

Effect of aryloxo ligand in 1-hexene, styrene polymerization catalyzed by nonbridged half-titanocenes of the type, $\text{Cp}^*\text{TiCl}_2(\text{OAr})$ ($\text{Cp}' = \text{C}_5\text{Me}_5, {}^i\text{BuC}_5\text{H}_4$) Structural analyses for $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6-{}^i\text{Bu}_2\text{C}_6\text{H}_3)$ and $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6-{}^i\text{Pr}_2-4-{}^i\text{BuC}_6\text{H}_2)$

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Abstract

Various (aryloxo)(pentamethylcyclopentadienyl)titanium(IV) dichloride complexes of the type, $\text{Cp}^*\text{TiCl}_2(\text{OAr})$ [$\text{Cp}^* = \text{C}_5\text{Me}_5$, $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ (**1**), $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ (**2**), $2,6-{}^i\text{Pr}_2\text{C}_6\text{H}_3$ (**3**), $2,6-{}^i\text{Pr}_2-4-{}^i\text{BuC}_6\text{H}_2$ (**4**), $2,6-{}^i\text{Bu}_2\text{C}_6\text{H}_3$ (**5**), $2,6-{}^i\text{Bu}_2-4\text{-MeC}_6\text{H}_2$ (**6**)], have been prepared, and structures for **4** and **5** have been determined by X-ray crystallography. The Ti–O–C (phenyl) bond angles for the Cp^* analogues containing the 2,6-diisopropyl-substituted phenoxo ligands (**3–4**, $173.0\text{--}174.6^\circ$) were larger than those for other Cp^* analogues ($155.5\text{--}162.3^\circ$), suggesting that both Cp^* and 2,6-diisopropyl-substituted aryloxo ligand force the unique bond angle leading to more O \rightarrow Ti π donation into Ti. Effect of aryloxo ligand in 1-hexene polymerization catalyzed by $\text{Cp}^*\text{TiCl}_2(\text{OAr})$ –MAO catalysts were explored, and **3–4** exhibited the exceptionally high catalytic activities. Various *tert*-BuCp analogues of the type, $({}^i\text{BuC}_5\text{H}_4)\text{TiCl}_2(\text{OAr})$ [$\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ (**7**), $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ (**8**), $2,6-{}^i\text{Pr}_2\text{C}_6\text{H}_3$ (**9**), $2,6-{}^i\text{Pr}_2-4-{}^i\text{BuC}_6\text{H}_2$ (**10**), $2,6-{}^i\text{Bu}_2\text{C}_6\text{H}_3$ (**11**), $2,6-{}^i\text{Bu}_2-4\text{-MeC}_6\text{H}_2$ (**12**)], have also been prepared, and explored effect of the aryloxo ligand in syndiospecific styrene polymerization in the presence of MAO cocatalyst. The catalytic activity increased in the order: **10** (activity 2680 kg sPs/mol Ti h) > **7**, **9** (1370) > **8** (534) > **11** (258) > **12** (54), strongly suggesting that role of anionic donor ligand was present in this catalysis.

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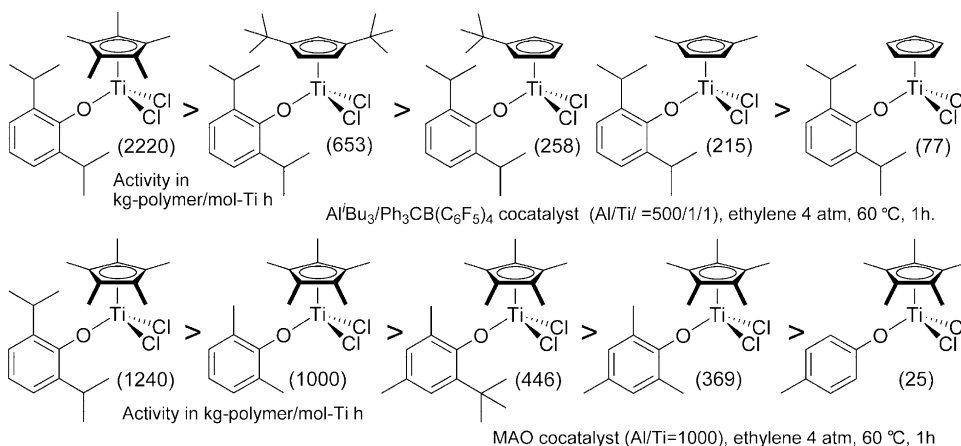
Keywords: Titanium; Olefin polymerization; Structure analysis; Ligand effect; Half-titanocene

1. Introduction

Design and synthesis of efficient transition metal complex catalysts for precise olefin polymerization are one of the most attractive subjects not only in the field of organometallic chemistry, catalysis, but also in the field of polymer chemistry, because evolution of new polyolefins that have never been prepared by conventional catalysts can be highly expected by designing the new catalysts [1]. *Nonbridged* half-metallocene type group 4 transition metal complexes containing anionic donor ligand of the type, $\text{Cp}'\text{M}(\text{L})\text{X}_2$ ($\text{Cp}' =$ cyclopentadienyl group; $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$; $\text{L} =$ anionic donor ligand such as OAr, NR_2 , NPR_3 ,

$\text{N} = \text{CR}_2$, etc.; $\text{X} =$ halogen, alkyl, etc.; $\text{R} =$ alkyl, aryl, etc.), have been one of the promising candidates as the efficient catalysts [2–24], because this type of complex catalysts recently displayed unique characteristics as olefin polymerization catalysts producing new polymers that had never been prepared by conventional Ziegler–Natta catalysts, by ordinary metallocene type [1] and/or so-called ‘constrained geometry’ (linked Cp–amide) type catalysts [1d–e]. We reported that half-titanocenes containing an aryloxo ligand of the type, $\text{Cp}'\text{TiCl}_2(\text{OAr})$ (OAr = aryloxy group), exhibited high catalytic activities for both olefin polymerization [4] and syndiospecific styrene polymerization [5]. In particular, these complex catalysts exhibited unique characteristics for copolymerization of ethylene with α -olefin [4b,6], styrene [7], norbornene [8a,b], and revealed that an efficient catalyst for desired polymerization can be tuned by modification of the cyclopentadienyl fragment, Cp' . More recently, we had

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Scheme 1. Effect of substituents on cyclopentadienyl and aryloxy ligands in ethylene polymerization [4a,b].

shown that efficient copolymerizations of ethylene with cyclohexene (CHE) [8c], 2-methyl-1-pentene (2M1P) [9], and with vinylcyclohexane [10] had been achieved as the first examples by using these complex catalysts.

