear complexes **5–8** exhibit higher catalytic activity than the binuclear complexes **9** and **10** do under the same conditions, which implies that there is no cooperative effect between the two metal centers⁴¹ in these binuclear catalyst systems. The binuclear complexes showing lower catalytic activity might be attributed to at least two factors. One is that any half part of the binuclear active cationic species formed during the polymerization can be considered as an electron-withdrawing group for another half part of the active species and will lower each other's catalytic activity. Another factor is that the binuclear active cationic species carries two positive charges and thus should show relatively lower solubility in solution, which will cause the binuclear complexes to exhibit lower catalytic activity. The catalytic activity of these binuclear catalysts changes in the same trend as observed in the mononuclear catalyst systems under similar conditions, and increases with the increase in the electron-donating ability of the aryl group on the Cp ring. In addition, the observed catalytic activity of these titanium complexes is also affected by the Al/Ti molar ratio with the highest catalytic activity being reached at the Al/Ti ratio about 200 for all catalysts. The catalytic activity of these catalysts is dependent on the polymerization temperature too, and increases with the increase in polymerization temperature. On the other hand, the molecular weight of the resultant polypropylene decreases with the increase in polymerization temperature. These results are in agreement with those reported previously for similar catalyst systems.⁴²

The gel permeation chromatography (GPC) analysis reveals that the polypropylene obtained with complexes **5–10** possesses relatively high molecular weight with unimodal molecular weight distribution ($M_w = 16\text{--}30 \times 10^4$, $M_w/M_n = 2.3\text{--}3.3$). A typical GPC diagram is shown in Fig. 4. The M_w value of the polypropylene obtained under similar conditions is obviously dependant on the structure of the catalyst and increases in the order of $7 < 10 < 6 < 8 < 9, 5$. These results indicate that the molecular weight of the produced polypropylene is mainly influenced by the size of the aryl

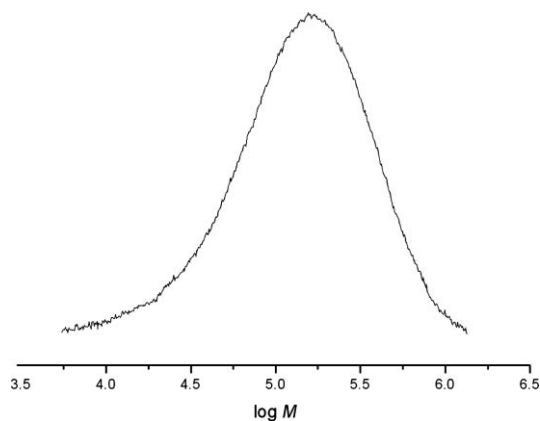


Fig. 4 The GPC trace of the polypropylene sample prepared with catalyst **8** (run 13 in Table 2).

group on the cyclopentadienyl ligand, which is reasonable since the bulky aryl group on the cyclopentadienyl ligand would stay in front of the central metal during the polymerization and therefore would lower the chain-transfer rate and increase the molecular weight of the resultant polymer. The binuclear complexes **9** and **10** produce polypropylene with molecular weight similar to or slightly higher than the one produced by their corresponding mononuclear complex **5** and **7**, indicating that the size of the substituent on the *para* position of the aryloxy ligand exerts little influence on the molecular weight of the resultant polymer. The 2,6-diisopropylphenoxy ligand was used in these complexes because it has been reported that the 2,6-diisopropylphenoxy complexes of this type show the best catalytic performance for the copolymerization of ethylene with α -olefins.⁴³

The ^1H NMR spectrum of a typical polypropylene sample is illustrated in Fig. 5. The resonances at 4.91 and 4.97 ppm could be assigned to the protons of the vinylidene end group, while the resonance at 5.03 ppm may be tentatively assigned to the olefinic proton in the isobutenyl end group $\text{Me}_2\text{C}=\text{CH}-$ which is possibly formed by isomerization of the terminal vinylidene as discussed in literature for a propylene isotactic polymerization system.⁴⁴ There is no other olefinic group, such as vinyl or internal olefin group can be seen from the ^1H NMR spectrum. The formation of the vinylidene end group is indicative of that the β -H elimination is a major chain transfer reaction for these systems. The ^{13}C NMR spectrum of the same polypropylene sample is shown in Fig. 6. The observed resonances of the methyl carbons (20.0–22.5 ppm) in the polymer are characteristic for atactic polypropylene.⁴⁵

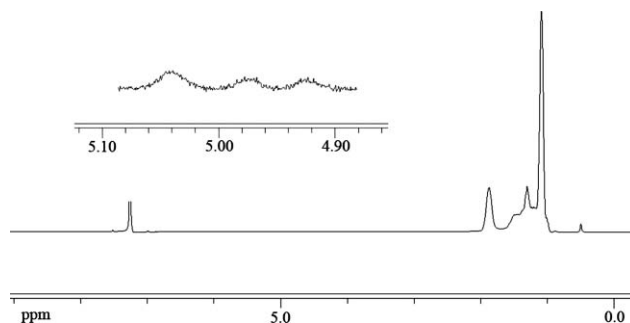


Fig. 5 ^1H NMR spectrum of the polypropylene obtained with catalyst **5** (run 2 in Table 2).

