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Constrained Geometry Tetramethylcyclopentadienyl-phenoxytitanium Dichlorides: Template Synthesis, Structures, and Catalytic Properties for Ethylene Polymerization

Yuetao Zhang,[†] Ying Mu,*[,†,§] Chunsheng Lü,[†] Guanghua Li,[‡] Jiansheng Xu,[†]
Yanrong Zhang,[†] Dongsheng Zhu,[†] and Shouhua Feng[‡]

School of Chemistry, Jilin University, 119 Jiefang Road, Changchun 130023, People's Republic of China, State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, School of Chemistry, Jilin University, 119 Jiefang Road, Changchun 130023, People's Republic of China, and Key Laboratory for Supramolecular Structure and Materials of Ministry of Education, Jilin University, Changchun 130023, People's Republic of China

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The synthesis of four new bidentate ligands, 2-(tetramethylcyclopentadienyl)-4,6-di-*tert*-butylphenol ($(TCDBP)H_2$, **5**), 2-(tetramethylcyclopentadienyl)-6-*tert*-butylphenol ($(TCBP)H_2$, **6**), 2-(tetramethylcyclopentadienyl)-6-phenylphenol ($(TCPP)H_2$, **7**), and 2-(tetramethylcyclopentadienyl)-6-methylphenol ($(TCMP)H_2$, **8**), as well as their corresponding constrained geometry tetramethylcyclopentadienyl-phenoxytitanium dichlorides $(TCDBP)TiCl_2$ (**9**), $(TCBP)TiCl_2$ (**10**), $(TCPP)TiCl_2$ (**11**), and $(TCMP)TiCl_2$ (**12**) are described. A new method for the synthesis of complexes **9**−**12** was developed. Molecular structures of **9**, **10**, and **11** were determined by single-crystal X-ray diffraction. The Cp(cent)−Ti−O angles of 106.8° for **9**, 107.1° for **10**, and 107.3° for **11** reveal their sterically open features as catalyst precursors. When activated with $^{i}Bu_3Al$ and $Ph_3C^+B(C_6F_5)_4^-$, complexes **9**−**12** exhibit reasonable catalytic activity for ethylene polymerization, producing polyethylenes with moderate molecular weights and melting points.

Introduction

Group 4 constrained geometry metallocene catalysts that have an appended chelating heteroatom donor group on the cyclopentadienyl ligand have received extensive attention in recent years.[1] In particular the constrained geometry catalysts with a pendant nitrogen donor on the cyclopentadienyl ligand, such as $Me_2Si(\eta^5\text{-}Me_4C_5)(^{t}BuN)TiCl_2$ (**I** in Chart 1), have been widely studied in industry[2] and academic institutions.[3] In comparison, the constrained geometry catalysts with a pendant oxygen donor on the cyclopentadienyl ligand have received less attention, although a number of catalysts of this type have also been reported.[4] Among oxygen-containing constrained geometry catalysts, 2-tetramethylcyclopentadienyl-4-methylphenoxytitanium dibenzyl (**II** in Chart 1) is particularly interesting due to its structural features and good catalytic activities.[5] However, the synthesis of this type of catalysts was found to be difficult.[5,6] Since Marks et al. reported the dibenzyl titanium complex **II**, there have been no further reports on the synthesis and catalytic properties of this type of catalyst until a recent communication which reported the synthesis and structures of a number of indenyl-phenoxy titanium and zirconium complexes.[7] We have recently modified the ligand by introducing

Chart 1

I **II**

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* To whom correspondence should be addressed. Tel: (+86)-431-8499136. Fax: (+86)-431-8949334. E-mail: ymu@mail.jlu.edu.cn.

[†] School of Chemistry.

[‡] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry.

[§] Key Laboratory for Supramolecular Structure and Materials of Ministry of Education.

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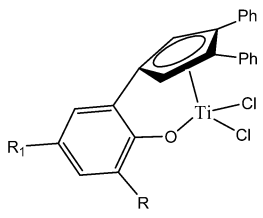
Chart 2