We previously reported that the catalytic activities for the ethylene polymerization were dependent upon the substituent on both cyclopentadienyl and the aryloxy ligands employed (Scheme 1) [4]. Since, as summarized in Table 1 [4a,b], the bond angle (173.0°) of Ti–O–C (phenoxy) for Cp*TiCl₂(O-2,6-*i*Pr₂C₆H₃) which was the most effective catalyst precursor is significantly different from those for the other Cp derivatives, Cp'TiCl₂(O-2,6-*i*Pr₂C₆H₃) (Cp' = Cp, 1,3-*t*Bu₂C₅H₃, 163.0–163.1°) and for Cp*TiCl₂(O-2,6-Me₂C₆H₃) (162.3°), we assumed that both Cp* and the diisopropyl group sterically force the more open Ti–O–C bond angle, which leads to more O → Ti π donation into Ti; this along with the more electron donating Cp* (as compared with Cp, *t*BuCp, Me₂Cp) stabilizes the active species, leading to higher activity [25]. Recently, it also turned out that the role of anionic donor ligand plays an essential role especially for ethylene copolymerizations such as 2M1P, CHE, styrene incorporations [8c,9,23b]. Therefore, we prepared various Cp* and *tert*-BuCp derivatives containing various aryloxy ligands of the type, Cp'TiCl₂(OAr) [Cp' = Cp* and Ar = 2,6-Me₂C₆H₃

(1), 2,4,6-Me₃C₆H₂ (2), 2,6-*i*Pr₂C₆H₃ (3), 2,6-*i*Pr₂-4-*t*BuC₆H₂ (4), 2,6-*t*Bu₂C₆H₃ (5), 2,6-*t*Bu₂-4-MeC₆H₂ (6); Cp' = *t*BuC₅H₄ and Ar = 2,6-Me₂C₆H₃ (7), 2,4,6-Me₃C₆H₂ (8), 2,6-*i*Pr₂C₆H₃ (9), 2,6-*i*Pr₂-4-*t*BuC₆H₂ (10), 2,6-*t*Bu₂C₆H₃ (11), 2,6-*t*Bu₂-4-MeC₆H₂ (12)] (Chart 1), and explored effect of the aryloxy ligand in both 1-hexene polymerization and syndiospecific styrene polymerization in the presence of MAO cocatalyst. Through this study, we explored effect of anionic donor ligand for precise olefin polymerization using these half-titanocenes.

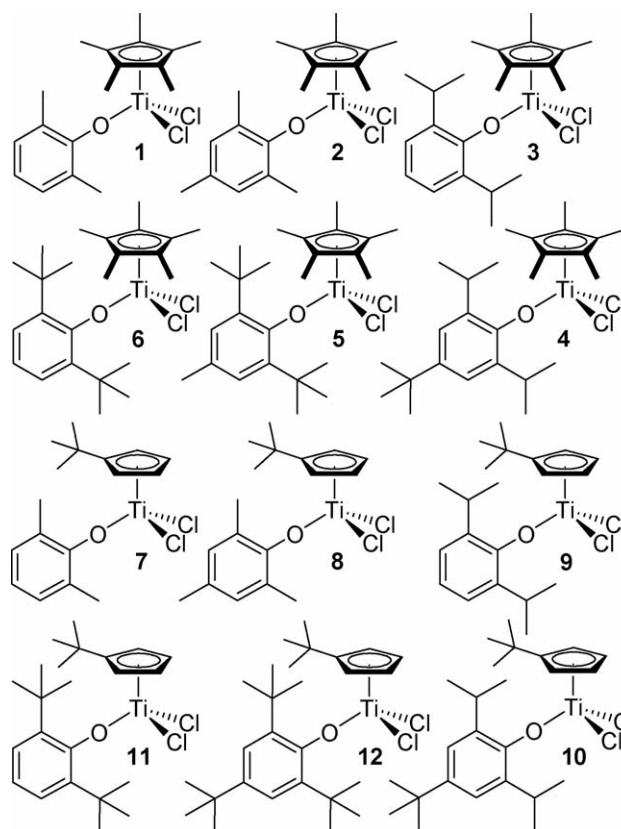


Chart 1.

Table 1
Selected bond distances (Å) and angles for Cp'TiCl₂(O-2,6-*i*Pr₂C₆H₃) [4a]

	Cp' = Cp	Cp' = 1,3- <i>t</i> Bu ₂ C ₅ H ₃	Cp' = Cp*
Bond distances (Å)			
Ti(1)–Cl(1)	2.262(1)	2.2553(8)	2.305(2)
Ti(1)–C(1) in Cp	2.282(8)	2.379(3)	2.367(7)
Ti(1)–C(2) in Cp	2.299(5)	2.378(3)	2.345(7)
Ti(1)–C(3) in Cp	2.325(5)	2.410(2)	2.368(7)
Ti(1)–O(1)	1.760(4)	1.773(3)	1.772(3)
Bond angles (°)			
Cl(1)–Ti–Cl(2)	104.23(7)	103.46(3)	103.45(5)
Cl(1)–Ti–O(1)	102.53(9)	103.62(6)	99.1(2)
Cl(2)–Ti–O(1)	102.53(9)	98.57(6)	104.1(2)
Ti–O–C(6) in phenyl	163.0(4)	163.1(2)	173.0(3)

2. Results and discussion

2.1. Syntheses of various $Cp^*TiCl_2(OAr)$ (**1–6**), $(^iBuC_5H_4)TiCl_2(OAr)$ (**7–12**), and structural analyses for $Cp^*TiCl_2(O-2,6-^iPr-4-^iBu-C_6H_2)$ (**4**) and $Cp^*TiCl_2(O-2,6-^iBu_2C_6H_3)$ (**5**)

Various Cp^* derivatives (**1–4**) of the type, $Cp^*TiCl_2(OAr)$, could be prepared in high yields from Cp^*TiCl_3 by adding 1.0 equiv. of the corresponding lithium phenoxides in Et_2O according to the reported procedure [4b], and the various *tert*-BuCp derivatives (**7–10**) could also be prepared from $(^iBuC_5H_4)TiCl_3$ in the same manner. However, attempts to isolate the 2,6-di-*tert*-butyl analogues (**5–6**, **11–12**) from Cp^*TiCl_3 or $(^iBuC_5H_4)TiCl_3$ were not successful, and the reaction mixture consisting of a certain amount of Cp^*TiCl_3 or $(^iBuC_5H_4)TiCl_3$ and the desired product were thus obtained. The desired complexes, $Cp^*TiCl_2(O-2,6-^iBu_2C_6H_3)$ (**5**, **11**), $Cp^*TiCl_2(O-2,6-^iBu_2-4-MeC_6H_2)$ (**6**, **12**) were found to be prepared in high yields if Cp^*TiCl_3 was treated with 1.0 equiv. of the corresponding LiOAr in toluene at 70 °C. The reaction at 70 °C was found to be important, and the reaction of Cp^*TiCl_3 with $LiO-^iBu_2C_6H_3$ at 50 °C after 10 h still afforded a mixture of **5** and Cp^*TiCl_3 . The resultant complexes were identified by 1H , ^{13}C NMR spectra, elemental analysis, and X-ray crystallography as shown below.

