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Synthesis of Various Nonbridged Titanium(IV) Cyclopentadienyl−Aryloxy Complexes of the Type CpTi(OAr)X_2 and Their Use in the Catalysis of Alkene Polymerization. Important Roles of Substituents on both Aryloxy and Cyclopentadienyl Groups

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*Summary: Various titanium complexes of the type Cp′Ti(OAr)Cl_2 (Cp′ = cyclopentadienyl; OAr = aryloxy) could be prepared in high yields from Cp′$TiCl_3$. These complexes show remarkable catalytic activities for alkene polymerization with MAO or Al^iBu_3−$Ph_3CB(C_6F_5)_4$: $(C_5Me_5)Ti(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)X_2$ (X = Cl (**2b**), Me (**8b**), CF_3SO_3 (**9b**)) showed the highest activities. The bond angle Ti−O−C (phenyl group) in **2b** (173.0°) is significantly different from those for other complexes (162.3−163.1°).*

Alkene 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 $(C_5Me_4SiR_2NR)MX_2$, and others.[3,4] On the other hand, however, there is only one example for the reaction catalyzed by nonbridged Cp′M(OR)X_2 (Cp′ = cyclopentadienyl group; X = halogen, etc.) complexes such as $Cp^*Ti(O^iPr)Me_2$ ($Cp^* = C_5Me_5$),[5] although the syntheses of Cp−aryloxy complexes such as $Cp^*Ti(O\text{-}2,6\text{-}Me_2C_6H_3)Cl_2$ (**2d**) were known.[6] We thus believe that it is still possible to develop this type of complex as a polymerization catalyst not only because the syntheses are relatively easy but also because the catalyst can be compared with the hybrid half-metallocene analogues.[2] In this paper, we wish to present syntheses of various titanium complexes of the type Cp′Ti(OAr)X_2 (OAr = aryloxy group) and their use in the catalysis of alkene polymerization in the presence of a cocatalyst. From these results, we also present an important effect of substituents on the activity.

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**)) 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). Complexes having other substituents on the cyclopentadienyl group such as $({}^nBuC_5H_4)Ti(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl_2$ (**3b**), $({}^tBuC_5H_4)Ti(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl_2$ (**4b**), $(1,3\text{-}Me_2C_5H_3)Ti(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl_2$ (**5b**), and $(1,3\text{-}{}^tBu_2C_5H_3)Ti(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl_2$ (**6b**), could also be prepared in the same manner from the trichloride analogues, which were synthesized by the reaction of $TiCl_4$ with the corresponding Cp′$SiMe_3$ in hexane (Scheme 2). These complexes could be

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(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. Eur. Patent 420,436. 1991. (b) Canich, J. A. M.; Hlatky, G. G.; Turner, H. W. U.S. Patent 542,236 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. Eur. Patent 416,815 A2, 1991. (d) Campbell, E. R., Jr. U.S. Patent 5,066,741, 1991. (e) LaPointe, R. E. Eur. Patent 468,651, 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) ligands: (a) Canich, J. A. M.; Turner, H. W. WP 92/12162, 1992. (b) Horton, A. D.; de With, J. *J. Chem. Soc., 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. *J. Chem. Soc., Chem. Commun.* **1996**, 2623. (g) Nomura, K.; Naga, N.; Takaoki, K.; Imai, A. *J. Mol. Catal.*, in press. (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.

(4) Examples of 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. U.S. Patent 5,079,205, 1992. (c) van der Linden, A.; Schaverien, 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, only one example was reported of 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. U.S. Patent 5,064,802, 1991.

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

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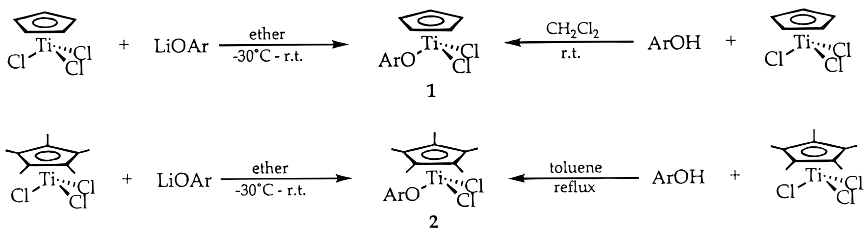
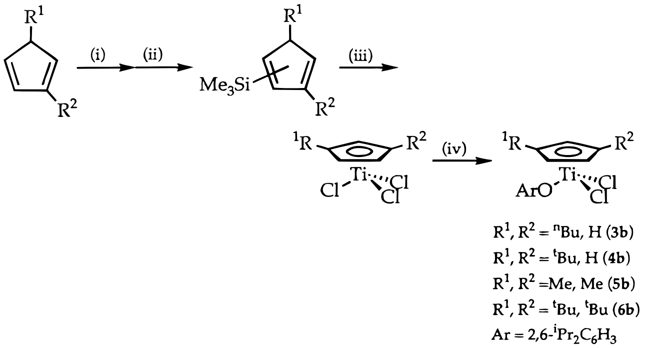
Scheme 1[a]



[a] Ar = 2,4,6-Me$_3$C$_6$H$_2$ (**a**), 2,6-^{i}Pr2C$_6$H$_3$ (**b**), 2-^{t}Bu-4,6-Me$_2$C$_6$H$_2$ (**c**), 2,6-Me$_2$C$_6$H$_3$ (**d**).