The calculated dyad, triad and pentad distributions for two typical polypropylene samples listed in Table 3 reveal that the polypropylene obtained with these catalysts is a kind of syndiotactically enriched atactic polypropylene with *r* (54–55%) being larger than *m* (45–46%) about 9%. By analyzing the triad distribution, it can be seen that the values of $4[\text{mm}][\text{rr}]/[\text{mr}]^2$ (1.07 and 0.99 for samples from run 2 and 14, respectively) are close to 1, which is in agreement with the statistical model of Bernoullian.⁴⁶ In addition, the ^{13}C NMR analysis indicates that the polypropylene produced by these catalysts is mainly made up of 1,2-insertion units with a little of 2,1-insertion and 1,3-enchainment units.⁴⁷ The DSC analysis on the polymer samples also confirms that the obtained polymers are atactic polypropylenes which all show a glass transition temperature (T_g) in the range of -7 to -3 °C, but no melting endotherm.

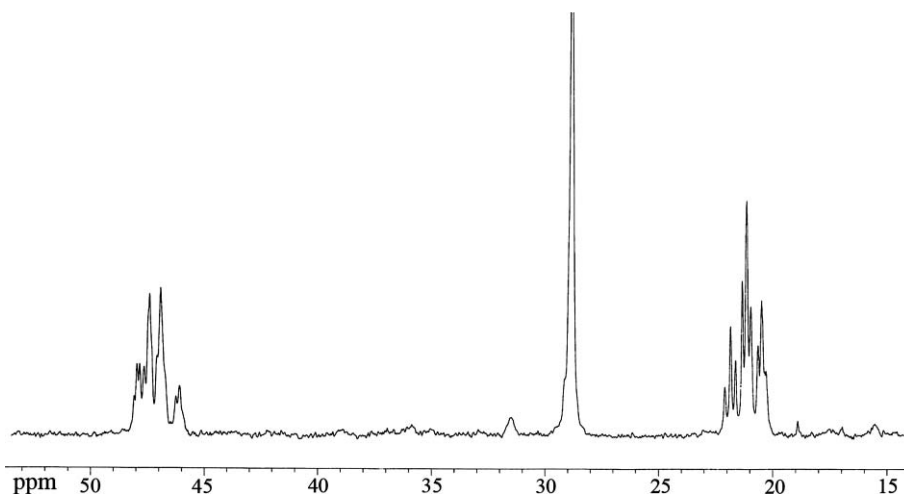
Table 3 Pentad, triad and dyad distribution and statistical analysis for typical polypropylenes

Sample	Pentads (%)									Triads (%)			Dyads (%)	
	<i>mmmm</i>	<i>mmmr</i>	<i>rmmr</i>	<i>mmrr</i>	<i>mmrm/rmrr</i>	<i>mrmm</i>	<i>rrrr</i>	<i>rrrm</i>	<i>mrmm</i>	<i>mm</i>	<i>mr</i>	<i>rr</i>	<i>m</i>	<i>r</i>
Run 2	4.91	9.81	6.65	12.17	22.94	13.66	7.88	14.56	7.42	21.37	48.77	29.86	45.75	54.25
Run 14	3.79	9.90	7.13	12.73	22.63	14.32	8.07	15.08	6.35	20.82	49.68	29.50	45.66	54.34

Table 4 Summary of propylene/1-hexene copolymerization catalyzed by complexes **5**, **6** and **7** activated with Al(*i*Bu)₃ and Ph₃CB(C₆F₅)₄^a

Run	Catalyst	1-hexene/mol L ⁻¹	Yield/g	Activity ^b	<i>M</i> _w ^c × 10 ⁻⁴	<i>M</i> _w / <i>M</i> _n ^c	1-hexene content ^d (mol%)
1	5	0.05	1.38	920	18.93	2.69	1.28
2	5	0.10	0.91	607	17.26	3.51	2.70
3	5	0.20	0.67	447	13.10	2.33	5.25
4	5	0.50	0.53	353	10.24	2.62	9.57
5	6	0.20	0.59	393	12.85	3.06	5.28
6	6	0.50	0.42	280	10.08	2.44	9.63
7	7	0.20	0.58	387	12.60	2.38	5.36
8	7	0.50	0.43	286	9.81	2.75	10.11

^a Polymerization conditions: toluene solution, temperature 70 °C, catalyst 3.0 μmol, B/Ti ratio 1.25, time 30 min, propylene pressure 5 bar. ^b Polymerization activity: kg polymer (mol Ti)⁻¹ h⁻¹. ^c Measured by GPC analysis. ^d Calculated by ¹³C NMR spectra.

