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Olefin Polymerization by (Cyclopentadienyl)(aryloxy)titanium(IV) Complexes−Cocatalyst Systems

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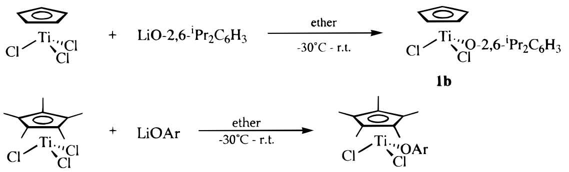
ABSTRACT: Various titanium(IV) complexes of the type $Cp'Ti(OAr)Cl_2$ (Cp′ = cyclopentadienyl; OAr = aryloxy) could be prepared in high yields from $Cp'TiCl_3$. $Cp^*Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)Me_2$ ($Cp^* = C_5Me_5$) could also be prepared from Cp^*TiMe_3 with $2,6\text{-}^iPr_2C_6H_3OH$ in high yield (77%). These complexes showed notable catalytic activities for ethylene polymerization with MAO or $Al^iBu_3{-}Ph_3CB(C_6F_5)_4$: $Cp^*Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)X_2$ [X = Cl (**2b**), Me (**8b**), CF_3SO_3 (**9b**)] showed the highest activities among these complexes. The effects of substituents on both cyclopentadienyl (pentamethylcyclopentadienyl) and aryloxy (2,6-diisopropylphenoxy) groups are important for the remarkable activity. The crystallographic analyses of $CpTi(O\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_2$ (**1b**), $Cp^*Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_2$ (**2b**), and $(1,3\text{-}^tBu_2C_5H_3)Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_2$ (**6b**) could be performed, and the bond angle of Ti−O−C (phenyl group) for **2b** (173.0°) was found to be significantly different from those for other complexes (162.3−163.1°), although no significant differences are observed for other bond lengths and angles among these compounds. $CpTi(O\text{-}2,4,6\text{-}Me_3C_6H_2)_2Cl$ (**7a**) and $CpTi(O\text{-}2,6\text{-}^iPr_2C_6H_3)_2Cl$ (**7b**) could be prepared from $CpTiCl_3$ with the corresponding phenol under the refluxing conditions of toluene, and the structure of **7a** could be determined by X-ray crystallography. These complexes also exhibited moderate catalytic activities for ethylene polymerization in the presence of MAO, which was prepared by removing toluene and an excess amount of $AlMe_3$, and the effect of the bulk of phenoxy ligand on the activity was demonstrated. **2b** was also found to be an effective catalyst precursor for ethylene/1-butene copolymerization, and the smaller r_Er_B values (0.25−0.36) compared to $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (2.45) were observed by microanalysis of the resultant copolymers.

Introduction

Olefin polymerization by homogeneous catalysis has been one of the most attractive subjects in the field of both organometallic chemistry and catalysis. There are many reports concerning this topic using metallocene analogues,[1] hybrid “half-metallocene” complexes[2] such as $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$, and others.[3,4] However, there was one example for the polymerization by nonbridged (cyclopentadienyl)(aryloxy)titanium(IV) complexes such as $Cp^*Ti(O^iPr)Me_2$ ($Cp^* = C_5Me_5$),[5] although the syntheses of these complexes such as $Cp^*Ti(O\text{-}2,6\text{-}Me_2C_6H_3)Cl_2$ (**2d**) were known.[6]

We have recently reported as a preliminary communication that $Cp^*Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_2$ (**2b**) showed an exceptionally high catalytic activity for ethylene polymerization in the presence of a cocatalyst such as MAO, or $Al^iBu_3/Ph_3CB(C_6F_5)_4$, and that a unique bond angle of Ti−O−C (phenyl group) in **2b** was observed by X-ray crystallography.[7] We believe that these results are very interesting to note because a highly active catalyst precursor can be prepared only with one or two steps as well as because there might be an another possibility to find a better catalyst. In this paper, we wish to introduce more detailed synthetic procedures of the various titanium complexes of the type $Cp'Ti(OAr)X_2$ (OAr = aryloxy group, Cp′ = cyclopentadienyl group) and $Cp'Ti(OAr)_2Cl$ and would also like to introduce the detailed results for the ethylene polymerization by these complexes in the presence of cocatalyst, including an important effect of substituents on both cyclopentadienyl and aryloxy groups for the activity. We also wish to show the results for the catalytic ethylene/1-butene copolymerization by **2b** or the $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**10**)−MAO system.

Scheme 1



Ar = $2,4,6\text{-}Me_3C_6H_2$ (**2a**), $2,6\text{-}^iPr_2C_6H_3$ (**2b**), $2\text{-}^tBu\text{-}4,6\text{-}Me_2C_6H_2$ (**2c**), $2,6\text{-}Me_2C_6H_3$ (**2d**), $4\text{-}MeC_6H_4$ (**2e**).

Results and Discussion

1. Synthesis of Various (Cyclopentadienyl)(aryloxy)titanium(IV) Complexes of the Type $Cp'Ti(OAr)X_2$ and $Cp'Ti(OAr)_2Cl$. $CpTi(OAr)Cl_2$ (**1**) or $Cp^*Ti(OAr)Cl_2$ (**2**) [Ar = $2,4,6\text{-}Me_3C_6H_2$ (**a**), $2,6\text{-}^iPr_2C_6H_3$ (**b**), $2\text{-}^tBu\text{-}4,6\text{-}Me_2C_6H_2$ (**c**), $4\text{-}MeC_6H_4$ (**e**)] could be prepared in high yields from $CpTiCl_3$ or Cp^*TiCl_3 by adding 1 equiv of the corresponding lithium phenoxides in diethyl ether (Scheme 1). These procedures were analogous to that for $Cp^*Ti(O\text{-}2,6\text{-}Me_2C_6H_3)Cl_2$[6] and highly efficient for preparing these types of complexes in high yields (84−99%). In addition, the products were almost pure in most cases after an extraction of the reaction product with toluene or Et_2O.

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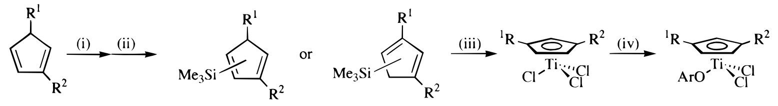
Scheme 2



(i) ^{n}BuLi/hexane or KH/THF; (ii) Me_3SiCl (excess); (iii) $TiCl_4$/ hexane; (iv) LiO-2,6-$^{i}Pr_2C_6H_3$/ Et_2O

R^1, R^2 = ^{n}Bu, H (**3b**)
R^1, R^2 = ^{t}Bu, H (**4b**)
R^1, R^2 =Me, Me (**5b**)
R^1, R^2 = ^{t}Bu, ^{t}Bu (**6b**)
Ar = 2,6-$^{i}Pr_2C_6H_3$

Complexes having other substituents in the cyclopentadienyl group such as ($^{n}BuC_5H_4$)Ti(O-2,6-$^{i}Pr_2C_6H_3$)Cl_2 (**3b**), ($^{t}BuC_5H_4$)Ti(O-2,6-$^{i}Pr_2C_6H_3$)Cl_2 (**4b**), (1,3-Me_2-C_5H_3)Ti(O-2,6-$^{i}Pr_2C_6H_3$)Cl_2 (**5b**), and (1,3-$^{t}Bu_2C_5H_3$)Ti(O-2,6-$^{i}Pr_2C_6H_3$)Cl_2 (**6b**), could also be prepared in the same manner from the trichloride analogues, Cp′$TiCl_3$, which were synthesized by the reaction of $TiCl_4$ with the corresponding Cp′$SiMe_3$ in hexane (Scheme 2). These reactions were also highly useful for preparing the corresponding complexes due to the relatively high yields in each step. KH was favorably used in place of ^{n}BuLi due to the low reactivity of 1,3-$^{t}Bu_2C_5H_4$ to prepare Cp′−metal species in high yield.

It should be noted that Cp*Ti(O-2,6-$^{i}Pr_2C_6H_3$)Me_2 (**8b**) could be prepared in relatively high yield (77%) as yellow microcrystals by the reaction of Cp*$TiMe_3$ with 1 equiv of 2,6-$^{i}Pr_2C_6H_3OH$ in Et_2O. Attempts for isolation of **8b** from **2b** by the reaction with MeMgBr, MeMgI, or MeLi were unsuccessful due to the difficulty to isolate from the reaction mixture containing **8b** and **2b**. The ^{1}H NMR spectrum of **8b** shows a resonance for the titanium−methyl protons (0.81 ppm, s, 3H) and the ^{13}C NMR spectrum shows a resonance for the methyl carbon (54.2 ppm) that we can regard as characteristic of titanium(IV)−methyl species. The results by mass spectroscopy and elemental analysis were also satisfactory for the formation of **8b**.

It should also be noted that Cp*Ti(O-2,6-$^{i}Pr_2$-C_6H_3)$(OTf)_2$ (**9b**: OTf = CF_3SO_3) could also be prepared in a moderate yield (59%) as deep brown microcrystals by the reaction of **2b** with AgOTf. The ^{13}C NMR spectrum shows a characteristic resonance for CF_3 carbons at 120.0 ppm (q, $^{1}J_{(C,F)} = 319$ Hz), whereas the other resonances are almost analogous to those for **2b** or **8b**.

It is also important to note that **1b** could be prepared quantitatively by the reaction of $CpTiCl_3$ with an excess amount of the phenol (in CH_2Cl_2 at room temperature), whereas the reaction did not take place if Cp*$TiCl_3$ was used in place of $CpTiCl_3$. On the other hand, reactions of $CpTiCl_3$ with an excess amount of 2,4,6-trimethylphenol or 2,6-diisopropylphenol under the refluxing conditions of toluene gave CpTi(O-2,4,6-$Me_3C_6H_2$)$_2$Cl (**7a**) or CpTi(O-2,6-$^{i}Pr_2C_6H_3$)$_2$Cl (**7b**) in high yields (87 and 85%, respectively), whereas the reaction of Cp*$TiCl_3$ with 2,6-$^{i}Pr_2C_6H_3OH$ under the same conditions afforded **2b** in high yield (94%).