The red platelet microcrystals of **4**, **5** were grown from the concentrated hot toluene solution layered by *n*-hexane upon standing at room temperature in the drybox, and their structures were determined at –30 °C. The molecular structures for **4** and **5** are shown in Figs. 1 and 2, respectively, and these structures showed that both complexes fold a rather distorted tetrahedral geometry around the titanium metal center. Selected bond distances, and bond angles for various $Cp^*TiCl_2(OAr)$ are summarized in Table 2, and these values in some reported Cp^* analogues [26–29] are also shown for comparison. No significant differences in bond lengths among these complexes were observed, and Ti–O bond distances (1.772–1.811 Å) were somewhat shorter than that (1.978 Å) for Ti–O (in CF_3SO_3) bond distance in $Cp^*TiMe(CF_3SO_3)(O-2,6-^iPr_2C_6H_3)$ [30] due to the π donation from oxygen to titanium. The Cl(1)–Ti–Cl(2) bond angles were found to be influenced by the substituents on the aryloxy ligand, and rather bulky di-*tert*-butyl analogue (**5**) possessed the smallest angle (98.10°) among these complexes.

It should be noted that the bond angles of Ti–O–C (phenyl) in **3–4** (173.0, 174.6°) were larger than those in the other Cp^* derivatives (155.5–162.3°) except $Cp^*TiCl_2(O-2,6-Ph_2-3,5-^iBu_2C_6H_3)$ (**14**, 176.9°) [31]. Although we assumed in the previous reports [4a,b] that both Cp^* and diisopropyl group *sterically* force the more open Ti–O–C bond angle, the bond angle for the di-*tert*-butyl analogue (**5**) was small (155.5°). The

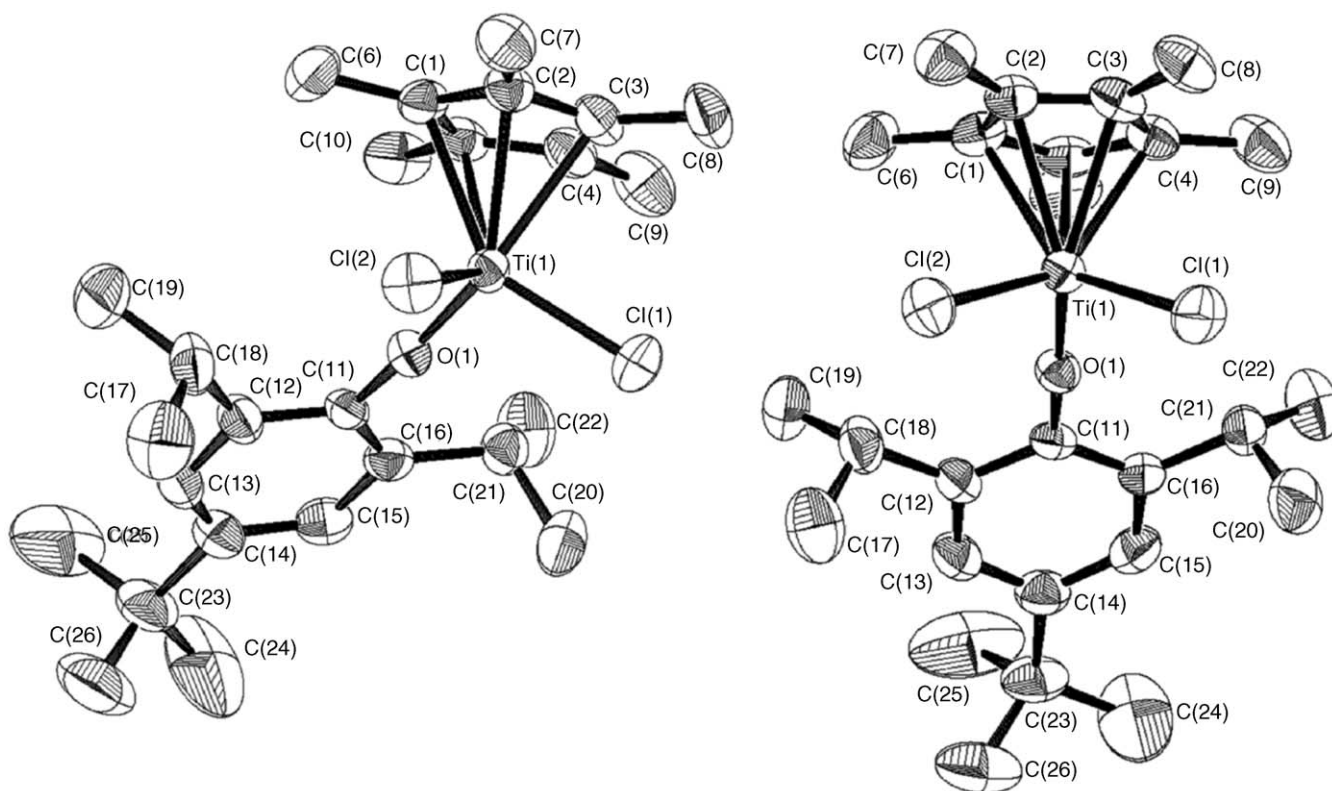


Fig. 1. ORTEP drawings for $Cp^*TiCl_2(O-2,6-^iPr-4-^iBuC_6H_2)$ (left: side view; right: front view). Thermal ellipsoids are drawn at a 50% probability level, and hydrogen atoms were omitted for clarity. Selected bond length (Å): Ti(1)–Cl(1) 2.263(2), Ti(1)–Cl(2) 2.2673(15), Ti(1)–O(1) 1.777(4), Ti(1)–C(1) 2.403(7), Ti(1)–C(2) 2.337(5), O(1)–C(11) 1.376(8), C(1)–C(2) 1.441(9), C(1)–C(5) 1.383(8), C(1)–C(6) 1.508(14), C(2)–C(3) 1.419(12), C(2)–C(7) 1.481(6), C(11)–C(12) 1.404(5). Selected bond angles (°): Cl(1)–Ti(1)–Cl(2) 103.71(7), Cl(1)–Ti(1)–O(1) 101.54(13), Cl(2)–Ti(1)–O(1) 102.86(12), Ti(1)–O(1)–C(11) 174.0(3), C(2)–C(1)–C(5) 108.7(7), C(1)–C(2)–C(3) 106.8(4), O(1)–C(11)–C(12) 118.6(6), O(1)–C(11)–C(16) 119.1(3), C(12)–C(11)–C(16) 122.2(6).