Scheme 2[a]



[a] Legend: (i) ^{n}BuLi/hexane or KH/THF; (ii) Me$_3$SiCl (excess); (iii) TiCl$_4$/hexane; (iv) LiO-2,6-^{i}Pr$_2$C$_6$H$_3$/Et$_2$O.

identified by ^{1}H and ^{13}C NMR, mass spectroscopy, elemental analysis, and X-ray crystallography.[7]

It turned out that **1b** could also be prepared quantitatively by the reaction of CpTiCl$_3$ with an excess amount of the phenol (in CH$_2$Cl$_2$ at room temperature), whereas the reaction did not take place if Cp*TiCl$_3$ was used in place of CpTiCl$_3$.[7] Interestingly, reactions of CpTiCl$_3$ with an excess amount of 2,4,6-trimethylphenol or 2,6-diisopropylphenol under reflux conditions in toluene gave CpTi(O-2,4,6-Me$_3$C$_6$H$_2$)$_2$Cl (**7a**) or CpTi(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$Cl (**7b**) in high yield (87 and 85%, respectively),[8] whereas the reaction of Cp*TiCl$_3$ with 2,6-^{i}Pr$_2$C$_6$H$_3$OH under the same conditions afforded **2b** in high yield (94%).

It is interesting to note that Cp*Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$)Me$_2$ (**8b**) could be prepared in high yield by the reaction of Cp*TiMe$_3$ with 2,6-^{i}Pr$_2$C$_6$H$_3$OH in Et$_2$O, although attempts at isolation of **8b** from **2b** by the reaction with MeMgBr, MeMgI, and MeLi were unsuccessful.[9] It also turned out that Cp*Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$)(OTf)$_2$ (**9b**; OTf = CF$_3$SO$_3$) could be prepared from **2b** with AgOTf in high yield.[10]

It is important to note that **2b** shows remarkable catalytic activity for polymerization of ethylene, propylene, and 1-hexene in the presence of MAO with Al^{i}Bu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ as a cocatalyst (Table 1). Complexes **8b** and **9b** were also found to be effective, and **2b** and **9b** with Al^{i}Bu$_3$/Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ showed the highest activities for ethylene polymerization.[11] It is also important to note that the activity as well as the molecular weight of the resultant polymer could be increased in 1-hexene polymerization (Table 1, runs 1−3),[12] if the MAO which was prepared by removing both toluene and excess AlMe$_3$ was used as a cocatalyst. The use of this MAO should also be a great advantage in this catalysis to obtain polymers having unimodal molecular weight distributions. It is also noteworthy that **2b** in the presence of MAO was also an effective catalyst for copolymerization of ethylene with 1-butene and of ethylene with 1-hexene (runs 12−14), and the activities were higher than those for homopolymerization of ethylene. The activity was almost the same as that of by [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ under the same conditions. More detailed polymerization studies, including the effect of cocatalysts, are in progress.

It turned out that other derivatives such as **1b**, **2a**,**c**,**d**, and **3b**−**6b** also show relatively high activity for ethylene polymerization under the same conditions. The activity catalyzed by Cp*Ti(OAr)Cl$_2$ (**2**) with MAO falls in the order OAr = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**2b**; 1240 kg of PE/((mol of Ti) h)) > O-2,6-Me$_2$C$_6$H$_3$ (**2d**; 1000) > O-2-^{t}Bu-4,6-Me$_2$C$_6$H$_2$ (**2c**; 446) > O-2,4,6-Me$_3$C$_6$H$_2$ (**2a**; 369) ≫ O-4-MeC$_6$H$_4$ (**2e**; 25),[13,14] and (C$_5$Me$_5$)Ti(O^{i}Pr)Me$_2$ showed lower catalytic activity (44 kg of PE/((mol of Ti) h)) under the same conditions. These results suggest that the bulk of the aryloxide ligand containing substituents at the 2,6-positions is important for high activity. On the other hand, the effect of cyclopentadienyl substituents on the activity with Cp′Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl$_2$−Al^{i}Bu$_3$/Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ catalysts increased in the order Cp* (**2b**; 2220 kg of PE/((mol of Ti) h)) ≫ 1,3-^{t}Bu$_2$C$_5$H$_3$ (**6b**; 653) > 1,3-Me$_2$C$_5$H$_3$ (**5b**; 215) > ^{n}BuC$_5$H$_4$ (**3b**; 302), ^{t}BuC$_5$H$_4$ (**4b**; 258) ≫ C$_5$H$_5$ (**1b**; 77).[15−17] It is evident

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[7] For detailed synthetic procedures of **1b**, **2a**−**c**,**e**, **3b**, **4b**, **5b**, and **6b** and analytical data, see the Supporting Information.