Table 1. Selected Bond Distances (Å) and Angles (deg) for 1b, 2b, 2d, and 6b[a]

compound	**1b**	**2b**	**2d**[b]	**6b**
		Bond Distances		
Ti(1)−Cl(1)	2.262(1)	2.305(2)	2.2736(6)	2.2553(8)
Ti(1)−C(1)	2.282(8)	2.367(7)	2.329(3)	2.379(3)
Ti(1)−C(2)	2.299(5)	2.435(7)	2.341(2)	2.378(3)
Ti(1)−C(3)	2.325(5)	2.368(7)	2.398(2)	2.410(2)
Ti(1)−Cp	1.99	2.03	2.034	2.04
Ti(1)−O(1)	1.760(4)	1.772(3)	1.785(2)	1.773(2)
O(1)−C(6)	1.368(6)[c]	1.367(5)	1.366(3)	1.365(3)
		Bond Angles		
Cl(1)−Ti(1)−Cl(2)	104.23(7)	103.45(5)	103.3(2)	103.46(3)
Cl(1)−Ti(1)−O(1)	102.53(9)	99.1(2)	101.7(1)	103.62(6)
Cl(2)−Ti(1)−O(1)	102.53(9)	104.1(2)	101.7(1)	98.57(6)
Ti(1)−O(1)−C(6)	163.0(4)[c]	173.0(3)	162.3(2)	163.1(2)
Cp−Ti(1)−O(1)	117.6	120.5	120.3	119.3
Cp−Ti(1)−Cl(1)	114.1	111.1	113.8	114.3
Cp−Ti(1)−Cl(2)	114.1	116.1	113.8	115.2

[a] **1b**: CpTi(O-2,6-$^{i}Pr_2C_6H_3$)Cl_2. **2b**: Cp*Ti(O-2,6-$^{i}Pr_2C_6H_3$)Cl_2. **2d**: Cp*Ti(O-2,6-$Me_2C_6H_3$)Cl_2. **6b**: (1,3-$^{t}Bu_2C_5H_3$)Ti(O-2,6-$^{i}Pr_2$-C_6H_3)Cl_2. [b] See ref 6. [c] Ti(1)−O(1)−C(4).

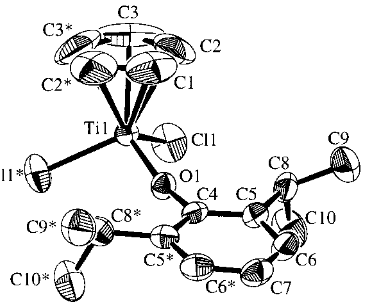


Figure 1. Crystal structure of CpTi(O-2,6-$^{i}Pr_2C_6H_3$)Cl_2 (**1b**).

2. Crystal Structure of CpTi(O-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl$_2$ (1b), Cp*Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl$_2$ (2b), (1,3-^{t}Bu$_2$C$_5$H$_3$)-Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl$_2$ (6b), and CpTi(O-2,4,6-Me$_3$-C$_6$H$_2$)$_2$Cl (7a). To explore the influence of substituents on both cyclopentadienyl and aryloxy groups, the crystal structures for **1b**, **2b**, and **6b** were determined by X-ray crystallography by using an Enraf-Nonius CAD4 (Mo Kα radiation, $\lambda = 0.710\,69$ Å) or Rigaku AFC7R (Cu Kα radiation, $\lambda = 1.541\,78$ Å) diffractometer (conditions: see Experimental Section). The selected bond lengths and bond angles for these complexes are summarized in Table 1.[8]

It is noteworthy that the bond angle of Ti−O−C (phenoxy group) for **2b** (173.0°) is significantly different from those for other complexes (**1b**, **2d**, and **6b**: 162.3−163.1°), although no significant differences are observed for other bond lengths and angles among these compounds (Table 1, and Ortep drawings: Figures 1−3). It seems likely that the Cp* ligand sterically forces the more open Ti−O−C angle, which leads to more O→Ti π donation into the titanium (Figure 1).

The crystal structure for **7a** could also be determined by using the Rigaku AFC7R (Cu Kα radiation, $\lambda = 1.541\,78$ Å) diffractometer,[8] and the selected bond angles and bond lengths are listed in Table 2 (Ortep drawing: Figure 4). It turned out that the bond angles of Ti−O−C (phenyl group) for **7a** (143.4 and 151.1°, respectively) were different from those for Cp′Ti(OAr)-Cl_2 complexes such as **1b** (163.0°), **2d** (162.3°), and **6d** (163.1°) whereas the other bond angles or bond distances were almost similar to those for other complexes. In addition, the Ti−O bond lengths for **7a** (1.819 and 1.804 Å) are longer than those for **1b**, **2b**, **2d**, or **6b** (1.760−1.785 Å). These are probably due to the steric

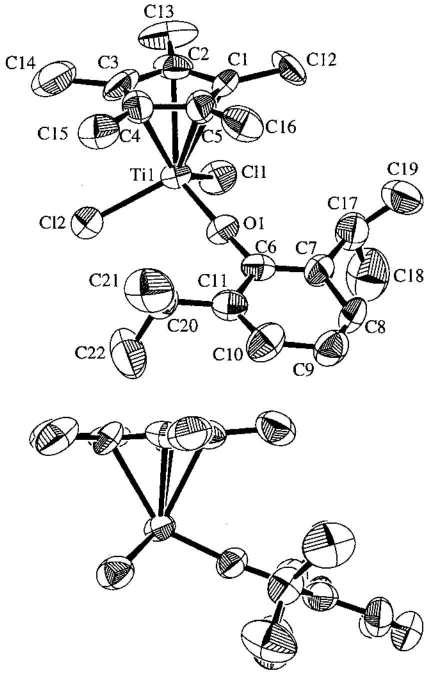


Figure 2. Crystal structure of Cp*Ti(O-2,6-$^iPr_2C_6H_3$)Cl_2 (**2b**): (top) ortep drawing of **2b**; (bottom) another view of **2b**.

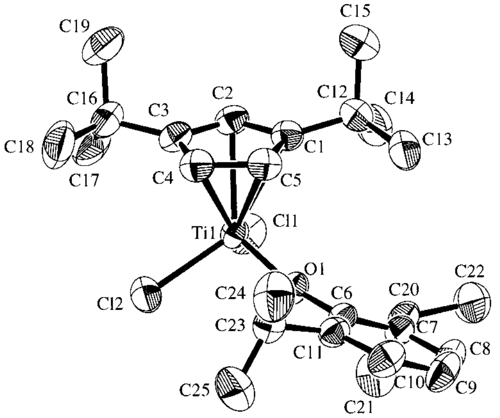


Figure 3. Crystal structure of (1,3-$^tBu_2C_5H_3$)Ti(O-2,6-$^iPr_2C_6H_3$)-Cl_2 (**6b**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for CpTi(O-2,4,6-$Me_3C_6H_2$)$_2$Cl (7a)

Bond Distances			
Ti(1)−Cl(1)	2.295(1)	Ti(1)−C(1)	2.336(7)
Ti(1)−C(2)	2.352(7)	Ti(1)−C(3)	2.343(6)
Ti(1)−Cp	2.03	Ti(1)−O(1)	1.819(3)
Ti(1)−O(1)	1.804(3)	O(1)−C(6)	1.373(5)
O(1)−C(12)	1.371(5)		
Bond Angles			
O(1)−Ti(1)−O(2)	104.6(2)	Cl(1)−Ti(1)−O(1)	104.5(1)
Cl(1)−Ti(1)−O(2)	102.4(1)	Ti(1)−O(1)−C(6)	143.4(3)
Ti(1)−O(2)−C(12)	151.3(3)	Cp−Ti(1)−O(1)	114.5
Cp−Ti(1)−O(2)	115.6	Cp−Ti(1)−Cl(1)	113.8

influence of two bulky phenoxy groups containing methyl groups in the 2,6-position.

3. Polymerization of Ethylene by the Nonbridged (Cyclopentadienyl)(aryloxy)titanium(IV) Complexes−Cocatalyst System. It should be noted that **2b** showed a remarkable catalytic activity for ethylene polymerization in the presence of a cocatalyst such as MAO or $Al^iBu_3/Ph_3CB(C_6F_5)_4$ (Table 3), and the acitivity was higher when $Al^iBu_3/Ph_3CB(C_6F_5)_4$ was used as a cocatalyst. The use of dry-MAO (d-MAO), which was prepared by removing toluene and an excess amount of $AlMe_3$ and used as a white solid,[9] in place of ordinary MAO (toluene solution) was found to be effective to increase the molecular weight of the resultant polymer with narrower polydispersities (runs 1 and 2). The increase in the M_n value is probably due to the decraese for the degree of chain transfer reaction by $AlMe_3$ in the polymerization.[10] **8b** and **9b** were effective as catalyst precursors: **2b** and **9b** with $Al^iBu_3/Ph_3CB(C_6F_5)_4$ showed the highest activities for ethylene polymerization (runs 3 and 7, respectively). The broad polydispersities were observed for the ethylene homopolymerization, whereas the narrow polydispersities were observed for polymerization of propylene and 1-hexene (see below). We believe at this stage that this is probably a result of polyethylene precipitation during the polymerization since these were performed at 60 °C.

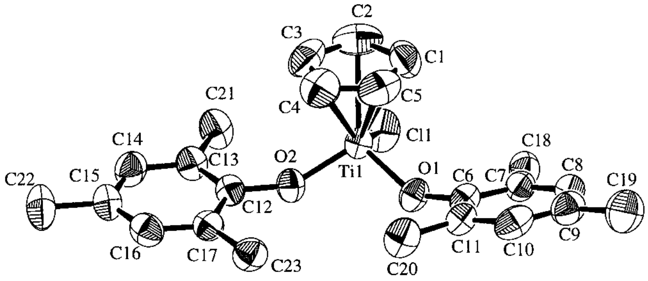


Figure 4. Crystal structure of CpTi(O-2,4,6-$Me_3C_6H_2$)$_2$Cl (**7a**).

Table 3. Polymerization of Ethylene by Cp*Ti(O-2,6-$^iPr_2C_6H_3$)X_2 [X = Cl (2b), Me (8b), OTf (9b)]−Cocatalyst Systems[a]

run no.	cat. (amt, μmol)	cocatalyst	Al/Ti[b]	polymer yield (g)	activity[c]	10^{-4} M_n[d]	M_w/M_n[d]
1	**2b** (4.6)	MAO[e]	1000	5.5	1200	2.77	14.8
2	**2b** (4.2)	d-MAO[f]	2000	5.2	1240	13.8	4.7[g]
3	**2b** (6.5)	Al^iBu_3/B[h]	500	14.4	2220	9.17	5.0[g]
4	**8b** (8.5)	d-MAO[f]	1000	6.1	718	15.1	6.0[g]
5	**8b** (3.1)	Al^iBu_3/B[h]	500	4.6	1480		
6	**9b** (3.7)	d-MAO[f]	1000	2.9	784		
7	**9b** (3.9)	Al^iBu_3/B[h]	500	8.2	2100	8.23	5.2[g]

[a] Reaction conditions: ethylene 4 kgf/cm^2, toluene 300 mL, 60 °C, 1 h. [b] Molar ratio of Al/Ti. [c] Polymerization activity [kg of polymer/(mol of Ti·h)]. [d] GPC data in *o*-dichlorobenzene vs polystyrene standard. [e] MAO 9.5 wt % (Al) in toluene. [f] MAO (toluene solution) was evaporated in vacuo and was used as a white solid. [g] Bimodal peaks were observed on GPC traces. [h] B = $Ph_3CB(C_6F_5)_4$, $Ph_3CB(C_6F_5)_4$/Ti = 1 (molar ratio).