**Fig. 6** ¹³C NMR spectrum of the polypropylene obtained with catalyst **5** (run 2 in Table 2).

Propylene/1-hexene copolymerization studies

Complexes **5**, **6** and **7** were briefly tested for the copolymerization of propylene with 1-hexene, and the results are listed in Table 4. The catalytic activities of these complexes in the copolymerization reactions were found to decrease with increasing the feed concentration of 1-hexene under similar conditions, and no comonomer effect was observed. Obvious comonomer effect has previously been observed in Me₂Si(Ind)₂ZrCl₂/MAO catalyzed propylene/1-hexene copolymerization reaction.²² The propylene/1-hexene copolymers were analyzed by ¹³C NMR and the ¹³C NMR spectrum of a typical copolymer sample is shown in Fig. 7. The assignments for the observed resonances are made according to the published literatures.^{48–50} The ¹³C NMR analysis indicates that the obtained copolymers are atactic and the comonomer 1-hexene is randomly incorporated into the polymer chains. Since no resonance in the region of 41–43 ppm for the αα carbon

in the HH dyad sequence²² has been observed in the ¹³C NMR spectra, it can be known that the 1-hexene units in the polymer chain are essentially isolated by propylene units. Based on the ¹³C NMR analysis, the comonomer content of the copolymer samples was calculated and listed in Table 4. In addition to the comonomer concentration, it seems that the comonomer incorporation is also affected by the structure of the catalyst. The comonomer content of the copolymers obtained with catalyst **7** is somewhat higher than that of the copolymers produced by catalyst **5** under similar conditions, due probably to that the catalytically active species of **7** is less bulky and carries more positive charge than the one of **5** does and therefore more favors the coordination of the bulky comonomer. DSC analysis on the copolymer samples indicates that the resulting copolymers are amorphous, and the crystallization process could not be observed. GPC analysis reveals that the molecular weight of the obtained propylene-1-hexene copolymers (*M*_w = 10–19 × 10⁴) produced by

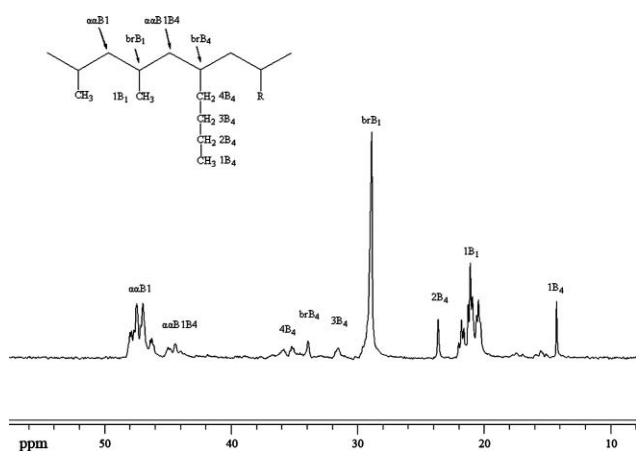


Fig. 7 ^{13}C NMR spectra of copolymer propylene-1-hexene together with assignments of the corresponding peaks. (Run 4 in Table 4.)

these catalysts is much higher than that of the copolymers obtained with the Cp_2ZrCl_2 catalyst system,²³ and the molecular weight distribution is basically unimodal and narrow, being characteristic for metallocene polyolefins.

Conclusions

A number of cyclopentadienyltitanium aryloxide complexes **5–10** have been synthesized in relatively high yields from the reaction of cyclopentadienyltitanium trichloride derivatives **1–4** with the corresponding lithium phenoxide. These new complexes were all characterized by elemental analyses, ^1H and ^{13}C NMR spectroscopy, and the molecular structures of complexes **6–8** were determined by X-ray crystallography. Upon activation with $^i\text{Bu}_3\text{Al}/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$, all complexes **5–10** exhibit good catalytic activities for propylene polymerization, and produce syndiotactically enriched atactic polypropylene with high molecular weight. The molecular weight of the resultant polymers is mainly influenced by the size of the aryl group on the cyclopentadienyl ligand in these complexes. Complexes **5** with 4'-trimethylsilylphenyl substituted cyclopentadienyl ligand produce atactic polypropylene with the highest molecular weight. Complexes **5**, **6** and **7** show reasonable catalytic activities for the copolymerization of propylene with 1-hexene, producing poly(propylene-co-1-hexene) with relatively high molecular weight ($M_w = 10\text{--}19 \times 10^4$) and comonomer incorporation (up to 10 mol% 1-hexene).