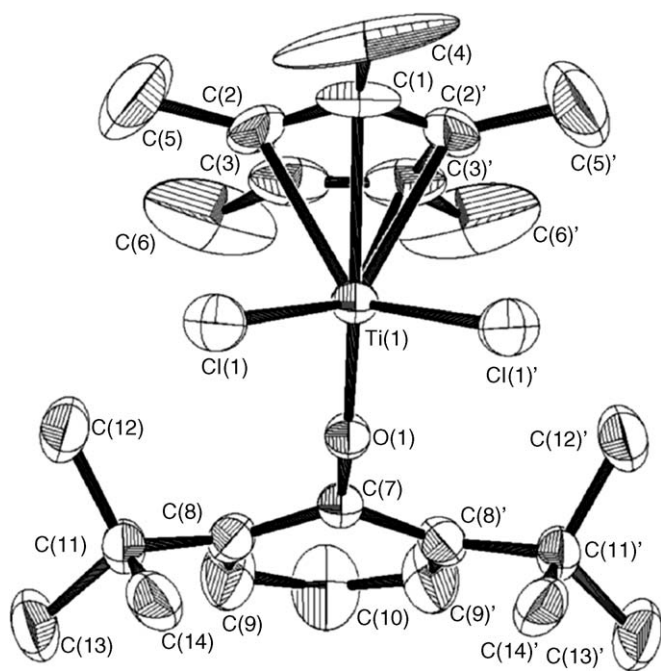


Fig. 2. ORTEP drawings for $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3)$. Thermal ellipsoids are drawn at a 50% probability level, and hydrogen atoms were omitted for clarity. Selected bond length (Å): $\text{Ti}(1)\text{—Cl}(1)$ 2.2674(10), $\text{Ti}(1)\text{—Cl}(1')$ 2.2674(10), $\text{Ti}(1)\text{—O}(1)$ 1.804(2), $\text{Ti}(1)\text{—C}(1)$ 2.359(4), $\text{Ti}(1)\text{—C}(2)$ 2.375(3), $\text{Ti}(1)\text{—C}(3)$ 2.370(3), $\text{O}(1)\text{—C}(7)$ 1.380(4), $\text{C}(1)\text{—C}(2)$ 1.405(4), $\text{C}(1)\text{—C}(4)$ 1.499(7), $\text{C}(2)\text{—C}(3)$ 1.391(5), $\text{C}(2)\text{—C}(5)$ 1.508(6), $\text{C}(7)\text{—C}(8)$ 1.409(3). Selected bond angles ($^\circ$): $\text{Cl}(1)\text{—Ti}(1)\text{—Cl}(1')$ 98.10(4), $\text{Cl}(1)\text{—Ti}(1)\text{—O}(1)$ 103.22(6), $\text{Ti}(1)\text{—O}(1)\text{—C}(7)$ 155.5(2), $\text{C}(1)\text{—C}(2)\text{—C}(3)$ 107.6(3), $\text{O}(1)\text{—C}(7)\text{—C}(8)$ 119.05(18), $\text{C}(7)\text{—C}(8)\text{—C}(9)$ 115.8(3).

similar large bond angle was observed in **14** whereas the value in $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-Ph}_2\text{C}_6\text{H}_3)$ (**13**) was rather small (160.6°). These results might suggest that the unique bond angle would be dependent upon the ligand set employed. Based on the analysis results in **3–4**, it is thus suggested that the unique bond angles in Ti—O—C (phenyl) were affected by substituents in both cyclopentadienyl and aryloxo ligands.

Table 2
Selected bond distances (Å) and angles for $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-R}_2\text{-4-R}'\text{C}_6\text{H}_2)$ (**1–5**)

	1 ^a (R,R' = Me,H)	2 ^b (R,R' = Me,Me)	3 ^c (R,R' = ⁱ Pr,H)	4 (R,R' = ⁱ Pr, ^t Bu)	5 (R,R' = ^t Bu,H)	13 ^d (R,R' = Ph,H)	14 ^e (R,R' = Ph,3,5- ^t Bu ₂)
Bond distances (Å)							
Ti(1)—Cl(1)	2.273(6)	2.262(2)	2.305(2)	2.268(1)	2.2674(10)	2.2693(13)	2.258(1)
Ti(1)—Cl(1) in Cp	2.329(3)	2.344(6)	2.367(7)	2.345(4)	2.359(4)	2.355(4)	2.340(3)
Ti(1)—C(2) in Cp	2.341(2)	2.389(7)	2.345(7)	2.417(4)	2.375(3)	2.348(4)	2.369(3)
Ti(1)—C(3) in Cp	2.398(2)	2.374(7)	2.368(7)	2.399(4)	2.370(3)	2.377(4)	2.420(3)
Ti(1)—O(1)	1.785(2)	1.781(4)	1.772(3)	1.779(3)	1.804(2)	1.811(3)	1.804(2)
Bond angles ($^\circ$)							
Cl(1)—Ti—Cl(2)	103.3(2)	103.2(1)	103.45(5)	103.68(5)	98.10(4)	98.70(5)	100.44(4)
Cl(1)—Ti—O(1)	101.7(1)	102.0(1)	99.1(2)	102.73(10)	103.22(6)	104.33(10)	103.68(7)
Cl(2)—Ti—O(1)	101.7(1)	101.6(1)	104.1(2)	101.83(10)	103.22(6)	105.20(10)	104.34(7)
Ti—O—C(6) in phenyl	162.3(2)	162.1(4)	173.0(3)	174.6(3)	155.5(2)	160.6(3)	176.90(19)

^a $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3)$ (**1**) cited from ref. [26].

^b $\text{Cp}^*\text{TiCl}_2(\text{O}-2,4,6\text{-Me}_3\text{C}_6\text{H}_2)$ (**2**) cited from ref. [27].

^c $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**3**) cited from ref. [4a].

^d $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-Ph}_2\text{C}_6\text{H}_3)$ (**13**) cited from ref. [28].

^e $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-Ph}_2\text{-3,5-}^t\text{Bu}_2\text{C}_6\text{H}_3)$ (**14**) cited from ref. [29].

Selected bond angles and distances for $\text{Cp}^*\text{Ti}(\text{X})(\text{Y})(\text{O}-2,6\text{-}^i\text{Pr}_2\text{-4-R}'\text{C}_6\text{H}_2)$ (X,Y = Cl,Cl, Me,Me, Me,CF₃SO₃, R' = H or ^tBu) are summarized in Table 3. Although no significant differences in the bond distances were observed among these complexes, the bond angles in X—Ti—Y were influenced by the anionic ligands (X,Y), probably due to the increased steric bulk of Me, CF₃SO₃ ligands compared to Cl. It should be noted that the bond angles in Ti—O—C (phenyl) were somewhat large in all cases ($166.2\text{--}174.6^\circ$), clearly suggesting that both Cp^* and the 2,6-diisopropyl-substituted aryloxo ligand form the unique bond angle, leading to more O → Ti π donation into the titanium.

2.2. Effect of aryloxo ligand in 1-hexene polymerization catalyzed by $\text{Cp}^*\text{TiCl}_2(\text{OAr})$ (**1–6**)—MAO catalyst systems

Table 4 summarizes 1-hexene polymerization results by **3** under various Al/Ti molar ratios. As reported previously [4c], the catalytic activity was affected by the Al/Ti molar ratio, and the ratio of 6000 showed the highest activity under these conditions. The resultant polymers were poly(1-hexene)s with atactic stereo-regularity [4c], and the polymers possessed high molecular weights with unimodal molecular weight distributions ($M_n = 3.01\text{--}4.61 \times 10^5$, $M_w/M_n = 1.42\text{--}1.74$). These polymerizations proceeded at remarkable rates, and the M_n values for the resultant polymers slightly increased for longer times (runs 4, 6–8). Fig. 3 shows time course plots of $\ln[1\text{-hexene}]_0$ in the polymerization [32]. Since a first order relationship between the monomer concentration and the reaction rate was seen, it is thus clear that the apparent decrease in the activity is not due to the deactivation of catalytically-active species but due to the decrease in the 1-hexene concentration.