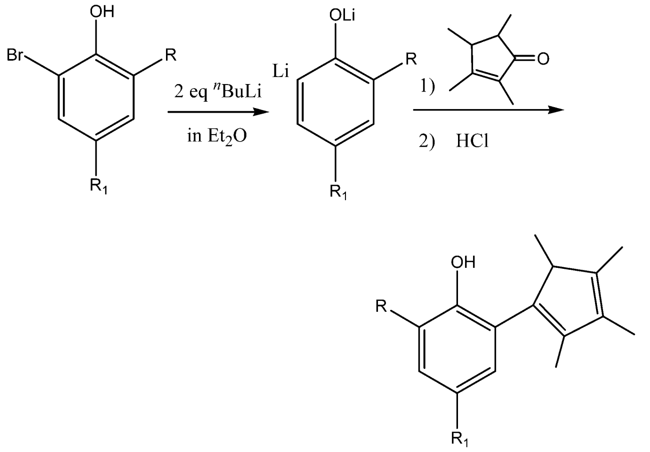
R = Ph (**1**), ^{t}Bu (**2**), ^{t}Bu (**3**), Me(**4**)
R$_1$=H(**1**, **2**, **4**), ^{t}Bu (**3**)

sterically bulky substituents to both the phenol and the cyclopentadienyl groups in order to prevent the formation of multinuclear species and biscyclopentadienyl complexes, and a number of 3,4-diphenylcyclopentadienyl-phenoxytitanium(IV) dichloride complexes (**1**−**4** in Chart 2) were synthesized.[8] Considering that similar complexes with a tetramethylcyclopentadienyl group instead of the diphenylcyclopentadienyl group in **1**−**4** should have better catalytic property than complexes **1**−**4** since the electron-donating Me groups on the Cp ring would increase the catalytic activity of the metallocene catalysts for the olefin polymerization reaction compared with the electron-withdrawing Ph groups,[9] we have further modified the ligand and successfully synthesized a series of new Me$_4$Cp-phenoxytitanium(IV) dichloride complexes for the first time by a new synthetic approach. We report here the preparation of 2-(tetramethylcyclopentadienyl)-4,6-di-*tert*-butylphenol (TCDBP)H$_2$, **5**), 2-(tetramethylcyclopentadienyl)-6-*tert*-butylphenol ((TCBP)H$_2$, **6**), 2-(tetramethylcyclopentadienyl)-6-phenylphenol ((TCPP)H$_2$, **7**), and 2-(tetramethylcyclopentadienyl)-6-methylphenol ((TCMP)H$_2$, **8**), the synthesis and characterization of the corresponding titanium(IV) dichloride complexes ((TCDBP)TiCl$_2$, **9**, (TCBP)TiCl$_2$, **10**, (TCPP)TiCl$_2$, **11**, and (TCMP)TiCl$_2$, **12**), as well as their catalytic performance in ethylene polymerization.

Results and Discussion

Synthesis of Ligands. The ligands **5**−**8** were synthesized by a modified literature procedure.[5,8] The reaction of the corresponding dilithium phenoxide, which was obtained by treating the given 2-bromophenol with 2 equiv of ^{n}BuLi, with 2,3,4,5-tetramethyl-2-cyclopentenone in Et$_2$O at room temperature followed by treating the reaction mixture with concentrated HCl produces **5**−**8**, respectively (Scheme 1). The synthetic reaction was also tried in toluene and THF, and similar results were obtained. Compounds **5** and **6** could be synthesized in higher yields, while **7** and **8** were obtained in lower yields. Compounds **5**−**8** were found to be stable under ambient temperature and pressure and could be left in air for a long time without detectable decomposition. ^{1}H NMR spectroscopic analysis indicates that freshly prepared samples of **5**−**8** are mixtures of three isomers. However, the ratio of the isomers changes with time. When the samples were left at room temperature, one of the isomers was found to become the major product after several days. It has been reported by Marks et al. that a single isomer was obtained of their ligand after vacuum distillation.[5] Similar behavior has also been observed for a *N*,*N*-dimethylaminophenyl-tetramethylcyclopentadiene ligand system.[10]

Scheme 1. Synthetic Procedure for Ligands 5−8



R = ^{t}Bu (**5**), ^{t}Bu (**6**), Ph(**7**), Me(**8**)
R$_1$=^{t}Bu (**5**), H(**6**, **7**, **8**)

Synthesis of Titanium(IV) Dichloride Complexes 9−12. Attempts to prepare the titanium(IV) complexes through amine elimination,[3a,11] alkane elimination,[5,12] or conventional lithium salt elimination[2a,8] routes were unsuccessful. Complexes **9**−**12** were finally synthesized by a template lithium salt elimination approach (Scheme 2), in which the given ligand **5**−**8** was first mixed with TiCl$_4$ in 1:1 molar ratio in order to form coordination intermediates, and the resulting coordination intermediates were then converted to the corresponding complexes **9**−**12** by reaction with 2 equiv of ^{n}BuLi at low temperature. The ^{1}H NMR spectrum of a mixture of **5** and TiCl$_4$ in CDCl$_3$ indicates clearly the formation of the coordination intermediates by comparison with the ^{1}H NMR spectrum of ligand **5** (Figure