Experimental

General comments

All manipulations involving air- and/or moisture-sensitive compounds were carried out under an argon atmosphere (ultra-high purity) using either standard Schlenk techniques or glove box techniques. Solvents were dried and distilled prior to use.⁵¹ Polymerization grade propylene was further purified by passage through columns of 4 Å molecular sieves and MnO. Al(*i*-Bu)₃, *n*-BuLi, TiCl₄, 2,6-bis-isopropylphenol, 1-bromo-4-methylbenzene, 1-bromo-4-isopropylbenzene, 1-bromo-3,5-bis-trifluoromethylbenzene, and

1-bromo-4-trimethylsilylbenzene were purchased from Aldrich. 2,3,4,5-tetramethyl-2-cyclopentenone⁵² and $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$,⁵³ were prepared according to literature procedures. ^1H and ^{13}C NMR spectra were measured using a Varian Mercury-300 NMR spectrometer. Elemental analyses were performed on a Perkin-Elmer 240c element analyzer. Viscosity-average molecular weights of the polypropylenes were determined in THN at 135 °C using Schott Geräte Mod. AVS/T2 Ubbelohde viscosimeter. Molecular weight and Molecular weight distribution of the polypropylenes and propylene-1-hexene copolymers were measured on a PL-GPC 220 at 140 °C with 1,2,4-trichlorobenzene as solvent. ^1H NMR spectra of the polymers were recorded on a Varian Mercury-300 NMR spectrometer with CDCl_3 as solvent. ^{13}C NMR spectra of the polymers were recorded on a Varian Unity-400 NMR spectrometer at 110 °C with $o\text{-C}_6\text{D}_4\text{Cl}_2$ as solvent. Glass transition temperatures (T_g) were measured by differential scanning calorimetry (DSC) on a NETZSCH DSC 204 with the heating/cooling rate at 10 °C min⁻¹ from -50 to 200 °C, upon the second heating scan.

Synthesis of 1-(4'-trimethylsilylphenyl)-2,3,4,5-tetramethylcyclopentadiene (L1). A solution of *n*-BuLi (12.5 mmol) was added dropwise to a solution of 1-bromo-4-trimethylsilylbenzene (2.86 g, 12.5 mmol) in Et₂O (60 mL) at -25 °C and the reaction mixture was allowed to warm to room temperature. After four hours, the solution was cooled to -15 °C, and a solution of 2,3,4,5-tetramethyl-2-cyclopentenone (1.72 g, 12.5 mmol) in Et₂O (20 mL) was added. The mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with 100 mL of H₂O and then acidified with 3 mL of concentrated HCl. The organic layer was separated, dried over MgSO₄, filtered and concentrated by distillation under reduced pressure. Pure product (3.12 g, 92.5%) was obtained as yellowish oil by column chromatography over silica (petroleum ether). Anal. calcd for C₂₈H₂₆Si (270.48): C 79.93, H 9.69. Found: C 79.65, H 9.52. ¹H NMR (CDCl₃, 300 MHz; 298 K): δ 7.51 (d, *J* = 8.1 Hz, 2 H, Ph), 7.24 (d, *J* = 8.4 Hz, 2 H, Ph), 3.20 (q, 1 H, Cp), 2.05 (d, *J* = 1.8 Hz, 3 H, Cp-Me), 1.93 (s, 3 H, Cp-Me), 1.87 (s, 3 H, Cp-Me), 0.97 (d, *J* = 7.5 Hz, 3 H, Cp-Me), 0.28 (s, 9 H, SiMe₃).

Synthesis of 1-(4'-isopropylphenyl)-2,3,4,5-tetramethyl-cyclopentadiene (L2). Ligand L2 was prepared in the same manner as L1 with 12.5 mmol of 1-bromo-4-isopropylbenzene as starting material. Pure product (2.80 g, 93.0%) was obtained as yellowish oil. Anal. calcd for C₁₈H₂₄ (240.37): C 89.94, H 10.06. Found: C 89.60, H 9.93. ¹H NMR (CDCl₃, 300 MHz; 298 K): δ 7.20 (m, 4 H, Ph), 3.18 (q, 1 H, Cp), 2.92 (m, 1 H, ⁱPr), 2.04 (d, *J* = 1.8 Hz, 3 H, Cp-Me), 1.94 (s, 3 H, Cp-Me), 1.87 (s, 3 H, Cp-Me), 1.28 (d, *J* = 6.9 Hz, 6 H, ⁱPr), 0.97 (d, *J* = 7.8 Hz, 3 H, Cp-Me).

Synthesis of 1-(4'-methylphenyl)-2,3,4,5-tetramethyl-cyclopentadiene (L3). Ligand **L3** was prepared in the same manner as **L1** with 12.5 mmol of 1-bromo-4-methylbenzene as starting material. Pure product (2.42 g, 91.6%) was obtained as yellowish oil. Anal. calcd for $C_{16}H_{20}$ (212.16): C 90.51, H 9.49. Found: C 90.27, H 9.30. 1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.19 (s, 4 H, Ph), 3.17 (q, 1 H, Cp), 2.02 (d, J = 1.8 Hz, 3 H, Cp-Me), 1.90 (s, 3 H, Cp-Me), 1.83 (s, 3 H, Cp-Me), 0.95 (d, J = 7.5 Hz, 3 H, Cp-Me).