$Cp^*_2TiCl_2$ and (2,6-$^iPr_2C_6H_3O$)$_2TiCl_2$ showed low catalytic activities for ethylene polymerization under the same conditions (Table 4, runs 13 and 14, respectively). These results strongly suggest that the observed polymerization activity by **2b** is not due to $Cp^*_2TiCl_2$ or (2,6-$^iPr_2C_6H_3O$)$_2TiCl_2$, which might be formed by the disproportionation in the catalyst solution. Since the activities by **2b**, **8b**, and by **9b** were almost the same, it is thus suggested that the same active species (such as Cp*Ti(O-2,6-$^iPr_2C_6H_3$)R^+, R = alkyl group) plays a role in this catalysis.

Ethylene polymerization by the other titanium(IV) complexes such as **1b**, **2a**, **2c**, **2d**, and **3**−**6b** were also examined to explore the effect of substituents on both cyclopentadienyl and aryloxy groups for the catalytic activity. The effect of substituents on the cyclopentadienyl group on the polymerization activity with Cp′Ti(O-2,6-$^iPr_2C_6H_3$)Cl_2−$Al^iBu_3/Ph_3CB(C_6F_5)_4$ catalysts increased in the order (Table 4) Cp* (**2b**: 2220 kg-PE/mol-Ti·h) ≫ 1,3-$^tBu_2C_5H_3$ (**6b**: 653) > $^nBuC_5H_4$ (**3b**:

Table 4. Polymerization of Ethylene by the $Cp'Ti(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl_2$ (Cp′ = Cyclopentadienyl)−Cocatalyst System[a]

run no.	complexes (amt, μmol)	cocatalyst	polymer yield (g)	activity[b]	10^{-4} M_n[c]	M_w/M_n[c]
2	**2b** (4.2)	d-MAO[d]	5.2	1240	13.8	4.7[e]
3	**2b** (6.5)	Al^iBu_3/B[f]	14.4	2220	9.17	5.0[e]
8	**1b** (18.3)	Al^iBu_3/B[f]	1.4	77		
9	**3b** (8.6)	Al^iBu_3/B[f]	2.6	302		
10	**4b** (15.1)	Al^iBu_3/B[f]	3.9	258	2.85	2.1
11	**5b** (24.2)	Al^iBu_3/B[f]	5.2	215	0.75	2.5
12	**6b** (7.2)	Al^iBu_3/B[f]	4.7	653	9.54	6.8[e]
13	$Cp^*_2TiCl_2$ (35.5)	Al^iBu_3/B[f]	2.5	70		
14	$(2,6\text{-}{}^iPr_2C_6H_3O)_2\text{-}{}^iTiCl_2$ (24.5)	Al^iBu_3/B[f]	1.4	57		

[a] Reaction conditions: ethylene 4 kgf/cm^2, 60 °C, 1 h, toluene 300 mL. [b] Polymerization activity [kg of PE/(mol of Ti•h)]. [c] GPC data in *o*-dichlorobenzene vs polystyrene standard. [d] d-MAO (see Table 3) was used, Al/Ti = 2000 (molar ratio). [e] Bimodal peaks were observed on GPC traces. [f] B = $Ph_3CB(C_6F_5)_4$, $Ph_3CB(C_6F_5)_4$/Al/Ti = 500, $Ph_3CB(C_6F_5)_4$/Ti = 1 (molar ratio).

Table 5. Polymerization of Ethylene by the $Cp^*Ti(OAr)Cl_2$−, and $Cp^*Ti(O^iPr)Me_2$−Cocatalyst Systems (OAr = Aryloxy Group)[a]

run no.	complexes (amt, μmol)	cocatalyst	polymer yield (g)	activity[b]	10^{-4} M_n[c]	M_w/M_n[c]
2	**2b** (4.2)	d-MAO[d]	5.2	1240	13.8	4.7[e]
3	**2b** (6.5)	Al^iBu_3/B[f]	14.4	2220	9.17	5.0[e]
15	**2d** (4.0)	d-MAO[d]	4.0	1000	27.4	4.5[e]
16	**2d** (7.2)	Al^iBu_3/B[f]	11.3	1570	4.99	3.4[e]
17	**2a** (8.4)	d-MAO[d]	3.1	369		
18	**2c** (13.0)	d-MAO[d]	5.8	446		
19	**2e** (13.0)	d-MAO[d]	0.33	25		
20	$Cp^*Ti(O^iPr)Me_2$ (55.1)	d-MAO[d]	2.4	44		

[a] Reaction conditions: ethylene 4 kgf/cm^2, 60 °C, 1 h, toluene 300 mL. [b] Polymerization activity [kg of PE/(mol of Ti•h)]. [c] GPC data in *o*-dichlorobenzene vs polystyrene standard. [d] d-MAO (see Table 3) was used, Al/Ti (molar ratio) = 1000 (run 3: Al/Ti = 2000). [e] Bimodal peaks were observed on GPC trace. [f] B = $Ph_3CB(C_6F_5)_4$, Al/Ti = 500, $Ph_3CB(C_6F_5)_4$/Ti = 1 (molar ratio).

302), $^tBuC_5H_4$ (**4b**: 258), 1,3-$Me_2C_5H_3$ (**5b**: 215) ≫ C_5H_5 (**1b**: 77). A similar observation was reported for polymerization of styrene with a series of $Cp'Ti(OMe)_3$ complexes and mentioned that the stabilization of the active site by more electron-releasing substituents is important for the high activity.[11] The effect of cyclopentadienyl substituents in this catalysis can thus be interpreted by the same reason.

The polymerization activity by the $Cp^*Ti(OAr)Cl_2$ (**2**)−d-MAO system increased in the order (Table 5) OAr = 2,6-$^iPr_2C_6H_3$ (**2b**: 1240 kg-PE/mol-Ti•h) > O-2,6-$Me_2C_6H_3$ (**2d**: 1000) > O-2-^{t}Bu-4,6-$Me_2C_6H_2$ (**2c**: 446) > O-2,4,6-$Me_3C_6H_2$ (**2a**: 369) ≫ O-4-MeC_6H_4 (**2e**: 25). In addition, $Cp^*Ti(O^iPr)Me_2$ showed low catalytic activity (run 20) under the same conditions. These results strongly suggest that the bulk of phenoxy ligand containing substituents in the 2,6-position is very important for the high activity.[12] These are, we believe, due to the steric effect, which would stabilize the catalytically active species under the polymerization conditions in the presence of cocatalyst. It is thus clear from these results that both Cp* and 2,6-diisopropylphenoxy groups are indispensable for the high catalytic activity.

As evident from the crystal structure (Table 1), the Cp* ligand in **2b** sterically forces the more open Ti−O−C (phenoxy group) angle. This suggests that the higher activity by **2b** is due to this unique bond angle, which can increase the stability of catalytically active species by more O→Ti π donation into the titanium. This is an explanation similar to that for styrene polymerization by $Cp'TiCl_3$, where the more electron-donating Cp* (as compared to Cp, BuCp, Me_2Cp, $^tBu_2Cp$) stabilizes the active species and leads to higher activity.[11]

Table 6. Polymerization of Ethylene by the $CpTi(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl_2$ (1b)−, $CpTi(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2Cl$ (7b)−, or $CpTi(O\text{-}2,4,6\text{-}Me_3C_6H_2)_2Cl$ (7a)−Cocatalyst System[a]

run no.	complex (μmol)	cocatalyst	polymer yield (g)	activity[b]	10^{-4} M_n[c]	M_w/M_n[c]
8	**1b** (18.3)	Al^iBu_3/B[d]	1.4	77		
21	**1b** (21.0)	d-MAO[e]	2.2	104	18.1	3.3
22	**7b** (18.1)	MAO[f]	1.4	77	23.0	2.3
23	**7b** (10.4)	d-MAO[e]	3.2	441	18.6	3.8
24	**7a** (29.1)	MAO[f]	1.3	45		
25	**7a** (12.2)	d-MAO[e]	5.4	442	25.7	2.7
26	$CpTiCl_3$ (18.7)	Al^iBu_3/B[d]	trace	trace		
14	$(2,6\text{-}{}^iPr_2C_6H_3O)_2\text{-}TiCl_2$ (24.5)	Al^iBu_3/B[d]	1.4	57		

[a] Reaction conditions: ethylene 4 kgf/cm^2, toluene 300 mL, 60 °C, 1 h. [b] Polymerization activity [kg of PE/mol of Ti•h)]. [c] GPC data in *o*-dichlorobenzene vs polystyrene standard. [d] B = $Ph_3CB(C_6F_5)_4$, Al/Ti = 500, $Ph_3CB(C_6F_5)_4$/Ti = 1 (molar ratio). [e] d-MAO (see Table 3) was used, Al/Ti = 1000 (molar ratio). [f] MAO 9.5 wt % (Al) toluene solution, Al/Ti = 1000.

It should also be noted that **7a** and **7b** showed moderate catalytic activities for ethylene polymerization when the d-MAO was used as a cocatalyst (Table 6). The activity by $CpTi(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)_nCl_{3-n}$ ($n = 1-3$) increased in the order **7b** [441 kg of PE/(mol of Ti•h)] > **1b** (104) ≫ $CpTiCl_3$ (trace).[13] It has also been reported that $(2,6\text{-}{}^tBu_2C_6H_3O)_3ZrCl$ was an effective catalyst precursor for ethylene polymerization to give polymers with narrower polydispersities than those by bis(phenoxy) complexes,[14] and the effect of the steric bulk of phenoxy ligand was suggested. Since it also does not seem likely that shorter Ti−O−C (phenyl) bond angles (compared with that in **1b)** or longer Ti−O lengths (compared with that in **1b**) in **7a** increase the stability of catalytically active species by the O→Ti π donation, as shown in **2b**, it is thus suggested that the effect of the phenoxy ligand on the activity with a series of $CpTi(OAr)_nCl_{3-n}$ complexes ($n = 2 > 1 \gg 0$) is probably due to the stabilization of the catalytically active species by the bulky phenoxy group under these polymerization conditions.