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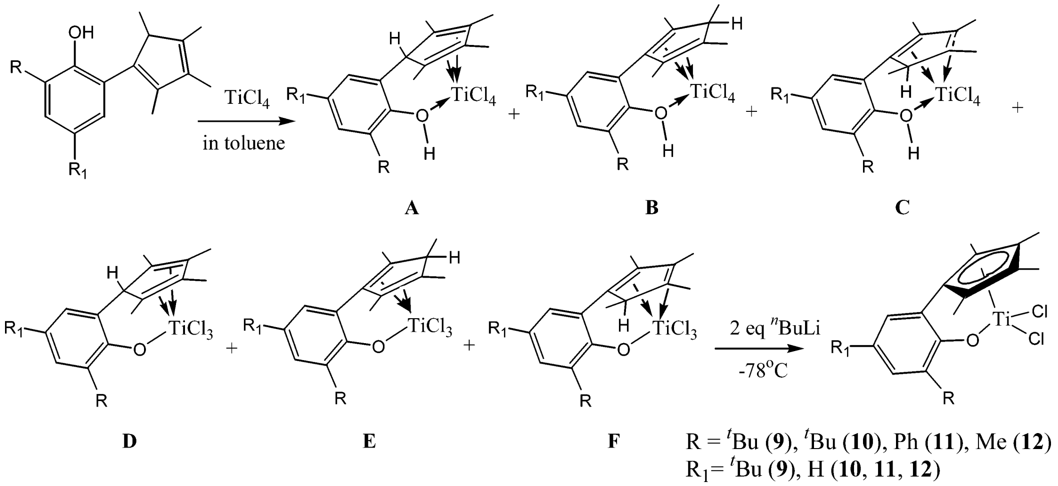
Scheme 2. Synthetic Procedure for Complexes 9−12



1). The complexity of the ^{1}H NMR spectrum of the mixture could be attributed to the existence of several forms of coordination intermediates such as **A**−**F** in Scheme 2. The partial formation of the Ti−O bond was confirmed by the observation of the HCl signal in the ^{1}H NMR spectrum. By following the reaction, it was found that the amount of HCl increases slowly with time. It has been reported that reactions of $TiCl_4$ with phenols usually need tens of hours to go to completion.[13] It is not clear so far whether the addition of ^{n}BuLi results in the deprotonation of the Me_4CpH group first or the formation of the Ti−Bu bond first. Both routes can lead to the final product. To our knowledge, this is the first time for metallocene type complexes to be synthesized by such a synthetic approach. The synthetic reactions for all complexes **9**−**12** were carried out in toluene. To simplify the purification steps, the synthesis of **9**−**12** was also tested in hexane. It was found that complexes **9** and **10** could be synthesized in lower yields, while complexes **11** and **12** could not be prepared in hexane. The successful synthesis of **9**−**12** further indicates the importance of the ligand modification for this type of complex. As mentioned in the previous report,[8] the R group at the *ortho* position of the phenolate might play a key role in preventing the formation of multinuclear species and biscyclopentadienyl complexes. Similar to the case of complexes **1**−**4**,[8] the yields of the synthetic reactions for **9**−**12** are quite different depending on the nature of the R group. The smallest methyl group results in the lowest yield of **12**, while the bulky ^{t}Bu group leads to higher yields of **9** and **10**. The complexes **9**−**12** were also found to be quite stable to air and moisture and could be exposed to air for several days without obvious decomposition. These complexes also exhibit good thermostability and can be heated to about 200 °C without decomposition. The ^{1}H and ^{13}C NMR spectra of **9**−**12** indicate that they all have C_s-symmetric structures in solution.

Crystal Structures of 9, 10, and 11. The molecular structures of complexes **9**, **10**, and **11** were determined by X-ray crystal structure analyses. The ORTEP drawings of the molecule structures are shown in Figures 2−4, respectively. The selected bond lengths and angles are summarized in Table 1. The general structural features of **9**, **10**, and **11** are comparable to those previously reported for **1**, **2**, and **II**. All molecules adopt C_s-symmetry with pseudo-tetrahedral geometry. The Cp(cent)−Ti−O angles for **9**, **10**, and **11** are 106.8°, 107.1°, and 107.3°, respectively, which are in line with those of complexes **1** (107.4°) and **2** (106.7°) and slightly smaller than the one in **II** (107.7°)[5] and that of the Cp(cent)−Ti−N angle in **I** (107.6°),[2a] indicating sterically open features for **9**, **10**, and **11** similar to complexes **I**, **II**, and **1**−**4** as catalyst precursors. The Ti−C_{ring} (av) distances of 2.348 Å for **9**, 2.335 Å for **10**, and 2.345 Å for **11** are similar to that in **I** (2.340 Å) and slightly