Synthesis of 1-(3',5'-bi-trifluoromethylphenyl)-2,3,4,5-tetramethyl-cyclopentadiene (L4). Ligand L4 was prepared in

the same manner as **L1** with 12.5 mmol of 1-bromo-3,5-bis(trifluoromethyl)benzene as starting material. Pure product (3.80 g, 91.0%) was obtained as yellowish oil. Anal. calcd for $C_{17}H_{16}F_6$ (334.30): C 61.08, H 4.82. Found: C 60.94, H 4.67. 1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.62 (s, 1 H, Ph), 7.44 (s, 2 H, Ph), 3.18 (q, 1 H, Cp), 2.06 (d, J = 1.8 Hz, 3 H, Cp-Me), 1.91 (s, 3 H, Cp-Me), 1.85 (s, 3 H, Cp-Me), 0.96 (d, J = 7.8 Hz, 3 H, Cp-Me).

Synthesis of 1-(4'-trimethylsilylphenyl)-2,3,4,5-tetramethyl-cyclopentadienyl titanium trichloride (1). A solution of *n*-BuLi (8.50 mmol) was added dropwise to a solution of 1-(4'-trimethylsilylphenyl)-2,3,4,5-tetramethyl-cyclopentadiene (2.00 g, 8.50 mmol) in THF (60 mL) at $-78^\circ C$ and the reaction mixture was allowed to warm to room temperature. After four hours, the mixture was cooled to $-15^\circ C$, and a solution of Me_3SiCl (8.90 mmol) in THF (20 mL) was slowly added. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The solvent and excess Me_3SiCl were removed under reduced pressure. The residue was extracted with toluene (30 mL) and slowly added to a solution of $TiCl_4$ (8.50 mmol) in 50 mL of toluene at $-78^\circ C$. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. The precipitate was filtered off and the solvent was removed to leave a red solid. Recrystallization from methylene chloride/*n*-hexane (1 : 3 in v/v) gave pure **1** (2.82 g, 78.2%). Anal. calcd for $C_{18}H_{25}Cl_3SiTi$ (423.71): C 50.90, H 6.17. Found: C 50.71, H 6.10. 1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.55 (d, J = 7.5 Hz, 2 H, Ph), 7.47 (d, J = 8.1 Hz, 2 H, Ph), 2.27 (s, 6 H, Cp-Me), 2.03 (s, 6 H, Cp-Me), 0.31 (s, 9 H, Si-Me₃). ^{13}C NMR ($CDCl_3$, 75 MHz; 298 K): δ 142.7, 141.3, 138.4, 135.9, 133.9, 133.6, 123.0, 15.3, 14.2, -1.2 .

Synthesis of 1-(4'-isopropylphenyl)-2,3,4,5-tetramethyl-cyclopentadienyl titanium trichloride (2). Complex **2** was synthesized in the same manner as complex **1** with 8.50 mmol of 1-(4'-isopropylphenyl)-2,3,4,5-tetramethyl-cyclopentadiene as starting material. Pure **2** (2.60 g, 78.0%) was obtained as red crystals by recrystallization from methylene chloride/*n*-hexane (1 : 3 in v/v). Anal. calcd for $C_{18}H_{25}Cl_3Ti$ (393.61): C 54.78, H 6.13. Found: C 54.37, H 6.08. 1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.22 (s, 4 H, Ph), 2.88 (m, 1 H, i -Pr), 2.40 (s, 6 H, Cp-Me), 2.35 (s, 6 H, Cp-Me), 1.21 (d, J = 7.2 Hz, 6 H, i -Pr). ^{13}C NMR ($CDCl_3$, 75 MHz; 298 K): δ 149.4, 143.4, 138.7, 136.2, 130.3, 126.4, 33.9, 23.8, 15.5, 14.6.

Synthesis of 1-(4'-methylphenyl)-2,3,4,5-tetramethyl-cyclopentadienyl titanium trichloride (3). Complex **3** was synthesized in the same manner as complex **1** with 8.50 mmol of 1-(4'-methylphenyl)-2,3,4,5-tetramethyl-cyclopentadiene as starting material. Pure **3** (2.36 g, 76.0%) was obtained as red crystals by recrystallization from methylene chloride/*n*-hexane (1 : 3 in v/v). Anal. calcd for $C_{16}H_{19}Cl_3Ti$ (365.55): C 52.57, H 5.24. Found: C 52.31, H 5.11. 1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.26 (s, 4 H, Ph), 2.47 (s, 6 H, Cp-Me), 2.43 (s, 6 H, Cp-Me), 2.41 (s, 3 H, Ph-Me). ^{13}C NMR ($CDCl_3$, 75 MHz; 298 K): δ 143.2, 138.7, 138.6, 136.1, 130.2, 130.1, 129.0, 21.3, 15.5, 14.6.