4. Copolymerization of Ethylene with α-Olefin by the $Cp^*Ti(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl_2$ (2b)−Cocatalyst System. It is noteworthy that **2b** is also an effective catalyst precursor for copolymerization of ethylene/1-butene and ethylene/1-hexene in the presence of d-MAO as a cocatalyst (Table 7). The activity in ethylene/1-hexene copolymerization was higher than that in homopolymerization of ethylene under the same conditions (runs 1 and 33). Higher polymerization activities were observed on ethylene/1-butene copolymerization and the activity was further enhanced upon the increase of 1-butene contents (runs 27 and 30). The molecular weight distributions for the resultant copolymers were narrower than those for ethylene homopolymer.

The catalytic copolymerization by the $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**10**)−MAO system were also performed to compare the reactivity under the same conditions, and the use of d-MAO was effective in this catalysis not only to obtain copolymer with a narrower molecular weight distribution but also to increase the molecular weight of the resultant copolymer (runs 31

Table 7. Copolymerization of Ethylene with α-Olefin by the Cp*Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl$_2$ (2b)− or [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (10)−d-MAO System[a]

run no.	complex (amt, μmol)	cocatalyst (Al/Ti)[b]	α-olefin	C$_4'$ (g)	temp. (°C)	polymer yield (g)	activity[c]	[α-olefin][d] (mol %)	$10^{-4}M_n$[e]	M_w/M_n[e]
2	**2b** (4.2)	d-MAO[f] (2000)			60	5.2	1240		13.8	4.7
27	**2b** (2.3)	d-MAO[f] (1000)	1-butene	10	70	16.8	7240	27.3	3.82	2.2
28	**2b** (1.2)	d-MAO[f] (1000)	1-butene	10	70	10.3	8880	25.8	3.81	2.3
29	**2b** (1.2)	d-MAO[f] (2000)	1-butene	10	70	11.1	9570	26.8	4.23	2.0
30	**2b** (2.1)	d-MAO[f] (1000)	1-butene	20	70	19.5	9290	37.5	8.37	2.06
31	**10** (2.7)	d-MAO[f] (1000)	1-butene	10	70	17.8	6550	32.4	5.75	3.4
32	**10** (2.7)	MAO[g] (1000)	1-butene	10	70	17.4	6440		3.14	6.4
1	**2b** (4.6)	MAO[g] (1000)			60	5.5	1200		2.77	14.8
33	**2b** (2.3)	MAO[g] (1000)	1-hexene[h]		60	4.7	2040	15.4[i]	2.71	1.9

[a] Reaction conditions: ethylene 6 kgf/cm^2 (runs 1, 2, and 33: 4 kgf/cm^2), toluene 200 mL (runs 1, 2 and 33: 300 mL), 1 h. [b] Molar ratio of Al/Ti. [c] Polymerization activity [kg of polymer/(mol of Ti·h)]. [d] α-Olefin in copolymers (mol %) determined by ^{13}C NMR spectra.[16] [e] GPC data in THF (run 30) or in *o*-dichlorobenzene (runs 1, 2, 27−29, and 31−33) vs polystyrene standard. [f] d-MAO (see Table 3) was used. [g] MAO 9.5 wt % (Al) in toluene. [h] 1-Hexene 10 mL. [i] η 0.81 dL/g.

Table 8. Monomer Sequence Distribution of Ethylene/1-Butene Copolymers Prepared by 2b− or 10−d-MAO Catalysts[a]

			triad sequence distribution[c] (%)								
run no.	complex	[1-butene][b] mol %	EEE	BEE + EEB	BEB	EBE	EBB + BBE	BBB	n_E[d]	n_B[e]	r_Er_B[f]
28	**2b**	25.8	37.3	30.3	6.6	20.8	4.8	0.2	3.4	1.1	0.27
29	**2b**	26.8	35.8	30.3	7.1	21.5	5.3	trace	3.3	1.1	0.25
30	**2b**	37.5	20.0	30.0	12.5	23.5	11.3	2.7	2.3	1.3	0.36
31	**10**	32.4	40.3	22.0	5.3	11.8	12.8	7.8	4.1	1.8	2.45

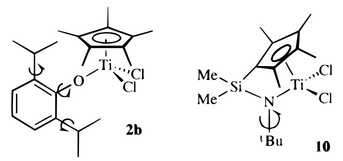
[a] Detailed polymerization conditions, see Table 7. [b] 1-Butene in copolymer. [c] Determined by ^{13}C NMR spectra.[16] [d] Average sequence number n_E = [EEE + (BEE + EEB) + BEB]/[BEB + (BEE + EEB)/2]. [e] Average sequence number n_B = [BBB + (BBE + EBB) + EBE]/[EBE + (BBE + EBB)/2]. [f] r_Er_B = 4[EE][BB]/[EB]^2, [EE] = [EEE] + [EEB + BEE]/2, [EB] = [EEB + BEE]/2 + [BEB] + [EBE] + [BBE + EBB]/2, [BB] = [BBB] + [BBE + EBB]/2.

and 32). It is important to note that the catalytic activities between **2b** and **10** (cocatalyst: d-MAO) are almost the same under the same conditions,[15] and we may say that **2b** is also an effective catalyst for ethylene/α-olefin copolymerization from the industrial viewpoints.

The structure and monomer sequence distribution of poly(ethylene-*co*-1-butene) prepared by **2b** were studied by ^{13}C NMR,[16] and the results are listed in Table 8. The same analysis of the copolymer prepared by **10** was also examined for the reference. The resonance derived from regioirregularly inserted 1-butene could not be detected in the ^{13}C NMR spectra of the copolymer prepared with **2b**.[17] This result suggests that the insertion of 1-butene proceeds selectively (same manner of 1,2-insertion or 2,1-insertion).

The triad sequence distributions in these copolymers showed that contents of EEE and BBB sequences in these copolymers were different between **2b** and **10** under the same conditions.[18] Noteworthy, the significant differences can also be seen for their diads as well as average sequence length (n_E and n_B) values in these catalyses. In addition, r_Er_B values (r_E and r_B are monomer reactive ratios of ethylene and 1-butene) for copolymers prepared by **2b** (0.25−0.36) were significantly different from that by **10** (2.45), and this result should be very interesting to emphasize the original nature of this catalysis. These differences are probably due to the difference of structure or an electronic nature of the catalytically active species. One possible explanation is due to rather rigid structure of **10** than **2b** that would affect the r_E and r_B (Chart 1). We believe that this information should be very important for the design of a suitable catalyst. The next step for our project is thus to explore a precise relationship between the above values and various factors such as catalyst structure, cocatalyst, comonomer used, etc., and this project is now in progress.

Chart 1



5. Polymerization of α-Olefin by the (C$_5$Me$_5$)Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl$_2$ (2b)−Cocatalyst System.

As shown in Table 9, **2b** shows moderate catalytic activity for 1-hexene polymerization in the presence of MAO (9.5 wt % (Al) toluene solution). The effect of phenoxy ligand is remarkable, as we can see by the results with **2b** (run 34) and Cp*TiCl$_3$ (run 36). The use of Cp* ligand is also important because the activity by **2b** was higher than that by **5b** (run 35). **2b** was also found to be an effective catalyst precursor for propylene polymerization although the polymerization activity was somewhat lower than that for ethylene.[19]

It is important to note that the activity as well as the molecular weight of the resultant poly(1-hexene) increased (Table 9, runs 40−44) when d-MAO was used as a cocatalyst.[9] The use of d-MAO should also be a great advantage in this catalysis to obtain the polymers having unimodal molecular weight distributions. It seems likely that the catalytically active sepcies can be more stabilized by removing AlMe$_3$, which would attack the aryloxy group to give the low-active species or decomposition.[10,20] The increase in the M_w value is probably due to the decrease for the degree of chain transfer reaction by AlMe$_3$.

These catalytic reactions proceeded at significant rates, especially at the initial stage and then decreased gradually, probably due to the decomposition of the active species or due to the increased viscosity in the reaction mixture (Figure 5). The turnover number (TON) of 10 320 could be attained on a larger reaction scale experiment (run 42, Table 9). The resultant poly-

Table 9. Polymerization of 1-Hexene by the Cp*Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl$_2$ (2b)−MAO Cocatalyst System[a]

run no.	complex (amt, μmol)	cocat.	time	polymer yield (g)	activity[b]	TON[c]	$10^{-4}M_w$[d]	M_w/M_n[d]
34	**2b** (10)	MAO	1 h	1.79	179	2130	17.4	1.87
							0.07	1.66[e]
35	**5b** (10)	MAO	1 h	0.30	30	357	2.06	1.38
							0.08	1.37[e]
36	Cp*TiCl$_3$ (15)	MAO	1 h	0.45	30	357	0.09	1.52
37	**2b** (10)[f]	MAO	15 min	1.282	513	1530	11.0	1.67
							0.07	1.67
38	**2b** (10)[f]	MAO	30 min	1.654	331	1970		
39	**2b** (10)[f]	MAO	1 h	2.139	214	2550	10.4	1.70
							0.06	1.65
40	**2b** (2.0)	d-MAO[g]	10 min	0.73	2190	4350	26.0	2.05
41	**2b** (2.0)	d-MAO[g]	30 min	1.07	1070	6370	29.9	2.04
42	**2b** (2.0)	d-MAO[g]	1 h	1.19	595	7080	31.5	2.26
43	**2b** (3.0)	d-MAO[g]	1 h	1.90	633	7540		
44	**2b** (3.0)[h]	d-MAO[g]	2 h	2.60	433	10320	29.9	2.26

[a] Reaction conditions: 1-hexene 15 g, cat. 5 μmol/g of toluene, MAO (9.5 wt % (Al) in toluene), Al/Ti = 1000 (molar ratio). [b] Polymerization activity [kg of polymer/(mol of Ti·h)]. [c] TON (turnover number) = (molar amount of C$_6'$ reacted)/(mol of Ti). [d] GPC data in THF vs polystyrene standard. [e] A peak with low M_w was observed on GPC trace. [f] **2b** and MAO was premixed at 0 °C for 10 min. [g] d-MAO (see Table 3) was used. [h] 1-Hexene 30 g, Al/Ti = 500 (molar ratio).