Under the optimized conditions by the above experiments, the 1-hexene polymerizations by $\text{Cp}^*\text{TiCl}_2(\text{OAr})$ (**1–6**) were performed in the presence of MAO cocatalyst. The results are summarized in Table 5. The activities by the Cp^* -aryloxo analogues (**3–4**) containing two isopropyl group in 2,6-position were much higher than those by the others (**1–2**, **5–6**), and the significant difference in the activity was not observed between **3** and **4**. The

Table 3
Selected bond distances (Å) and angles (°) for Cp*Ti(X)(Y)(O-2,6-*i*-Pr₂-4-R'C₆H₂)

	R' = H ^a , X, Y = Cl, Cl	R' = <i>t</i> -Bu, X, Y = Cl, Cl	R' = H ^b , X, Y = Me, Me	R' = H ^b , X, Y = Me, CF ₃ SO ₃
Bond distances (Å)				
Ti(1)—Cl(1) or C in Me	2.305(2)	2.268(1)	2.101(3)	2.093(8)
Ti(1)—C(1) in Cp	2.367(7)	2.345(4)	2.338(3)	2.346(6)
Ti(1)—C(2) in Cp	2.345(7)	2.417(4)	2.350(2)	2.377(6)
Ti(1)—C(3) in Cp	2.368(7)	2.399(4)	2.374(2)	2.353(6)
Ti(1)—O(1)	1.772(3)	1.779(3)	1.790(2)	1.778(4)
Bond angles (°)				
X—Ti—Y	103.45(5)	103.68(5)	99.8(1) ^c	97.4(3) ^d
X—Ti—O(1), X = Cl or C in Me	99.1(2)	102.73(10)	101.9(1) ^e	102.1(2) ^e
Y—Ti—O(1)	104.1(2)	101.83(10)	102.9(1)	106.6(2)
Ti—O—C in phenyl	173.0(3)	174.6(3)	168.7(1)	166.2(4)

^a Cp*TiCl₂(O-2,6-*i*-Pr₂C₆H₃) (**3**) cited from ref. [4a].

^b Cp*TiMe(Y)(O-2,6-*i*-Pr₂C₆H₃) (Y = Me, CF₃SO₃) cited from ref. [30].

^c Me—Ti—Me bond angle.

^d Me—Ti—O in CF₃SO₃ bond angle.

^e O(1)—Ti—C in Me bond angle.

Table 4
1-Hexene polymerization by Cp*TiCl₂(O-2,6-*i*-Pr₂C₆H₃) (**3**)—MAO catalyst system^a

Run no.	Al/Ti ^b	Time (min)	Yield (mg)	Activity ^c	TON ^d	M _n ^e (×10 ⁻⁴)	M _w /M _n ^e
1	2000	20	162	972	3850	28.4	1.74
2	3000	20	210	1260	4990	30.1	1.74
3	4000	20	384	2300	9130	37.2	1.65
4	6000	20	445	2670	10600	46.1	1.42
5	8000	20	327	1960	7770	40.0	1.64
6	6000	10	192	2300	4560	38.2	1.47
4	6000	20	445	2670	10600	46.1	1.42
7	6000	30	518	2070	12300	47.6	1.48
8	6000	60	588	1180	14000	57.6	1.40

^a Polymerization conditions: 1-hexene 10 mL, *n*-hexane 10 mL, catalyst 0.5 μmol (**3** 2.0 μmol/mL toluene), MAO (prepared by removing toluene and AlMe₃), 25 °C.

^b Molar ratio of Al/Ti.

^c Activity in kg polymer/mol Ti h.

^d TON (turnover numbers) = (molar amount of 1-hexene consumed)/(mol Ti).

^e GPC data in THF vs. polystyrene standards.

results clearly indicate that both Cp* and aryloxo ligand containing diisopropyl group in 2,6-position are very important factors for exhibiting the high activity. These results would also suggest that the unique bond angles in Ti—O—C (phenyl) for **3–4**

affect the high catalytic activity by more O → Ti π donation into the titanium, which leads to stabilize the catalytically active species for exhibiting the higher catalytic activity in 1-hexene polymerization.

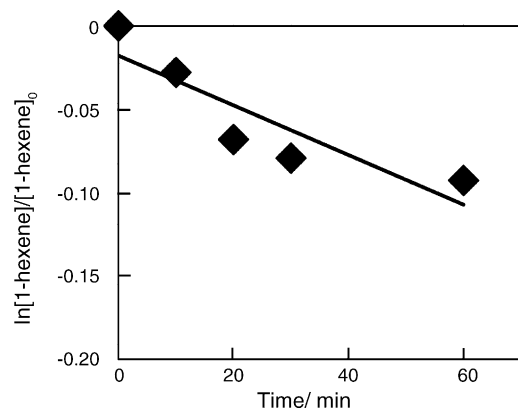


Fig. 3. Time course plots vs. ln[1-hexene]/[1-hexene]₀ for 1-hexene polymerization by **1**—MAO catalyst system, and [1-hexene] is the 1-hexene concentration at the prescribed time and [1-hexene]₀ is the initial concentration.

Table 5

1-Hexene polymerization by Cp*TiCl₂(OAr) [OAr = O-2,6-Me₂C₆H₃ (**1**), O-2,4,6-Me₃C₆H₂ (**2**), O-2,6-*i*-Pr₂C₆H₃ (**3**), O-2,6-*i*-Pr₂-4-*t*-BuC₆H₂ (**4**), O-2,6-*t*-Bu₂C₆H₃ (**5**), O-2,6-*t*-Bu-4-MeC₆H₂ (**6**)—MAO catalyst systems^a

Run no.	Catalyst	Yield (mg)	Activity ^b	M _n ^c (×10 ⁻⁴)	M _w /M _n ^c
9	1	40	240	14.2	1.66
10	2	58	348	13.2	1.66
4	3	445	2670	46.1	1.42
11	4	448	2690	26.1	1.80
12	5	26	156	23.7	1.93
13	6	36	216	28.4	1.63

^a Polymerization conditions: 1-hexene 10 mL, *n*-hexane 10 mL, catalyst 0.5 μmol (complex 2.0 μmol/mL toluene), MAO (prepared by removing toluene and AlMe₃) 3.0 mmol, 25 °C, 20 min.

^b Activity in kg polymer/mol Ti h.

^c GPC data in THF vs. polystyrene standards.

Table 6
Effect of aryloxy ligand for styrene polymerization by (*t*-BuC₅H₄)TiCl₂(OAr) [OAr = O-2,6-Me₂C₆H₃ (**7**), O-2,4,6-Me₃C₆H₂ (**8**), O-2,6-*i*-Pr₂C₆H₃ (**9**), O-2,6-*i*-Pr₂-4-*t*-BuC₆H₂ (**10**), O-2,6-*t*-Bu₂C₆H₃ (**11**), O-2,6-*t*-Bu₂-4-MeC₆H₂ (**12**)]—MAO catalyst systems^a

Run no.	Catalyst	Acetone insoluble ^b				Acetone soluble ^f (mg)
		Yield, mg (%) ^c	Activity ^d	M_n^e ($\times 10^{-4}$)	M_w/M_n^e	
14	7	228 (92)	1370	5.3	2.05	20
15	8	89 (79)	534	5.9	1.91	23
16	9	229 (91)	1370	5.7	2.05	22
17	10	446 (83)	2680	5.2	2.18	91
18	11	43 (33)	258	5.1	2.01	87
19	12	9 (25)	54	4.6	1.98	27

^a Conditions: catalyst 1.0 μ mol, styrene/toluene = 5/9 mL, MAO 3.0 mmol (Al/Ti = 3000), 10 min at 25 °C.