Synthesis of 1-(3',5'-di-trifluoromethylphenyl)-2,3,4,5-tetramethyl-cyclopentadienyl titanium trichloride (4). Complex **4** was synthesized in the same manner as complex **1** with 8.50 mmol of 1-(3',5'-di-trifluoromethylphenyl)-2,3,4,5-tetramethyl-cyclopentadiene as starting material. Pure **4** (3.18 g, 76.9%) was obtained as red crystals by recrystallization from methylene

chloride/*n*-hexane (1 : 3 in v/v). Anal. calcd for $C_{17}H_{15}Cl_3F_6Ti$ (487.52): C 50.90, H 6.17. Found: C 50.62, H 6.03. 1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.93 (s, 1 H, Ph), 7.85 (s, 2 H, Ph), 2.45 (s, 6 H, Cp-Me), 2.44 (s, 6 H, Cp-Me). ^{13}C NMR ($CDCl_3$, 75 MHz; 298 K): δ 138.6, 137.2, 135.7, 135.0, 132.1, 130.6, 122.4, 121.9, 15.3, 14.0.

Synthesis of 1-(4'-trimethylsilylphenyl)-2,3,4,5-tetramethyl-cyclopentadienyl-TiCl₂(O-2,6-di-isopropyl-C₆H₃) (5). A solution of *n*-BuLi (3.80 mmol) was added dropwise to a solution of 2,6-diisopropylphenol (0.680 g, 3.80 mmol) in Et_2O (30 mL) at $-25^\circ C$. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The solvent was removed *in vacuo* and the residue was washed with hexane. The obtained white powder was dissolved in toluene (10 mL), and then a solution of 1-(4'-trimethylsilylphenyl)-2,3,4,5-tetramethyl-cyclopentadienyl titanium trichloride (1.48 g, 3.50 mmol) in toluene (15 mL) was added at room temperature. The reaction mixture was heated to $80^\circ C$ and stirred for 12 h. The mixture was filtered and the precipitate was washed with toluene (2×5 mL). The filtrate was concentrated to leave a black-red residue. Recrystallization from CH_2Cl_2 -*n*-hexane (1 : 3) gave pure **5** as red crystals (1.60 g, 80.6%). Anal. calcd for $C_{30}H_{42}Cl_2OSiTi$ (565.52): C 63.60, H 7.65. Found: C 62.49, H 7.20. 1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.56 (d, J = 8.1 Hz, 2 H, Ph), 7.47 (d, J = 8.1 Hz, 2 H, Ph), 6.99 (m, 3 H, Ph), 3.02 (m, 2 H, Ar- i -Pr), 2.30 (s, 6 H, Cp-Me), 2.29 (s, 6 H, Cp-Me), 1.03 (d, J = 7.2 Hz, 12 H, Ar- i -Pr), 0.30 (s, 9 H, Si-Me). ^{13}C NMR ($CDCl_3$, 75 MHz; 298 K): δ 159.9, 140.7, 139.6, 136.8, 133.6, 133.1, 130.8, 129.6, 123.5, 123.1, 26.7, 23.7, 13.9, 13.2, -1.2 .

Synthesis of 1-(4'-isopropylphenyl)-2,3,4,5-tetramethyl-cyclopentadienyl-TiCl₂(O-2,6-di-isopropyl-C₆H₃) (6). Complex **6** was synthesized in the same manner as complex **5** except that 3.50 mmol of 1-(4'-isopropylphenyl)-2,3,4,5-tetramethyl-cyclopentadienyl titanium trichloride was used instead of 1-(4'-trimethylsilylphenyl)-2,3,4,5-tetramethyl-cyclopentadienyl titanium trichloride. Pure **6** (1.47 g, 78.5%) was obtained as red crystals by recrystallization from methylene chloride/*n*-hexane (1 : 3 in v/v). Anal. calcd for $C_{30}H_{40}Cl_2OTi$ (535.42): C 67.16, H 7.70. Found: C 66.75, H 7.35. 1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.42 (d, J = 8.1 Hz, 2 H, Ph), 7.25 (d, J = 8.1 Hz, 2 H, Ph), 6.99 (m, 3 H, Ph), 3.02 (m, 2 H, Ar- i -Pr), 2.93 (m, 1 H, i -Pr), 2.29 (s, 12 H, Cp-Me), 1.27 (d, J = 7.2 Hz, 12 H, Ar- i -Pr), 1.03 (d, J = 6.9 Hz, 6 H, i -Pr-Me). ^{13}C NMR ($CDCl_3$, 75 MHz; 298 K): δ 159.8, 148.7, 139.6, 137.2, 133.7, 130.7, 130.4, 130.2, 126.2, 123.5, 123.1, 33.9, 26.7, 23.9, 23.7, 13.9, 13.4.