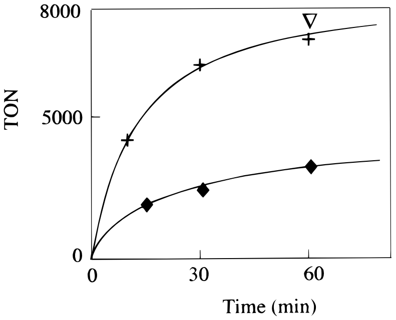


Figure 5. Time course for polymerization of 1-hexene by the Cp*Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl$_2$ (**2b**)−MAO catalyst system. Reaction conditions: 1-hexene 15 g, room temperature, MAO (9.5 wt % (Al) toluene solution) or d-MAO, Al/Ti = 1000 (molar ratio), catalyst 5 μmol/g of toluene. Key: (◆) 10 μmol (MAO toluene solution); (+) 2 μmol (MAO solid); (▽) 3 μmol (MAO solid). TON (turnover number) = (molar amount of 1-hexene reacted)/(mol of Ti).

(1-hexene) was atactic polymer [experimental pentad distribution of the polymer (run 40), mmmm:(mmmr + rmmr + mmrr):(mmrm + rmrr):(rmrm + rrrr):mrrr: mrrm = 0.135:0.339:0.238:0.200:0.071:0.018, respectively],[21] while 2,1- or other insertion units could not be found.

Experimental Section

General Procedure. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques unless otherwise specified. All chemicals used were reagent grade and were purified by the standard purification procedures. Tetrahydrofuran, diethyl ether, hexane, and dichloromethane were purchased from Kanto Chemical Co., Ltd. as anhydrous grade and stored in the presence of molecular sieves. Toluene for synthesis of various complexes was purchased as the same grade and stored over sodium/potassium alloy. CpTiCl$_3$, Cp*TiCl$_3$, Cp*TiMe$_3$, and Cp*$_2$TiCl$_2$ were purchased from Strem Chemical Co., Ltd. [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$, 1,3-^{t}Bu$_2$C$_5$H$_4$, 1,3-Me$_2$C$_5$H$_4$, ^{t}BuC$_5$H$_5$, and ^{n}BuC$_5$H$_5$ were purchased from Kanto Chemical Co., Ltd. Cp*Ti(O^{i}Pr)Me$_2$[5] and Cp*Ti(O-2,6-Me$_2$C$_6$H$_3$)Cl$_2$[6] were prepared according to the previous reports. (2,6-^{i}Pr$_2$C$_6$H$_3$O)$_2$TiCl$_2$ was also prepared according to the previous report (e.g., EP 241560). All deuterated NMR solvents were stored over molecular sieves in a drybox.

All ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 spectrometer (270.2 MHz, ^{1}H). All chemical shifts are given in ppm and are referenced to Me$_4$Si. Obvious multiplicities and routine coupling constants are usually not listed. All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. The chemical shift values and coupling constants of the titanium(IV) complexes prepared in this paper are listed in Table 10. All ^{13}C NMR spectra for the ethylene/1-butene and ethylene/1-hexene copolymers were performed by using a Bruker AM-400 spectrometer (100.614 MHz, ^{13}C: invgate method, *o*-dichlorobenzene-d_4) at 135 °C.

All the mass spectra (negative) were recorded by using a JEOL JMS-700 double focusing mass spectrometer equipped with a frit-CI interface. The sample solutions in dehydrated toluene were introduced into the ion source of the mass spectrometer at the rate of 2−5 μL/min. Microanalysis (C, H, N) for the complexes prepared were performed on a Perkin-Elmer PE2400 microanalyzer.

Synthesis of (C$_5$H$_5$)Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl$_2$ (1b). Method 1. LiO-2,6-^{i}Pr$_2$C$_6$H$_3$ (840 mg, 4.56 mmol) was added in one portion to a Et$_2$O solution (30 mL) containing CpTiCl$_3$ (1.00 g, 4.56 mmol) at −25 °C. The reaction mixture was warmed slowly to room temperature and was stirred for 10 h. The mixture was then filtered through Celite, and the filter cake was washed with Et$_2$O (15 mL × 2). The combined filtrate and 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$_2$Cl$_2$ layered by a small amount of Et$_2$O. The chilled (−30 °C) solution gave red microcrystals (1.40 g). The microcrystals were pure enough by ^{1}H and ^{13}C NMR. Yield: 85%. The sample for the X-ray crystallography was further recrystallized from Et$_2$O (−25 °C).

Method 2. HO-2,6-^{i}Pr$_2$C$_6$H$_3$ (2.52 g, 14.1 mmol) was added in small portions to a CH$_2$Cl$_2$ solution (30 mL) containing CpTiCl$_3$ (1.03 g, 4.70 mmol) at −25 °C. The reaction mixture was warmed slowly to room temperature and was stirred for 10 h. The solvent was then removed in vacuo, and the resultant solid was extracted with toluene. The solution was taken to dryness under reduced pressure to give a red solid. The solid containing **1b** was recrystallized with a minimum amount of Et$_2$O (−25 °C, first crop 1.0 g). The mother liquor was concentrated, and the chilled solution gave a second crop (700 mg). Total yield: 1.70 g (>99%). MS: calcd for C$_{17}$H$_{22}$Cl$_2$OTi, 361.13; found (M$^-$), 360.1. Anal. Calcd: C, 56.54; H, 6.14. Found: C, 56.86; H, 6.19.

Synthesis of Cp*Ti(O-2,4,6-Me$_3$C$_6$H$_2$)Cl$_2$ (2a). Synthesis of **2a** was carried out by the same procedure as that in **1b** (method 1) except that LiO-2,4,6-Me$_3$C$_6$H$_2$ (505 mg, 3.52 mmol) and Cp*TiCl$_3$ (1.02 g, 3.52 mmol) in place of LiO-2,6-^{i}Pr$_2$C$_6$H$_3$ and CpTiCl$_3$ and that toluene (20 mL × 2) in place of Et$_2$O was used to extract the product. Yield: 1.32 g (96.4%). The resultant red solid was further purified as red microcrystals by recrystallization from CH$_2$Cl$_2$ layered by *n*-hexane at −25

Table 10. ^{1}H and ^{13}C NMR Data for Various Nonbridged (Cyclopentadienyl)(aryloxy)titanium(IV) Complexes (Solvent = C_6D_6)

complexes	^{1}H NMR (δ in ppm)	^{13}C NMR (δ in ppm)
$CpTi(O\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_2$ (**1b**)	1.25 (d, 12H, $J = 6.9$ Hz, $(CH_3)_2CH-$), 3.43 (m, 2H, $(CH_3)_2CH-$), 6.12 (s, 5H, C_5H_5), 6.94−7.06 (m, 3H, C_6H_3)	23.7, 27.2, 120.4, 123.8, 123.8, 124.9, 138.5, 164.8
$Cp^*Ti(O\text{-}2,4,6\text{-}Me_3C_6H_2)Cl_2$ (**2a**)	1.94 (s, 15H, $C_5(CH_3)_5$), 2.15 (s, 3H, $CH_3C_6H_2$), 2.32 (s, 6H, $CH_3C_6H_2$), 6.66 (br s, 2H, C_6H_2)	12.8, 17.3, 20.8, 128.6, 129.3, 132.0, 132.3, 160.7
$Cp^*Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_2$ (**2b**)	1.31 (d, 12H, $J = 6.9$, $(CH_3)_2CH-$), 1.94 (s, 15H, $C_5(CH_3)_5$), 3.44 (m, 2H, $(CH_3)_2CH-$), 6.99−7.11 (m, 3H, C_6H_3)	12.7, 24.2, 26.9, 123.6, 124.0, 132.0, 139.6, 159.8
$Cp^*Ti(O\text{-}2\text{-}^tBu\text{-}4,6\text{-}Me_2C_6H_2)Cl_2$ (**2c**)	1.54 (s, 9H, $(CH_3)_3C-$), 1.97 (s, 15H, $C_5(CH_3)_5$), 2.12 (s, 3H, $CH_3C_6H_2$), 2.41 (s, 3H, $CH_3C_6H_2$), 6.75 (m, 1H, C_6H_2), 7.06 (m or d, 1H, C_6H_2)	13.2, 19.1, 21.1, 31.0, 35.3, 125.6, 129.9, 131.0, 132.2, 132.6, 139.3, 161.9
$Cp^*Ti(O\text{-}4\text{-}MeC_6H_4)Cl_2$ (**2e**)	1.98 (s, 15H, $C_5(CH_3)_5$), 2.10 (s, 3H, $CH_3C_6H_4$), 6.58−6.96 (m, 4H, C_6H_4)	12.8, 20.8, 119.6, 130.0, 132.4, 132.6, 163.6
$(^nBuC_5H_4)Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_2$ (**3b**)	0.82 (t, 3H, $J = 7.6$, CH_3CH_2-), 1.12−1.42 (m, 4H, C_4H_9), 1.27 (d, 12H, $(CH_3)_2CH-$), 2.62 (t, 2H, $J = 3.1$, C_4H_9), 3.42−3.57 (m, 2H, $(CH_3)_2CH-$), 6.08 (t, 2H, $J = 2.2$, $^nBuC_5H_4$), 6.15 (t, 2H, $J = 2.7$, $^nBuC_5H_4$), 6.96−7.09 (m, 3H, C_6H_3)	13.8, 22.6, 23.8, 27.2, 30.8, 32.3, 120.0, 120.3, 123.7, 124.8, 138.6, 141.6, 164.4
$(^tBuC_5H_4)Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_2$ (**4b**)	1.25 (s, 9H, $(CH_3)_3C-$), 1.27 (d, 12H, $J = 6.2$, $(CH_3)_2CH-$), 3.51 (m, 2H, $(CH_3)_2CH-$), 5.90 (t, 2H, $J = 3.1$, $^tBuC_5H_4$), 6.48 (t, 2H, $J = 3.1$, $^tBuC_5H_4$), 6.95−7.10 (m, 3H, C_6H_3)	23.8, 27.2, 30.8, 33.9, 118.9, 119.0, 123.8, 124.9, 138.6, 150.8, 164.8
$(1,3\text{-}Me_2C_5H_3)Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_2$ (**5b**)	1.23 (d, 12H, $J = 6.9$, $(CH_3)_2CH-$), 2.05 (s, 6H, $(CH_3)_2C_5H_3$), 3.43 (m, 2H, $(CH_3)_2CH-$), 5.83 (d, 2H, $J = 2.3$, $(CH_3)_2C_5H_3$), 5.91 (m, 1H, $(CH_3)_2C_5H_3$), 6.90−7.13 (m, 3H, C_6H_3)	16.4, 23.8, 27.1, 120.2, 122.1, 123.7, 124.6, 136.4, 138.8, 163.4
$(1,3\text{-}^tBu_2C_5H_3)Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_2$ (**6b**)	1.24 (s, 18H, $(CH_3)_3C-$), 1.33 (d, 12H, $J = 6.2$, $(CH_3)_2CH-$), 3.74 (m, 2H, $(CH_3)_2CH-$), 6.33 (d, 2H, $J = 2.4$, $^tBu_2C_5H_3$), 6.92−7.08 (m, 4H, C_6H_3 and $^tBu_2C_5H_3$)	24.2, 27.1, 30.1, 34.4, 115.3, 119.3, 123.9, 124.6, 139.6, 151.1, 163.8
$CpTi(O\text{-}2,4,6\text{-}Me_3C_6H_3)_2Cl$ (**7a**)	2.19 (s, 6H, $4\text{-}CH_3C_6H_2Me_2$), 2.36 (s, 12H, $2,6\text{-}(CH_3)_2C_6H_2Me$), 6.11 (s, 5H, C_5H_5), 6.73 (br s, 4H, C_6H_2)	18.2, 20.7, 118.7, 126.8, 129.4, 131.7, 165.0
$CpTi(O\text{-}2,6\text{-}^iPr_2C_6H_3)_2Cl$ (**7b**)	1.25 (d, 24H, $J = 6.9$, $(CH_3)_2CH-$), 3.43 (m, 4H, $(CH_3)_2CH-$), 6.12 (s, 5H, C_5H_5), 6.94−7.06 (m, 6H, C_6H_3)	23.7, 27.1, 120.5, 123.8, 125.0, 138.5, 164.8
$Cp^*Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)Me_2$ (**8b**)	0.81 (s, 6H, $TiCH_3$), 1.37 (d, 6H, $J = 7$, $(CH_3)_2CH-$), 1.82 (s, 15H, $C_5(CH_3)_5$), 3.31 (m, 2H, $(CH_3)_2CH-$), 7.09 (t, 1H, $J = 9$, C_6H_3), 7.23 (s, 2H, C_6H_3)	11.4, 24.0, 27.0, 54.2, 121.8, 122.3, 123.3, 138.4, 158.8
$Cp^*Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)(CF_3SO_3)_2$ (**9b**)	1.48 (d, 6H, $J = 6.6$, $(CH_3)_2CH-$), 2.07 (s, 15H, $C_5(CH_3)_5$), 3.38 (m, 2H, $(CH_3)_2CH-$), 7.17 (s, 2H, C_6H_3), 7.37 (br s, 1H, C_6H_3)	12.2, 27.4, 24.3, 24.6, 120.0, 124.2 ($^2J_{(C,F)} = 319$ Hz), 126.4, 139.1, 140.3, 160.1