^b Syndiotactic polystyrene (sPS).

^c Yield (%) = yield (mg) of sPS/polymer yield (mg) in whole polystyrene produced.

^d Activity in kg sPS/mol Ti h.

^e GPC data in THF vs polystyrene standards.

^f Atactic polystyrene prepared by MAO.

2.3. Effect of aryloxy ligand in syndiospecific styrene polymerization catalyzed by (*t*-BuC₅H₄)TiCl₂(OAr) (**7**–**12**)—MAO catalyst systems

Table 6 summarizes the results for syndiospecific styrene polymerization by various *tert*-BuCp analogues, (*t*-BuC₅H₄)TiCl₂(OAr) (**7**–**12**), under the optimized conditions according to the previous report [5b]. The *tert*-BuCp analogues were chosen because the molecular weight distributions for resultant syndiotactic polystyrenes (as the acetone insoluble fraction) prepared by (1,3-Me₂C₅H₃)TiCl₂(OAr) (Ar = 2,6-Me₂C₆H₃, 3,5-Me₂C₆H₃) complexes were bimodal in the presence of MAO [5a], or Al(*t*-Bu)₃-Al(*n*-C₈H₁₇)₃/borate cocatalyst [33]. In contrast, the resultant polymers prepared by **7**–**12**—MAO catalysts possessed high molecular weights with unimodal molecular weight distributions as well as with perfect syndiotactic stereo-regularity ($M_n = 4.6$ – 5.9×10^4 , $M_w/M_n = 1.91$ – 2.18). No significant differences in the M_n values were observed, and the facts may be explained by our previous assumption that these values (dominant chain-transfer reactions) were not influenced by the anionic donor ligand but highly influenced by the Cp' employed [5b].

It is important to note that the catalytic activity increased in the order: **10** (activity 2680 kg sPS/mol Ti h) > **7**, **9** (1370) > **8** (534) > **11** (258) > **12** (54). These results clearly indicate that the catalytic activities are strongly influenced by both *ortho*- and *para*- substituents in the aryloxy ligand [34,35]. Although it has been invoked that cationic Ti(III) plays an essential role for syndiospecific styrene polymerization by Cp'TiX'₃ (X' = Cl, OMe, etc.) [36], the role of anionic donor ligands towards the activity was present in this catalysis. This would suggest a possibility that a neutral Ti(III) or a cationic Ti(IV) species also plays a role for this polymerization with this unique catalyst system, as we previously suggested [5b]. We believe that the contents in this paper should be helpful for understanding the reaction mechanism for both syndiospecific styrene polymerization and ethylene/styrene copolymerization.

3. Experimental

3.1. General procedure

All experiments were carried out under a nitrogen atmosphere in a vacuum atmosphere drybox unless otherwise specified. Anhydrous grade of toluene (Kanto Kagaku Co. Ltd) was transferred into a bottle containing molecular sieves (mixture of 3A and 4A 1/16, and 13X) in the drybox, and was used without further purification. Styrene of polymerization grade (Idemitsu Petrochemicals Co.) was stored in a freezer after passing through alumina short column under nitrogen flow in the dry box, and the styrene was further purified by the same procedure in the dry box prior to use. Cp*TiCl₂(O-2,6-Me₂C₆H₃) (**1**) [26], Cp*TiCl₂(O-2,4,6-Me₃C₆H₂) (**2**) [4b], Cp*TiCl₂(O-2,6-*i*-Pr₂C₆H₃) (**3**) [4b], (*t*-BuC₅H₄)TiCl₂(O-2,6-*i*-Pr₂C₆H₃) (**7**) [4b] were prepared according to the previous reports. Toluene and AlMe₃ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt.% (Al) toluene solution, Tosoh Finechem Co.] were taken to dryness under reduced pressure (at ca. 50 °C for removing toluene, AlMe₃, and then heated at >100 °C for 1 h for completion) in the drybox to give white solids.

Molecular weights and the molecular weight distributions of the poly(1-hexene), polystyrenes were measured by gel-permeation chromatography (GPC). HPLC grade THF was used for GPC and were degassed prior to use. GPC were performed at 40 °C on a Shimadzu SCL-10A using a RID-10A detector (Shimadzu Co. Ltd.) in THF (containing 0.03 wt.% 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL/min). GPC columns (ShimPAC GPC-806, 804 and 802, 30 cm \times 8.0 mm ϕ , spherical porous gel made of styrene/divinylbenzene copolymer, ranging from <10² to 2 \times 10⁷ MW) were calibrated versus polystyrene standard samples. Elemental analyses were performed by using PE2400II Series (Perkin-Elmer Co.).

3.2. Synthesis of Cp*TiCl₂(O-2,6-*i*-Pr₂-4-*t*-BuC₆H₂) (**4**)

Into a Et₂O solution (30 mL) containing Cp*TiCl₃ (1.00 g, 3.46 mmol), LiO-2,6-*i*-Pr₂-4-*t*-BuC₆H₂ (1.0 equiv.) was added in

one portion at -25°C , and the reaction mixture was warmed slowly to room temperature, was stirred for 10 h. The mixture was then filtered through Celite pad, and the filter cake was washed with Et_2O ($2 \times 15\text{ mL}$). The combined filtrate and the wash were taken to dryness under reduced pressure to give a red-orange solid. The solid was then dissolved in a minimum amount of CH_2Cl_2 layered by *n*-hexane in the freezer (-25°C). The chilled solution gave red (platelet) microcrystals. Yield 1.363 g (81%). $^1\text{H NMR}$ (C_6D_6): δ 1.31 (s, 9H, $(\text{CH}_3)_3\text{C}-$), 1.34 (d, 12H, $J=7.0\text{ Hz}$, $(\text{CH}_3)_2\text{CH}-$), 1.91 (s, 15H, $\text{C}_5(\text{CH}_3)_5-$), 3.40–3.58 (m, 2H, $(\text{CH}_3)_2\text{CH}-$), 7.28 (s, 2H, C_6H_2). $^{13}\text{C NMR}$ (C_6D_6): δ 12.7, 24.4, 27.1, 31.7, 34.3, 120.3, 131.9, 139.0, 146.3, 158.1. Anal. calcd. for $\text{C}_{26}\text{H}_{40}\text{Cl}_2\text{OTi}$: C, 64.06; H, 8.27. Found: C, 64.29; H, 8.14 (%).