Synthesis of 1-(4'-methylphenyl)-2,3,4,5-tetramethyl-cyclopentadienyl-TiCl₂(O-2,6-di-isopropyl-C₆H₃) (7). Complex **7** was synthesized in the same manner as complex **5** except that 3.50 mmol of 1-(4'-methylphenyl)-2,3,4,5-tetramethyl-cyclopentadienyl titanium trichloride was used instead of 1-(4'-trimethylsilylphenyl)-2,3,4,5-tetramethyl-cyclopentadienyl titanium trichloride. Pure **7** (1.40 g, 79.1%) was obtained as red crystals by recrystallization from methylene chloride/*n*-hexane (1 : 3 in v/v). Anal. calcd for $C_{28}H_{36}Cl_2OTi$ (507.36): C 66.15, H 7.35. Found: C 65.27, H 7.18. 1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.41 (d, J = 8.1 Hz, 2 H, Ph), 7.23 (d, J = 8.1 Hz, 4 H, Ph), 7.02 (m, 3 H, Ph), 3.04 (m, 2 H, Ar- i -Pr), 2.39 (s, 3 H, Ar-Me), 2.30 (s, 6 H, Cp-Me), 2.27 (s, 6 H, Cp-Me), 1.05 (d, J = 7.2 Hz,

12 H, Ar-ⁱPr). ¹³C NMR (CDCl₃, 75 MHz; 298 K): δ 159.8, 139.6, 137.9, 137.3, 133.3, 131.0, 130.4, 130.0, 128.9, 123.5, 123.1, 26.7, 23.7, 21.2, 13.9, 13.2.

Synthesis of 1-(3',5'-(CF₃)₂-phenyl)-2,3,4,5-tetramethyl-cyclopentadienyl-TiCl₂(O-2,6-di-isopropyl-C₆H₃) (8). Complex **8** was synthesized in the same manner as complex **5** except that 3.50 mmol of 1-(3',5'-(CF₃)₂-phenyl)-2,3,4,5-tetramethyl-cyclopentadienyl titanium trichloride was used instead of 1-(4'-trimethylsilylphenyl)-2,3,4,5-tetramethyl-cyclopentadienyl titanium trichloride. Pure **8** (1.69 g, 76.8%) was obtained as red crystals by recrystallization from methylene chloride/*n*-hexane (1 : 3 in v/v). Anal. calcd for C₂₉H₃₂Cl₂F₆O₂Ti (629.34): C 55.25, H 5.28. Found: C 54.91, H 5.12. ¹H NMR (CDCl₃, 300 MHz; 298 K): δ 8.05 (s, 2 H, Ph), 7.91 (s, 1 H, Ph), 6.97 (m, 3 H, Ph), 3.06 (m, 2 H, Ar-ⁱPr), 2.32 (s, 6 H, Cp-Me), 2.28 (s, 6 H, Cp-Me), 1.07 (d, *J* = 6.9 Hz, 12 H, Ar-ⁱPr). ¹³C NMR (CDCl₃, 75 MHz; 298 K): δ 159.8, 139.4, 135.2, 133.4, 132.0, 131.9, 131.5, 130.7, 124.1, 123.3, 121.7, 26.9, 23.6, 13.8, 13.0.

Synthesis of (3,3',5,5'-tetra-isopropyl-4,4'-biphenolate)-bi-[1-(4'-trimethylsilylphenyl)-2,3,4,5-tetramethyl-cyclopentadienyl-TiCl₂] (9). Complex **9** was synthesized in the same manner as complex **5** except that 1.90 mmol of 3,3',5,5'-tetra-isopropyl-4,4'-biphenol was used instead of 2,6-bi-isopropylphenol. Pure **9** (1.43 g, 72.5%) was obtained as red crystals by recrystallization from methylene chloride/*n*-hexane (1 : 3 in v/v). Anal. calcd for C₆₀H₈₂Cl₄O₂Si₂Ti₂ (1129.02): C 63.70, H 7.49. Found: C 62.81, H 7.20. ¹H NMR (CDCl₃, 300 MHz; 298 K): δ 7.56 (d, *J* = 4.5 Hz, 4 H, Ph), 7.49 (d, *J* = 4.5 Hz, 4 H, Ph), 7.14 (s, 4 H, Ph), 3.05 (m, 4 H, Ar-ⁱPr), 2.32 (s, 24 H, Cp-Me), 1.09 (d, *J* = 4.2 Hz, 24 H, Ar-ⁱPr), 0.31 (s, 18 H, Si-Me). ¹³C NMR (CDCl₃, 75 MHz; 298 K): δ 159.7, 140.5, 139.8, 136.7, 136.4, 133.7, 133.1, 130.8, 129.6, 129.0, 121.6, 26.7, 23.7, 13.9, 13.3, -1.2.