°C. MS: calcd for $C_{19}H_{26}Cl_2OTi$, 389.18; found (M^-), 388.46. Anal. Calcd: C, 58.63; H, 6.73. Found: C, 58.60; H, 6.80.

Synthesis of $Cp^*Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_2$ (2b). Method 1. Synthesis of **2b** was carried out by the same procedure as that in **2a** except that Cp^*TiCl_3 (1.55 g, 5.35 mmol) and $LiO\text{-}2,6\text{-}^iPr_2C_6H_3$ (990 mg, 5.38 mmol) in place of $LiO\text{-}2,4,6\text{-}Me_3C_6H_2$ were used. The yield (2.30 g) was almost quantitative. The resultant solid was purified as red needles by recrystallization from CH_2Cl_2 layered by *n*-hexane in the freezer (−25 °C). The sample for the X-ray crystallography was further recrystallized from CH_2Cl_2 layered by *n*-hexane at 5 °C.

Method 2. $HO\text{-}2,6\text{-}^iPr_2C_6H_3$ (1.29 g, 7.25 mmol) was added in small portions to a stirred toluene solution (50 mL) containing Cp^*TiCl_3 (1.00 g, 3.45 mmol) at −25 °C. The mixture was warmed to room temperature and was then refluxed for 1 day under N_2. The solution was then filtered through Celite, and the filter cake was washed with toluene (20 mL). The combined filtrate and wash were taken to dryness under reduced pressure to give a red solid. The resultant solid was dissolved in hot CH_2Cl_2, and the chilled (−25 °C) solution layered by *n*-hexane gave red needles. Yield: 1.40 g (94%). MS: calcd for $C_{22}H_{32}Cl_2OTi$, 431.26; found (M^-), 429.9. Anal. Calcd: C, 61.27; H, 7.48. Found (1): C, 61.34; H, 7.37; N, 0. Found (2): C, 60.96; H, 7.78; N, 0.

Synthesis of $Cp^*Ti(O\text{-}2\text{-}^tBu\text{-}4,6\text{-}Me_2C_6H_2)Cl_2$ (2c). Synthesis of **2c** was carried out by the same procedure as that in **2a** except that Cp^*TiCl_3 (1.02 g, 3.52 mmol) and $LiO\text{-}2\text{-}^tBu\text{-}4,6\text{-}Me_2C_6H_2$ (650 mg, 3.52 mmol) in place of $LiO\text{-}2,4,6\text{-}Me_3C_6H_2$ were used. The yield (1.51 g) was almost quantitative. MS: calcd for $C_{22}H_{32}Cl_2OTi$, 431.26; found (M^-), 430.46. Anal. Calcd: C, 61.27; H, 7.48. Found: C, 61.12; H, 7.56.

Synthesis of $Cp^*Ti(O\text{-}4\text{-}MeC_6H_4)Cl_2$ (2e). Synthesis of **2e** was carried out by the same procedure as that in **2a** except that Cp^*TiCl_3 (970 mg, 3.35 mmol) and $LiO\text{-}4\text{-}MeC_6H_4$ (384 mg, 3.37 mmol) in place of $LiO\text{-}2,4,6\text{-}Me_3C_6H_2$ were used. Yield (first and second crops): 1.04 g (86%).

Synthesis of $(^nBuC_5H_4)Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_2$ (3b). (a) Preparation of $(^nBuC_5H_4)TiCl_3$. ^nBuLi (1.6 M hexane solution, 15.42 mL, 24.67 mmol) was added over 30 min to an *n*-hexane solution (40 mL) containing $^nBuC_5H_5$ (3.00 g, 24.55 mmol) at −30 °C. The reaction mixture was then warmed slowly to room temperature and was stirred overnight. The mixture was cooled (ca. 0 °C) and white precipitates ($^nBuC_5H_4Li$) were then collected by filtration, washed quickly with cold *n*-hexane, and then dried in vacuo. The resultant solid ($^nBuC_5H_4Li$, 2.5 g, 19.51 mmol) was placed in a Schlenk tube, and THF (50 mL) was added. The mixture was cooled to −30 °C, and Me_3SiCl (2.76 g, 25.36 mmol) was then added in small portions over 30 min. The reaction mixture was warmed slowly to room temperature and was stirred overnight. The solvent and Me_3SiCl remaining were removed in vacuo; then the residue was extracted with *n*-hexane. The solution was then placed in a rotary evaporator to remove *n*-hexane, and $^nBuC_5H_4{-}SiMe_3$ was obtained as a major product (yield 92% from $^nBuC_5H_4Li$). $^nBuC_5H_4{-}SiMe_3$ (1.00 g, 5.14 mmol) dissolved in *n*-hexane (10 mL) was added dropwise over 30 min to an *n*-hexane solution (50 mL) of $TiCl_4$ (976 mg, 5.14 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature and was stirred overnight. The solution was then filtered through Celite and the filter cake was washed with *n*-hexane. The combined filtrate and wash were concentrated to 20 mL and then placed in the freezer (−30 °C). The chilled solution gave yellow microcrystals of $(^nBuC_5H_4)TiCl_3$, which were washed quickly with cold *n*-hexane and then dried in vacuo.

(b) Preparation of $(^nBuC_5H_4)Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_2$ (3b). The synthetic procedure of **3b** was the same as that in **2b** (method 1) except that $LiO\text{-}2,6\text{-}^iPr_2C_6H_3$ (682 mg, 3.70 mmol) and $(^nBuC_5H_4)TiCl_3$ (1.02 g, 3.70 mmol) in place of Cp^*TiCl_3 were used. Yield: 1.16 g (75%). MS: calcd for $C_{21}H_{30}Cl_2OTi$, 417.23; found (M^-), 416.46.

Synthesis of $(^tBuC_5H_4)Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_2$ (4b). The synthetic procedure of $(^tBuC_5H_4)TiCl_3$ was analogous to that for $(^nBuC_5H_4)TiCl_3$ except that $^tBuC_5H_5$ in place of $^nBuC_5H_5$ was used; then **4b** can be prepared by the reaction of $(^tBuC_5H_4)TiCl_3$ with $LiO\text{-}2,6\text{-}^iPr_2C_6H_3$ (conditions similar to

Table 11. Summary of Crystallographic Data, Collection Parameters, and Refinement Parameters[a]

compound[b]	**1b**	**2b**	**6b**	**7a**
empirical formula	$C_{17}H_{22}Cl_2OTi$	$C_{22}H_{32}Cl_2OTi$	$C_{25}H_{38}Cl_2OTi$	$C_{23}H_{27}ClO_2Ti$
formula weight	361.17	431.30	473.38	418.92
cryst size (mm^3)	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.20	0.20 × 0.25 × 0.20	0.20 × 0.20 × 0.20
color/shape	red/prismatic	red/prismatic	red/prismatic	red/prismatic
crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic
a (Å)	16.576(4)	6.966(1)	10.683(1)	14.475(3)
b (Å)	8.422(2)	17.394(2)	17.174(2)	20.155(2)
c (Å)	12.898(3)	9.748(1)	14.433(1)	7.473(2)
β (deg)		100.96(1)	96.385(8)	
V (Å^3)	1800.7	1159.6(2)	2631.8(4)	2169.81(6)
space group	$Cmc2_1$	$P2_1$	$P2_1/n$	$P2_12_12_1$
Z	4	2	4	4
D_{calc} (g/cm^3)	1.332	1.235	1.195	1.282
F_{000}	752.00	456.00	1008.00	880.00
diffractometer	Enraf-Nonius CAD4	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R
radiation, λ (Å)	Mo Kα, 0.710 69	Cu Kα, 1.541 78	Cu Kα, 1.541 78	Cu Kα, 1.541 78
T (K)	295	296	296	296
$2\theta_{max}$ (deg)	52.6	130.1	130.2	130.2
no. of reflns	1062	2033	4667	2158
R_{int}		0.028	0.018	
no. of obsvns ($I > 3\sigma(I)$)	818	1676	3339	1722
no. of variables	102	234	415	281
residuals: R; R_w	0.032; 0.038	0.046; 0.065	0.032; 0.043	0.037; 0.049
GOF	1.17	2.02	1.20	1.37
max (minimun) peak in final diff map e-/Å^3	0.24 (−0.18)	0.74 (−0.26)	0.18 (−0.18)	0.25 (−0.18)

[a] Structure solution: direct methods. Refinement: full-matrix least-squares. Function minimized: $\sum\omega(|F_o| - |F_c|)^2$. Least squares weights: $\omega = 1/[\sigma^2(F) + (pF)^2/4]$, p-factor 0.05. [b] **1b**: CpTi(O-2,6-$^iPr_2C_6H_3$)Cl_2. **2b**: Cp*Ti(O-2,6-$^iPr_2C_6H_3$)Cl_2. **6b**: (1,3-$^tBu_2C_5H_3$)Ti(O-2,6-$^iPr_2C_6H_3$)Cl_2. **7a**: Cp(O-2,4,6-$Me_3C_6H_2$)$_2$Cl.

those in **3b**).[22] Yield: 80% (from ($^tBuC_5H_4$)$TiCl_3$). MS: calcd for $C_{21}H_{30}Cl_2OTi$, 417.23; found (M^-), 416.44. Anal. Calcd: C, 60.45; H, 7.25. Found: C, 60.61; H, 7.47.