3.3. Synthesis of $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Bu}_2\text{C}_6\text{H}_3)$ (**5**)

Into a toluene solution (30 mL) containing Cp^*TiCl_3 (1.00 g, 3.46 mmol) equipped with a sealed Schlenk tube, $\text{LiO}-2,6\text{-}^i\text{Bu}_2\text{C}_6\text{H}_3$ (1.0 equiv.) was added in one portion at room temperature. The reaction mixture was stirred at 70°C for 10 h. The mixture was then filtered through Celite pad, and the filter cake was washed with toluene ($2 \times 15\text{ mL}$). The combined filtrate and the wash were taken to dryness under reduced pressure to give a red-orange solid. The solid was then dissolved in a minimum amount of CH_2Cl_2 layered by *n*-hexane in the freezer (-25°C). The chilled solution gave red microcrystals. Yield 1.235 g (78%). $^1\text{H NMR}$ (C_6D_6): δ 1.44 (s, 18H, $(\text{CH}_3)_3\text{C}-$), 1.82 (s, 15H, $\text{C}_5(\text{CH}_3)_5-$), 6.82 (t, 1H, $J=7.7\text{ Hz}$, C_6H_3), 7.16 (d, 2H, $J=7.7\text{ Hz}$, C_6H_3). $^{13}\text{C NMR}$ (C_6D_6): δ 13.8, 32.1, 36.3, 121.8, 125.3, 133.5, 139.9, 166.9. Anal. calcd. for $\text{C}_{24}\text{H}_{36}\text{Cl}_2\text{OTi}$: C, 62.76; H, 7.90. Found: C, 62.36; H, 7.73 (%).

3.4. Synthesis of $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Bu}_2\text{-4-MeC}_6\text{H}_2)$ (**6**)

Synthetic procedure for **6** was the same as that for **5** except $\text{LiO}-2,6\text{-}^i\text{Bu}_2\text{-4-MeC}_6\text{H}_2$ was used in stead of $\text{LiO}-2,6\text{-}^i\text{Bu}_2\text{C}_6\text{H}_3$ and amount of Cp^*TiCl_3 was 0.85 g (2.94 mmol). Yield 1.232 g (89%). $^1\text{H NMR}$ (C_6D_6): δ 1.47 (s, 18H, $(\text{CH}_3)_3\text{C}-$), 1.85 (s, 15H, $\text{C}_5(\text{CH}_3)_5-$), 2.20 (s, 3H, $\text{CH}_3\text{C}_6\text{H}_2$), 7.04 (s, 2H, C_6H_2). $^{13}\text{C NMR}$ (C_6D_6): δ 13.4, 21.1, 32.3, 36.2, 126.0, 130.6, 133.3, 139.9, 165.4. Anal. calcd. for $\text{C}_{25}\text{H}_{38}\text{Cl}_2\text{OTi}$: C, 63.43; H, 8.09. Found: C, 63.31; H, 8.05 (%).

3.5. Synthesis of $(^i\text{BuC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3)$ (**7**)

Synthetic procedure for **7** was the same as that for **4** except that $(^i\text{BuC}_5\text{H}_4)\text{TiCl}_3$ (500 mg, 1.82 mmol) was used instead of Cp^*TiCl_3 , and $\text{LiO}-2,6\text{-Me}_2\text{C}_6\text{H}_3$ was used in stead of $\text{LiO}-2,6\text{-}^i\text{Pr}_2\text{-4-}^i\text{BuC}_6\text{H}_2$. The resultant solid after filtration was then dissolved in a minimum amount of Et_2O layered by *n*-hexane in the freezer (-25°C). The chilled solution gave red microcrystals. Yield 422 mg (64%). $^1\text{H NMR}$ (C_6D_6): δ 1.20 (s, 9H, $(\text{CH}_3)_3\text{C}-$), 2.22 (s, 6H, $\text{CH}_3\text{C}_6\text{H}_2$), 5.76 (t, 2H, $J=2.7\text{ Hz}$, $^i\text{BuC}_5\text{H}_4$), 6.34 (t, 2H, $J=2.6\text{ Hz}$, $^i\text{BuC}_5\text{H}_4$), 6.74 (t, 1H,

$J=7.5\text{ Hz}$, C_6H_3), 6.80 (d, 2H, $J=7.3\text{ Hz}$, C_6H_3). $^{13}\text{C NMR}$ (C_6D_6): δ 17.7, 31.0, 34.0, 119.4, 119.6, 124.3, 128.1, 129.1, 150.9, 167.2. Anal. calcd. for $\text{C}_{17}\text{H}_{23}\text{Cl}_2\text{OTi}$: C, 56.38; H, 6.40. Found: C, 56.69; H, 6.20 (%).

3.6. Synthesis of $(^i\text{BuC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,4,6\text{-Me}_3\text{C}_6\text{H}_2)$ (**8**)

Synthetic procedure for **8** was the same as that for **7** except that $\text{LiO}-2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ was used in stead of $\text{LiO}-2,6\text{-Me}_2\text{C}_6\text{H}_3$ and $(^i\text{BuC}_5\text{H}_4)\text{TiCl}_3$ (1.00 g, 3.63 mmol) was used. Yield 1.057 g (78%). $^1\text{H NMR}$ (C_6D_6): δ 1.21 (s, 9H, $(\text{CH}_3)_3\text{C}-$), 2.08 (s, 3H, $\text{CH}_3\text{C}_6\text{H}_2$), 2.24 (s, 6H, $\text{CH}_3\text{C}_6\text{H}_2$), 5.81 (t, 2H, $J=3.3\text{ Hz}$, $^i\text{BuC}_5\text{H}_4$), 6.37 (t, 2H, $J=3.3\text{ Hz}$, $^i\text{BuC}_5\text{H}_4$), 6.59 (s, 2H, C_6H_2). $^{13}\text{C NMR}$ (C_6D_6): δ 17.7, 21.0, 31.0, 34.0, 119.3, 119.5, 127.8, 129.6, 133.6, 150.6, 165.9. Anal. calcd. for $\text{C}_{18}\text{H}_{24}\text{Cl}_2\text{OTi}$: C, 57.63; H, 6.45. Found: C, 57.89; H, 6.51 (%).

3.7. Synthesis of $(^i\text{BuC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{-4-}^i\text{BuC}_6\text{H}_2)$ (**10**)

Synthetic procedure for **10** was the same as that for **8** except that $\text{LiO}-2,6\text{-}^i\text{Pr}_2\text{-4-}^i\text{BuC}_6\text{H}_2$ was used in stead of $\text{LiO}-2,4,6\text{-Me}_3\text{C}_6\text{H}_2$. Yield 1.362 g (79%). $^1\text{H NMR}$ (C_6D_6): δ 1.23 (s, 9H, $(\text{CH}_3)_3\text{C}-$), 1.30 (s, 9H, $(\text{CH}_3)_3\text{C}-$), 1.34 (d, 12H, $J=6.6\text{ Hz}$, $(\text{CH}_3)_2\text{CH}-$), 3.53–3.58 (m, 2H, $(\text{CH}_3)_2\text{CH}-$), 5.87 (t, 2H, $J=2.7\text{ Hz}$, $^i\text{BuC}_5\text{H}_4$), 6.43 (t, 2H, $J=2.7\text{ Hz}$, $^i\text{BuC}_5\text{H}_4$), 7.29 (s, 2H, C_6H_2). $^{13}\text{C NMR}$ (C_6D_6): δ 24.0, 27.4, 30.8, 31.6, 33.8, 34.9, 119.0, 120.4, 138.0, 147.2, 150.6, 163.3. Anal. calcd. for $\text{C}_{25}\text{H}_{38}\text{Cl}_2\text{OTi}$: C, 63.43; H, 8.09. Found: C, 63.30; H, 7.92 (%).