[8] For experimental details, see the Supporting Information.

[9] **8b**: yield 77% (from Cp*TiMe$_3$). For experimental details, see the Supporting Information.

[10] **9b**: yield 59%. For experimental details, see the Supporting Information.

[11] It was also revealed that Cp*$_2$TiCl$_2$ and (2,6-^{i}Pr$_2$C$_6$H$_3$O)$_2$TiCl$_2$ showed low catalytic activities for ethylene polymerization under the same conditions (70 and 57 kg of PE/((mol of Ti) h), respectively). These results suggest that the observed polymerization activity with **2b** is not due to Cp*$_2$TiCl$_2$ or (2,6-^{i}Pr$_2$C$_6$H$_3$O)$_2$TiCl$_2$ which might be formed by the disproportionation but is rather due to **2b**. For detailed results, see the Supporting Information.

[12] Broad polydispersities were observed for the ethylene homopolymerization as compared to the narrow M_w/M_n values observed for the polypropylene, poly-1-hexene, and ethylene/α-olefin copolymerizations. This is probably a result of polyethylene precipitation during the polymerization, since these reactions were run at 60 °C.

[13] For experimental details, see the Supporting Information.

[14] The activity for ethylene polymerization with **2d**−Al^{i}Bu$_3$−Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ catalyst under the same conditions of run 7 was 1570 kg of polymer/((mol of Ti) h). The activity was lower than that with **2b**−Al^{i}Bu$_3$−Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ catalyst (2220 kg of polymer/((mol of Ti) h)).

[15] For experimental details, see the Supporting Information.

[16] 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; p 315. They mentioned that these results suggested stabilization of the active site by electron-releasing substituents.

[17] (a) Randall, J. C. *J. Polym., Sci., Polym. Phys. Ed.* **1973**, *11*, 275. (b) *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1989**, *C29* (2&3), 201. (c) *Annual Book of ASTM Standards*; ASTM: Philadelphia, PA, 1994; p D5017−91.

Table 1. Alkene Polymerization Catalyzed by Cp*Ti(O-2,6-$^iPr_2C_6H_3)X_2$ (X = Cl (2b), Me (8b), OTf (9b)) in the Presence of Cocatalyst

run no.	cat. (amt/μmol)	cocat.	Al/Ti[a]	olefin	temp/°C	time	polymer yield/g	activity[b]	10^{-4} M_n	M_w/M_n[c]
1	**2b** (10)	MAO[d]	1000	1-hexene[e]	r.t.	1 h	1.79	179	17.4	1.87[f]
2	**2b** (2.0)	MAO[g]	1000	1-hexene[e]	r.t.	10 min	0.73	2190	26.0	2.05
3	**2b** (2.0)	MAO[g]	1000	1-hexene[e]	r.t.	30 min	1.07	1070	29.9	2.04
4	**2b** (4.6)	MAO[d]	1000	ethylene[h]	60	1 h	5.5	1200	2.77	14.8
5	**2b** (4.2)	MAO[g]	2000	ethylene[h]	60	1 h	5.2	1240	13.8	4.7
6	**2b** (6.5)	Al^{i}Bu$_3$/B[i]	500	ethylene[h]	60	1 h	14.4	2220	9.17	5.0
7	**8b** (8.5)	MAO[g]	1000	ethylene[h]	60	1 h	6.1	718	15.1	6.0
8	**8b** (3.1)	Al^{i}Bu$_3$/B[i]	500	ethylene[h]	60	1 h	4.6	1480		
9	**9b** (3.7)	MAO[g]	1000	ethylene[h]	60	1 h	2.9	784		
10	**9b** (3.9)	Al^{i}Bu$_3$/B[i]	500	ethylene[h]	60	1 h	8.2	2100	8.23	5.2
11	**2b** (13.2)	MAO[d]	1000	propylene[j]	60	1 h	7.5	568	7.79	1.9
12	**2b** (2.3)	MAO[g]	1000	ethylene/1-hexene[i,k]	60	1 h	4.7[l]	2040	2.71	1.9
13	**2b** (2.3)	MAO[g]	1000	ethylene/1-butene[m]	70	1 h	16.8[n]	7240	3.82	2.2
14	**2b** (2.1)	MAO[g]	1000	ethylene/1-butene[o]	70	1 h	19.5[n]	9290	8.37	2.06
16	CGC−Ti[p] (2.7)	MAO[g]	1000	ethylene/1-butene[m]	70	1 h	17.8[n]	6550	5.75	3.4