Synthesis of (1,3-$Me_2C_5H_3$)Ti(O-2,6-$^iPr_2C_6H_3$)Cl_2 (5b). The synthetic procedure of (1,3-$Me_2C_5H_3$)$TiCl_3$ was analogous to that for ($^nBuC_5H_4$)$TiCl_3$ except that $^tBuC_5H_5$ in place of $^nBuC_5H_5$ was used; then **5b** can be prepared by the reaction of (1,3-$Me_2C_5H_3$)$TiCl_3$ with LiO-2,6-$^iPr_2C_6H_3$ (similar conditions as those in **3b**).[22] Yield: 85% (from (1,3-$Me_2C_5H_3$)$TiCl_3$). MS: calcd for $C_{19}H_{26}Cl_2OTi$, 389.18; found (M^-), 388.48. Anal. Calcd: C, 58.63; H, 6.73. Found (1): C, 58.68; H, 7.09; N, 0. Found (2): C, 58.92; H, 7.09; N, 0.

Synthesis of (1,3-$^tBu_2C_5H_3$)Ti(O-2,6-$^iPr_2C_6H_3$)Cl_2 (6b). (a) Preparation of (1,3-$^tBu_2C_5H_3$)$TiCl_3$. KH (678 mg, 16.91 mmol) was added to a THF solution (30 mL) of 1,3-$^tBu_2C_5H_4$ (3.00 g, 16.82 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature and was then refluxed for 3 h. The mixture was cooled (ca. 0 °C), and Me_3SiCl (3.66 g, 33.65 mmol) was then added in small portions over 30 min. The solution was then warmed to room temperature and was stirred for 5 h. The solvent and Me_3SiCl remaining were removed in vacuo; then the residue was extracted with *n*-hexane. The solution was then placed in a rotary evaporator, and a pale yellow liquid containing 1,3-$^tBu_2C_5H_3$−$SiMe_3$ as a major product was obtained. Yellow microcrystals of (1,3-$^tBu_2C_5H_3$)$TiCl_3$ could be then prepared from 1,3-$^tBu_2C_5H_3$−$SiMe_3$ and $TiCl_4$ by the same procedure as that for ($^nBuC_5H_4$)-$TiCl_3$. ^1H NMR (C_6D_6): δ 1.18 (s, 18H, (CH_3)$_3$C−), 6.27 (d, 2H, $J = 2.4$ Hz, $^tBu_2C_5H_3$), 6.69 (t, 1H, $J = 2.6$ Hz, $^tBu_2C_5H_3$).

(b) Preparation of (1,3-$^tBu_2C_5H_3$)Ti(O-2,6-$^iPr_2C_6H_3$)Cl_2 (6b). The synthetic procedure of **6b** was the same as that in **2b** (method 1) except that LiO-2,6-$^iPr_2C_6H_3$ (567 mg, 3.08 mmol) and (1,3-$^tBu_2C_5H_3$)$TiCl_3$ (1.02 g, 3.08 mmol) in place of Cp*$TiCl_3$ were used. Yield: 1.05 g (72%). Samples for the X-ray crystallography was prepared by recrystallization with a minimum amount of Et_2O layered by *n*-hexane at −30 °C. MS: calcd for $C_{25}H_{38}Cl_2OTi$, 473.33; found (M^-), 472.57. Anal. Calcd: C, 63.43; H, 8.09. Found: C, 63.63; H, 7.98; N, 0.

Synthesis of CpTi(O-2,4,6-$Me_3C_6H_3$)$_2$Cl (7a). HO-2,4,6-$Me_3C_6H_3$ (5.0 g, 36.7 mmol) was added in small portions to a toluene solution (50 mL) of $CpTiCl_3$ (1.0 g, 4.56 mmol) at −25 °C. The reaction mixture was warmed slowly to room temperature and was then refluxed for 10 h. The mixture was then filtered through Celite, and the filter cake was washed with toluene (20 mL). The combined filtrate and wash were taken to dryness under reduced pressure to remove toluene, and 2,4,6-$Me_3C_6H_2OH$ remained upon heating. The resultant solid containing the phenol (trace amount) was dissolved in Et_2O (30 mL) and was then cooled to −25 °C. The chilled solution gave red−orange microcrystals, and the microcrystals were further purified with a minimum amount of Et_2O at −30 °C. Yield: 1.02 g (87%). Samples for the X-ray crystallography were prepared by recrystallization with a minimum amount of Et_2O at 5 °C. MS: calcd for $C_{23}H_{27}ClO_2Ti$, 418.78; found (M^-), 418.47. Anal. Calcd: C, 65.96; H, 6.50. Found: C, 65.91; H, 6.69.

Synthesis of CpTi(O-2,6-$^iPr_2C_6H_3$)$_2$Cl (7b). Synthesis of **7b** is the same as that for **7a** except that $CpTiCl_3$ (1.03 g, 4.70 mmol) and HO-2,6-$^iPr_2C_6H_3$ (3.0 g, 16.79 mmol) in place of HO-2,4,6-$Me_3C_6H_2$ were used. Yield: 2.01 g (85%). MS: calcd for $C_{29}H_{39}ClO_2Ti$, 502.93; found (M^-), 502.67.

Synthesis of Cp*Ti(O-2,6-$^iPr_2C_6H_3$)Me_2 (8b). HO-2,6-$^iPr_2C_6H_3$ (773 mg, 4.34 mmol) was added in small portions to a Et_2O solution (30 mL) containing Cp*$TiMe_3$ (990 mg, 4.34 mmol) at −30 °C. The reaction mixture was warmed to room temperature and was stirred for 10 h. The mixture was then dried in vacuo, and the resultant yellow solid was dissolved in a minimum amount of Et_2O. The chilled solution (−30 °C) gave yellow microcrystals (970 mg), which were dried in vacuo. The concentrated mother liquor in the freezer afforded a second crop (330 mg). Yield: 1.30 g (77%). MS: calcd for $C_{24}H_{38}OTi$, 390.42; found (M^-), 390.55. Anal. Calcd: C, 73.83; H, 9.81. Found: C, 73.38; H, 9.70, N, 0.

Synthesis of Cp*Ti(O-2,6-$^iPr_2C_6H_3$)(OTf)$_2$ (9b). AgOTf (928 mg, 3.61 mmol) was added in small portions to a CH_2Cl_2 solution (30 mL) containing **2b** (760 mg, 1.76 mmol) at −30 °C. The mixture was warmed to room temperature and was stirred for 10 h. The reaction mixture was then filtered through Celite, and the filtrate was dried in vacuo. The resultant solid was dissolved in a minimum amount of CH_2Cl_2, and the chilled (−25 °C) solution gave deep brown microcrystals (660 mg). Yield: 59% (600 mg). Anal. Calcd for $C_{24}H_{32}F_6O_7S_2Ti$, 418.78: C, 43.77; H, 4.90. Found: C, 43.84; H, 5.11; N, 0.

Polymerization of Ethylene and Propylene. Polymerization of ethylene (Tables 3−6) was performed by using a 1 L scale autoclave and the typical reaction procedure is as follows. Toluene (300 mL) and MAO (9.5 wt % (Al) toluene solution) or d-MAO (prepared from ordinary MAO by removing toluene and $AlMe_3$) were added into the autoclave filled with N_2, and the reaction apparatus then introduced ethylene to 4 kgf/cm^2. The toluene solution containing complex was then introduced into the autoclave under pressurized conditions. In the case of the polymerization with $Ph_3CB(C_6F_5)_4$, the borate in toluene solution was added soon after the addition of complex. The reaction mixture was stirred for 1 h at 4 kgf/cm^2 (60 °C), and the polymerization was terminated with the addition of EtOH (15 mL). The solution was then poured into EtOH (200 mL), and the resultant polymer was adequately washed with EtOH and then dried in vacuo for several hours. Molecular weights and the molecular weight distributions of the polymers were measured at 145 °C by means of gel-permiation chromatography (Waters 150 CV) using *o*-dichlorobenzene as the solvent and the calibration with standard polystyrene samples. The polymerization of propylene was also performed in the same manner.

Copolymerization of Ethylene with 1-Butene and Ethylene with 1-Hexene. The catalytic copolymerization of ethylene/1-butene was carried out in the same manner as that on ethylene except that 1-butene was introduced before introducing ethylene (400 mL scale autoclave, reaction temperature 70 °C). The copolymerization of ethylene/1-hexene was carried out in the same manner as that on ethylene polymerization, except that 1-hexene was added before introducing ethylene.

Polymerization of 1-Hexene. A typical procedure for polymerization of 1-hexene is as follows. 1-Hexene (15 g) and a prescribed amount of d-MAO were added to a Schlenk tube (50 mL) under N_2, and the polymerization was started by the addition of a toluene solution (2.0 g) containing **2b** (2.0 μmol). The reaction mixture was stirred for 1 h at room temperature, and the polymerization was terminated with the addition of EtOH. The reaction product was extracted with $CHCl_3$, which was washed with HCl aqueous solution and then dried in vacuo.