Synthesis of (3,3',5,5'-tetra-isopropyl-4,4'-biphenolate)-bi-[1-(4'-methylphenyl)-2,3,4,5-tetramethyl-cyclopentadienyl-TiCl₂] (10). Complex **10** was synthesized in the same manner as complex **9** except that 3.50 mmol of 1-(4'-methylphenyl)-2,3,4,5-tetramethyl-cyclopentadienyl titanium trichloride was used instead of 1-(4'-trimethylsilylphenyl)-2,3,4,5-tetramethyl-cyclopentadienyl titanium trichloride. Pure **10** (1.27 g, 71.8%) was obtained as red crystals by recrystallization from methylene chloride/*n*-hexane (1 : 3 in v/v). Anal. calcd for C₅₆H₇₀Cl₄O₂Ti₂ (1012.70): C 66.25, H 7.15. Found: C 65.13, H 6.92. ¹H NMR (CDCl₃, 300 MHz; 298 K): 7.47 (d, *J* = 5.1 Hz, 4 H, Ph), 7.30 (d, *J* = 5.1 Hz, 4 H, Ph), 7.21 (s, 4 H, Ph), 3.14 (m, 4 H, Ar-ⁱPr), 2.46 (s, 6 H, Ar-Me), 2.38 (s, 12 H, Cp-Me), 2.35 (s, 12 H, Cp-Me), 1.18 (d, *J* = 3.9 Hz, 24 H, Ar-ⁱPr). ¹³C NMR (CDCl₃, 75 MHz; 298 K): δ 159.7, 139.8, 137.9, 137.3, 136.3, 133.3, 130.9, 130.4, 130.0, 128.9, 121.6, 26.9, 23.8, 21.2, 14.0, 13.2.

X-Ray structure determinations of **6**, **7** and **8**

Crystals of **6**, **7** and **8** suitable for X-ray structure determination were obtained from a saturated solution of CH₂Cl₂-*n*-hexane (1 : 3, v/v) at room temperature. The data were collected at 293 K on the Rigaku RAXIS-RAPID diffractometer using Mo Kα radiation. The structures were solved by direct methods⁵⁴ 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

Table 5 Crystal data and structure refinement for complexes **6**, **7** and **8**

	6	7	8
Empirical formula	C ₃₀ H ₄₀ Cl ₂ O ₂ Ti	C ₂₈ H ₃₆ Cl ₂ O ₂ Ti	C ₂₉ H ₃₂ Cl ₂ F ₆ O ₂ Ti
<i>M_w</i>	535.42	507.37	629.35
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>	<i>Pc</i>
<i>a</i> /Å	22.757(5)	8.3715(17)	12.1002 (17)
<i>b</i> /Å	8.7719(18)	17.975(4)	8.7661(12)
<i>c</i> /Å	15.626(3)	36.081(7)	15.896(2)
<i>α</i> /°	90	90	90
<i>β</i> /°	103.38(3)	90	111.918(3)
<i>γ</i> /°	90	90	90
<i>V</i> /Å ³	3034.7(11)	5429.6(19)	1564.2(4)
<i>Z</i>	4	8	2
<i>D_c</i> /g cm ⁻³	1.172	1.241	1.336
<i>F</i> (000)	1136	2144	648
<i>μ</i> /mm ⁻¹	0.477	0.529	0.500
No. of reflections	22 357	47 290	10 396
No. of independent reflections	5298	6203	5719
<i>R_{int}</i>	0.0852	0.0659	0.0324
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b	0.0543/0.1082	0.0447/0.1063	0.0439/0.1044
GOF	1.044	1.037	1.011
Largest diffraction peak and hole/e Å ⁻³	0.204, -0.287	0.226, -0.320	0.352, -0.258

$$^a R_1 = \sum \|F_o| - |F_c|\| / \sum |F_o|. \quad ^b wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

position. All calculations were performed using the SHELXTL crystallographic software packages.⁵⁵ Details of the crystal data, data collections, and structure refinements are summarized in Table 5.

Polymerization reactions

The propylene polymerization experiments were carried out as follows: a dry 250 mL steel autoclave was charged with 60 mL of toluene, thermostated at desired temperature and saturated with 1.0 bar of propylene. The polymerization reaction was started by addition of a mixture of a catalyst and Al(^{*i*}Bu)₃ in toluene (5 mL) and a solution of Ph₃CB(C₆F₅)₄ in toluene (5 mL) at the same time. The reaction mixture was stirred for 30 min under 5 bar of propylene. The polymerization was then quenched by injecting acidified methanol [HCl (3 M)/methanol = 1 : 1]. The polymer was collected by filtration, washed with water and methanol, and dried to a constant weight under vacuum. For the copolymerization experiments, appropriate amounts of 1-hexene were added in toluene.

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