3.8. Synthesis of $(^i\text{BuC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Bu}_2\text{C}_6\text{H}_3)$ (**11**)

Synthetic procedure for **11** was the same as that for **5** except $(^i\text{BuC}_5\text{H}_4)\text{TiCl}_3$ (0.51 g, 1.85 mmol) was used instead of Cp^*TiCl_3 . Yield 0.666 g (81%). $^1\text{H NMR}$ (C_6D_6): δ 1.28 (s, 9H, $(\text{CH}_3)_3\text{C}-$), 1.48 (s, 18H, $(\text{CH}_3)_3\text{C}-\text{C}_6\text{H}_2$), 5.76 (t, 2H, $J=2.7\text{ Hz}$, $^i\text{BuC}_5\text{H}_4$), 6.40 (t, 2H, $J=2.7\text{ Hz}$, $^i\text{BuC}_5\text{H}_4$), 6.84 (t, 1H, $J=7.9\text{ Hz}$, C_6H_3), 7.19 (d, 2H, $J=7.7\text{ Hz}$, C_6H_3). $^{13}\text{C NMR}$ (C_6D_6): δ 31.2, 32.4, 34.4, 36.3, 120.4, 123.1, 126.0, 139.7, 151.9, 171.4. Anal. calcd. for $\text{C}_{23}\text{H}_{34}\text{Cl}_2\text{OTi}$: C, 62.03; H, 7.70. Found: C, 62.12; H, 7.85 (%).

3.9. Synthesis of $(^i\text{BuC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Bu}_2\text{-4-MeC}_6\text{H}_2)$ (**12**)

Synthetic procedure for **12** was the same as that for **5** except that $(^i\text{BuC}_5\text{H}_4)\text{TiCl}_3$ (0.60 g, 2.18 mmol) was used instead of Cp^*TiCl_3 , and $\text{LiO}-2,6\text{-}^i\text{Bu}_2\text{-4-MeC}_6\text{H}_2$ was used in stead of $\text{LiO}-2,6\text{-}^i\text{Bu}_2\text{C}_6\text{H}_3$. Yield 0.656 g (66%). $^1\text{H NMR}$ (C_6D_6): δ 1.30 (s, 9H, $(\text{CH}_3)_3\text{C}-$), 1.49 (s, 18H, $(\text{CH}_3)_3\text{C}-\text{C}_6\text{H}_2$), 2.20 (s, 3H, $\text{CH}_3\text{C}_6\text{H}_2$), 5.81 (t, 2H, $J=2.7\text{ Hz}$, $^i\text{BuC}_5\text{H}_4$), 6.42 (t, 2H, $J=2.7\text{ Hz}$, $^i\text{BuC}_5\text{H}_4$), 7.08 (s, 2H, C_6H_2). $^{13}\text{C NMR}$ (C_6D_6): δ 21.2, 31.0, 32.1, 34.1, 35.9, 119.9, 126.4, 131.7, 139.3, 151.1, 169.8. Anal. calcd. for $\text{C}_{24}\text{H}_{36}\text{Cl}_2\text{OTi}$: C, 62.76; H, 7.90. Found: C, 62.91; H, 7.97 (%).

3.10. 1-Hexene polymerization

Typical procedure for 1-hexene polymerization was as follows: prescribed amount of MAO, 1-hexene (10.0 mL) and *n*-hexane (10.0 mL) were added to a round bottom flask (50 mL) in the drybox, and the polymerization was started by the addition of a toluene solution (0.25 mL) containing the catalyst (0.5 μ mol). The reaction mixture was stirred for prescribed time at 25 °C, and the polymerization was terminated with the addition of EtOH. The reaction product was extracted with CHCl₃ which was washed with a mixed solution of EtOH and HCl aqueous solution and then rinsed with water. The chloroform extract was dried over Na₂SO₄, and chloroform and 1-hexene remained was then removed in vacuo. The resultant poly(1-hexene)s possessed atactic stereoregularity with favored repeated 1,2-insertion mode [4c].

3.11. Polymerization of styrene

Typical polymerization procedure (described in Table 6, complex 7) is as follows: into a 25 mL round bottom flask, MAO (3.0 mmol, 174 mg), prescribed amount of toluene (9.0 mL), and then styrene (5.0 mL) were added in the dry box. A toluene solution containing titanium complex (1.0 μ mol/mL toluene, 1.0 mL) was added into the solution to start the polymerization at 25 °C, and the reaction mixture was stirred for 10 min. The polymerization was then terminated with the addition of ethanol containing HCl, and the resultant white solid was collected by

filtration, and was dried in vacuo. The resultant solid was then separated into two fractions by using acetone as the extraction solvent, and was dried in vacuo for 6 h at 60 °C. Typical ¹H and ¹³C NMR spectra for resultant polymer (acetone insoluble fraction, SPS) were the same as those reported previously [5].

3.12. Crystallographic analysis

All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo K α radiation. The selected crystal collection parameters are listed in Table 7, and the detailed results (CIF files, and X-ray structure reports) were described in Supplementary materials. All structures were solved by direct method and expanded using Fourier techniques [37], and the nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations for complexes were performed using the crystal structure [38,39] crystallographic software package.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2006.03.030.

Table 7
Crystal and data collection parameters for Cp*TiCl₂(OAr) [OAr = O-2,6-*i*Pr₂-4-*t*Bu-C₆H₂ (4), O-2,6-*i*Bu₂C₆H₃ (5)]^a

Complex	4	5
Formula	C ₂₆ H ₄₀ Cl ₂ OTi	C ₂₄ H ₃₆ Cl ₂ OTi
Formula weight	487.41	459.35
Habits	Red, platelet	Red, platelet
Crystal size (mm)	0.47 × 0.33 × 0.10	0.50 × 0.17 × 0.07
Crystal system	Monoclinic	Orthorhombic
Space group	C2/c (#15)	Pnma (#62)
<i>a</i> (Å)	28.172(14)	7.822(3)
<i>b</i> (Å)	12.534(6)	17.091(8)
<i>c</i> (Å)	20.261(10)	18.628(6)
β (°)	129.225(19)	
<i>V</i> (Å ³)	5542.3(47)	2490.2(15)
Z value	8	4
<i>D</i> _{calcd} (g/cm ³)	1.168	1.225
<i>F</i> ₀₀₀	2080.00	976.00
Temp (K)	243	243
λ (Mo K α) (Å)	0.71069	0.71069
2 θ max (°)	50.0°	50.0°
No. of reflections measured:	2741	2275
total		
No. of observations (<i>I</i> > 10.000(<i>I</i>))	3082	2233
No. of variables	311	159
Residuals: <i>R</i> ₁ ; <i>R</i> _w	0.0666; 0.1799	0.0580; 0.1274
GOF	1.006	1.080
Max (minimum) peak in final diff. map (e/Å ³)	0.64 (−0.63)	0.44 (−0.040)

^a Detailed analysis results are shown in Supplementary data.

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