Crystal Structure Determinations for $CpTi(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl_2$ (1b), $Cp^*Ti(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl_2$ (2b), $(1,3\text{-}{}^tBu_2C_5H_3)Ti(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl_2$ (6b), and $CpTi(O\text{-}2,4,6\text{-}Me_3C_6H_2)_2Cl$ (7a). The crystal structures for **1b**, **2b**, **6b**, and **7a** were determined by X-ray crystallography by using an Enraf-Nonius CAD4 (Mo Kα radiation, $\lambda = 0.710\,69$ Å) or Rigaku AFC7R (Cu Kα radiation, $\lambda = 1.541\,78$ Å) diffractometer under the conditions listed in Table 11. Preparation procedures for these crystals were described above. For more detailed analysis conditions, see the Supporting Information.

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Supporting Information Available: Typical ^{13}C NMR spectra of poly(1-hexene) and poly(ethylene-*co*-1-butene)s prepared by **2b** and **10**. Experimental detailes for X-ray crystallography for **1b**, **2b**, **6b**, and **7a** (total 20 pages). See any current masthead page for ordering and Internet access instructions.

References and Notes

(1) For example: (a) Brintzinger, K. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Guram, A. S.; Jordan, R. F. in *Comprehensive Organometallic Chemistry*; 2nd ed.; Lappert, M. F., Ed.; Pergamon: Oxford, U.K., 1995; Vol. 4, p 589.

(2) For example: (a) Canich, J. A. M. EP 420436, 1991. (b) Canich, J. A. M.; Hlatky, G. G.; Turner, H. W. USP 542236, 1990. (c) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. EP 416815 A2, 1991. (d) Campbell, R. E., Jr. USP 5066741, 1991. (e) LaPointe, R. E. EP 468651, 1991. (f) Okuda, J.; Schattenmann, F. J.; Wocaldo, S.; Massa, W. *Organometallics* **1995**, *14*, 789. (g) Devore, D. D.; Timmers, F. J.; Hasha, D. L.; Rosen, R. K.; Marks, T. J.; Deck, P. A.; Stern, C. L. *Organometallics* **1995**, *14*, 3132. (h) du Plooy, K. E.; Moll, U.; Wocadlo, S.; Massa, W.; Okuda, J. *Organometallics* **1995**, *14*, 3129. (i) Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572. (j) McKnight, A. L.; Masood, M. A.; Waymouth, R. M.; Straus, D. A. *Organometallics* **1997**, *16*, 2879.

(3) Examples (recent report) for catalytic alkene polymerization using group 4 metal complexes containing bis(amide) ligand: (a) Canich, J. A. M.; Turner, H. W. WP 92/12162, 1992. (b) Horton, A. D.; de With, J. *Chem. Commun.* **1996**, 1375. (c) Cloke, F. G. N.; Geldbach, T. J.; Hitchcock, P. B.; Love, J. B. *J. Organomet. Chem.* **1996**, *506*, 343. (d) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008. (e) Scollard, J. D.; McConville, D. H.; Payne, N. C.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241. (f) Tinkler, S.; Deeth, R. J.; Duncalf, D. J.; McCamley, A. *Chem. Commun.* **1996**, 2623. (g) Nomura, K.; Naga, N.; Takaoki, K.; Imai, A. *J. Mol. Catal. A* **1998**, *130*, L209. (h) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830. (i) Horton, A. D.; de With, J.; van der Linden, A. J.; van der Weg, H. *Organometallics* **1996**, *15*, 2672. (j) Clark, H. C. S.; Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B.; Mainwright, A. P. *J. Organomet. Chem.* **1995**, *501*, 333. (k) Bei, X.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3282. (l) Tsukahara, T.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3303. (m) Kim, I.; Nishihara, Y.; Jordan, R. F. *Organometallics* **1997**, *16*, 3314. (n) Shah, S. A. A.; Dorn, H.; Voigt, A.; Roesky, H. W.; Parisini, E.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **1996**, *15*, 3176. (o) Schrock, R. R.; Schattenmann, F.; Aizenberg, M.; Davis, W. M. *Chem. Commun.* **1998**, 199.

(4) Examples for catalytic alkene polymerization using group 4 complexes that contain aryloxide ligands: (a) Miyatake, T.; Mizunuma, K.; Seki, Y,; Kakugo, M. *Macromol. Chem., Rapid Commun.* **1989**, *10*, 349. (b) Canich, J. A. M. USP 5079205, 1992. (c) van der Linden, A.; Schraverien, C. J.; Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008. (d) Fokken, S.; Spaniol, T. P.; Kang, H.-C.; Massa, W.; Okuda, J. *Organometallics* **1996**, *15*, 5069. (e) Sernetz, F. G.; Mülhaupt, R.; Fokken, S.; Okuda, J. *Macromolecules* **1997**, *30*, 1562. (f) Fokken, S.; Spaniol, T. P.; Okuda, J. *Organometallics* **1997**, *16*, 4240.

(5) As far as we know, one example was reported for ethylene polymerization using the $Cp^*Ti(O^iPr)Me_2{-}[HNEt_3]^+[B(C_6F_5)_4]^-$ system (4.08 kg of polymer/mol of Ti, ethylene 1 atm, benzene, room temperature, 20 min): Stevens, J. C.; Neithamer, D. R. USP 5064802, 1991.

(6) Gomez-Sal, P.; Martin, A.; Mena, M.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1991**, *419*, 77.

(7) Nomura, K.; Naga, N.; Miki, M.; Yanagi, K.; Imai, A. *Organometallics* **1998**, *17*, 2152.

(8) For more detailed crystallographic data, see the Supporting Information.

(9) Examples for the preparation of MAO solid, also see: (a) Ishihara, N.; Takakura, Y.; Miura, T. JP Kokai, H6-329714, 1994. (b) Sishta, C.; Hathorn, R.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 1112. (c) Resconi, L.; Bossi, S.; Abis, L. *Macromolocules* **1990**, *23*, 4489. (d) Deck, P. A.; Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 1772.

(10) Example concerning the effect of $AlMe_3$ in MAO on syndiospecific polymerization of styrene by $Cp^*TiCl_3{-}MAO$ system: (a) Tomotsu, N. *Polym. Prepr. Jpn.* **1993**, 42. (b) Tomotsu, N.; Ishihara, N. *Catal. Surveys Jpn.* **1997**, *1*, 89. (c) Tomotsu, N.; Ishihara, N.; Newman, T. H.; Malanga, M. T. *J. Mol. Catal. A* **1998**, *128*, 167. They reported that contamination of $AlMe_3$ in d-MAO decreases the activity.

(11) A similar observation was reported for polymerization of styrene with a series of $Cp'Ti(OMe)_3$ complexes: Newman, T. H.; Campbell, R. E.; Malanga, M. T. *Metcon '93*, **1993**, 315 (also see in ref 10b,c). They mentioned that these results were due to a stabilization of the active site by electron-releasing substituents.

(12) Similar attempts were made for styrene polymerization by using various $Cp^*TiX_3{-}MAO$ catalysts ($X = Cl, OMe, O^iPr$,

$OCH(CF_3)_2$, OC_6H_5, O-4-MeC_6H_4).[11] However, no significant effect was observed by increasing the activity.

(13) Similar attempts were performed for ethylene polymerization by Cp_2ZrCl_2−, Cp_2Zr(O-2,6-$^tBu_2C_6H_3$)Cl−, Cp_2Zr(O-2,6-$^iPr_2C_6H_3$)Cl−, and Cp_2Zr(O-2,6-$Me_2C_6H_3)_2$−MAO systems: Repo, T.; Gerhard, J.; Salo, M.; Polano, M.; Leskelä, M. *J. Organomet. Chem.* **1997**, *541*, 363. However, no significant difference for the activity was observed in these catalyses.

(14) It was reported by J. A. M. Canich[4b] that (2,6-$^tBu_2C_6H_3O)_3$-ZrCl was an effective catalyst precursor for ethylene polymerization in the presence of MAO. It was suggested that the high activity by this complex was due to the effect of the steric bulk of aryloxy group especially having substituents in the 2,6-positions.

(15) The activity for copolymerization of etylene/1-butene catalyzed by the **10**−$Al^iBu_3/Ph_3CB(C_6F_5)_4$ system under the same conditions of run 31 was 12 400 kg of polymer/(mol of Ti•h) (**10** 1.4 μmol, Al/Ti = 500, $Ph_3CB(C_6F_5)_4$/Ti = 1, $M_n = 7.04 \times 10^4$, $M_w/M_n = 2.2$).

(16) These calculations were made by the following paper using ^{13}C NMR spectra of copolymers: (a) Randall, J. C. *J. Polym., Sci., Polym. Phys. Ed.* **1973**, *11*, 275. (b) Idem. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1989**, *C29* (2&3), 201.

(17) If the 1-butene in the BEB sequence is inserted in a different manner (1,2-insertion and 2,1-insertion), $S_{\alpha\beta}$ (31.78), $S_{\alpha\delta}$ (34.22), and $S_{\beta\gamma}$ (27.77 ppm: calculated δ) (S = second carbon) could be formed between the ethyl side chains of these 1-butenes. These resonances from S carbon could not be found in the poly(ethylene-*co*-1-butene) prepared by **2b**.

(18) The result for the triad sequence distribution for copolymer prepared by the $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$−$Al^iBu_3/Ph_3CB(C_6F_5)_4$ system[15] was as follows, EEE/(BEE + EEB)/BEB/EBE/(EBB + BBE)/BBB = 36.7/26.2/5.8/16.8/11.9/2.6 ($C_4{}'$ 31.3 mol %). It was revealed that the distribution was somewhat dependent upon the cocatalyst, but the significant change was not observed.

(19) Polymerization activity = 568 kg of pp/(mol of Ti•h), $M_n = 7.79 \times 10^4$, $M_w/M_n = 1.9$ [Conditions: **2b** 13.2 μmol, MAO (9.5 wt % (Al) toluene solution, Al/Ti = 1000), propylene 4 kgf/cm^2, toluene 300 mL, 60 °C, 1 h, 1 L scale autoclave].

(20) Example explored for the role of MAO for the syndiospecific polymerization of styrene: (a) Miyashita, A. *Polym. Prepr. Jpn.* **1993**, *42*, 2295. (b) Miyashita, A.; Nabika, M.; Suzuki, T. *Abstr. Symp. Organomet. Chem. Jpn., 40th* **1993**, 46.

(21) This calculation was made on the basis of the following paper using ^{13}C NMR spectrum: Asakura, T.; Demura, M.; Nishiyama, Y. *Macromolecules* **1991**, *24*, 2334. For more details, see Supporting Information.

(22) Detailed description for the synthesis of these complexes can be seen in the Supporting Information of our preliminary communication.[7]

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