[a] Molar ratio of Al/Ti. [b] kg of polymer/((mol of Ti) h). [c] GPC data in THF (runs 1−3, and 14) or in *o*-dichlorobenzene (runs 4−13, 15, and 16) vs polystyrene standard. [d] MAO 9.5 wt % (Al) in toluene. [e] 1-Hexene 15 g, cat. 5 μmol/g of toluene. [f] Small amount of low M_n peak was also observed on GPC trace. [g] MAO (toluene solution) was evaporated in vacuo and was used as white solids. [h] Ethylene 4 kgf/cm^2, toluene 300 mL. [i] B = $Ph_3C^+B(C_6F_5)_4^-$, $Ph_3C^+B(C_6F_5)_4^-/Ti = 1$ (molar ratio). [j] Propylene 4 kgf/cm^2. [k] Ethylene 4 kgf/cm^2, 1-hexene 10 mL. [l] 1-Hexene 15.4 mol % by ^{13}C NMR,[17] η 0.81 dL/g. [m] Ethylene 6 kgf/cm^2, 1-butene 10 g, toluene 200 mL. [n] 1-Butene 21.0 (run 13), 32.0 (run 14), and 26.8 (run 15) mol %, respectively, by ^{13}C NMR.[17] [o] Ethylene 6 kgf/cm^2, 1-butene 20 g, toluene 200 mL. [p] [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$. For experimental details, see the Supporting Information.

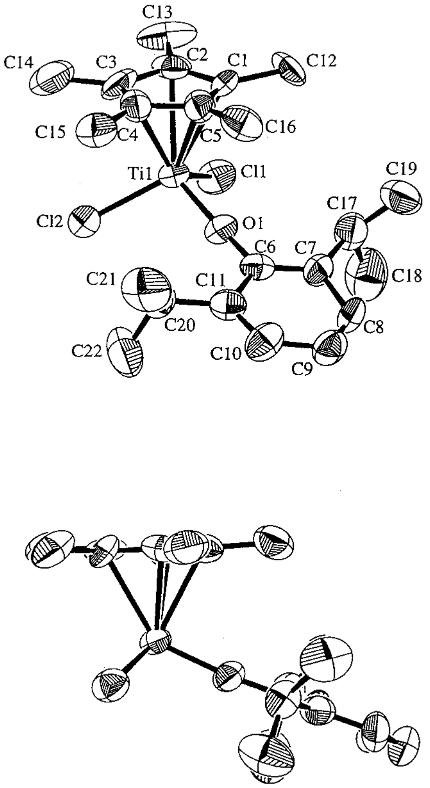

Figure 1. Crystal structure of Cp*Ti(O-2,6-$^iPr_2C_6H_3)Cl_2$ (**2b**): (top) Ortep drawing of **2b**; (bottom) another view of **2b**.

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

	1b	2b	2d[b]	6b
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)
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] Legend: **1b**, CpTi(O-2,6-$^iPr_2C_6H_3)Cl_2$; **2b**, Cp*Ti(O-2,6-$^iPr_2C_6H_3)Cl_2$; **2d**, Cp*Ti(O-2,6-$Me_2C_6H_3)Cl_2$; **6b**, (1,3-$^tBu_2C_5H_3$)Ti(O-2,6-$^iPr_2C_6H_3)Cl_2$. [b] See ref 6. [c] Ti(1)−O(1)-C(4).

from these results that both Cp* and 2,6-diisopropylphenoxy groups are indispensable for notable catalytic activity.

Table 2 summarizes selected bond distances and angles for **1b**, **2b**,**d** and **6b** determined by X-ray crystallography. It is noteworthy that *the bond angle Ti−O−C (phenoxy group) for **2b** (173.0°) is significantly different from those of the others (162.3−163.1°)*, although no significant differences were observed for both the bond lengths and the angles among these compounds (Figure 1). 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. This along with the more electron-donating Cp* (as compared to Cp, BuCp, Me$_2$Cp, and ^{t}Bu$_2$Cp) stabilize the active species and leads to higher activity.[16] We are thus studying more concerning this catalysis: the results, including both the reaction chemistry and the effect of cocatalysts, will be introduced soon.

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Supporting Information Available: Text giving experimental details for the preparation of **1b**, **2a**−**c**,**e**, **3b**, **4b**, **5b**, **6b**, **7a**,**b**, **8b**, and **9b** with all analysis data and experimental details for the polymerization of ethylene, propylene, and 1-hexene and copolymerization of ethylene with 1-butene and of ethylene with 1-hexene and text, tables, and figures giving experimental details for X-ray crystallography for **1b**, **2b**, and **6b** (38 pages). Ordering information is given on any current masthead page.

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