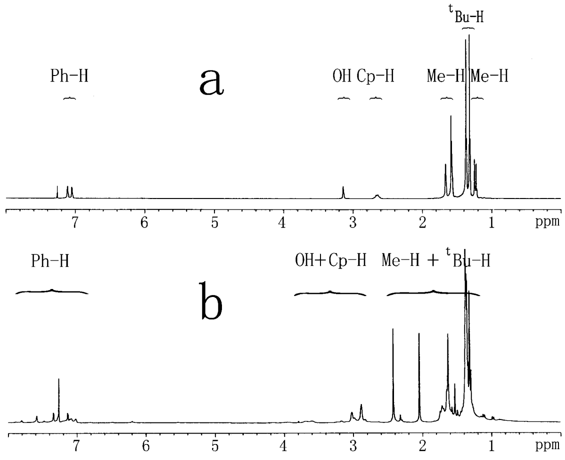


Figure 1. ^{1}H NMR spectra of ligand **5** (a) and the mixture of $TiCl_4$ and **5** (b).

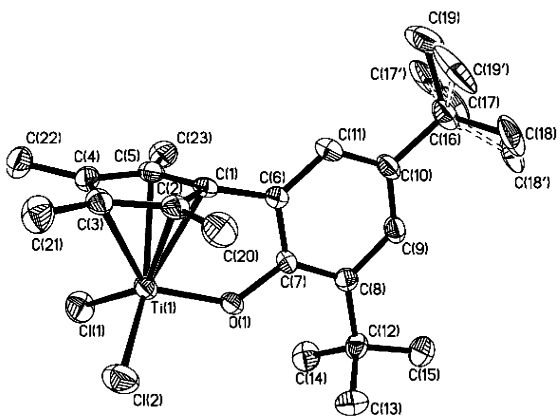


Figure 2. Structure of complex **9** (thermal ellipsoids are drawn at the 30% probability level).

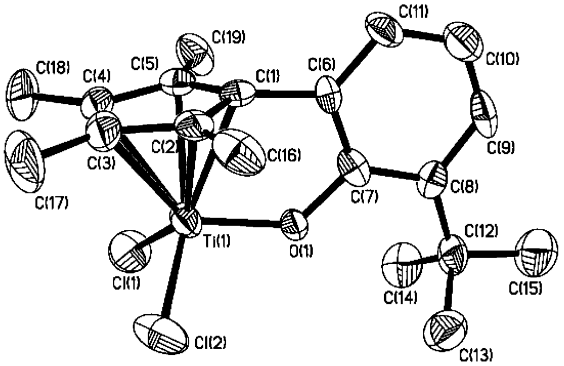


Figure 3. Structure of complex **10** (thermal ellipsoids are drawn at the 30% probability level).

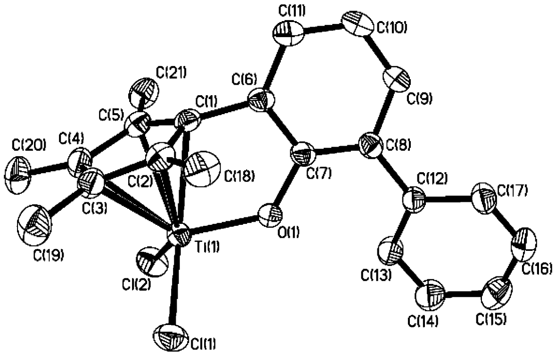


Figure 4. Structure of complex **11** (thermal ellipsoids are drawn at the 30% probability level).

Table 1. Selected Bond Lengths (Å) and Angles (deg)

	Complex **9**		
Ti(1)–O(1)	1.832(3)	Ti(1)–C(1)	2.300(4)
Ti(1)–C(2)	2.323(4)	Ti(1)–C(3)	2.377(4)
Ti(1)–C(4)	2.405(5)	Ti(1)–C(5)	2.333(4)
Ti(1)–Cl(1)	2.2648(17)	Ti(1)–Cl(2)	2.2719(16)
O(1)–C(7)	1.380(5)	Cp(cent)–Ti(1)	2.014
C(1)–C(6)	1.484(6)	O(1)–Ti(1)–Cl(1)	107.32(11)
O(1)–Ti(1)–Cl(2)	104.39(10)	Cl(1)–Ti(1)–Cl(2)	104.38(7)
Cp(cent)–Ti(1)–O(1)	106.8	Ti(1)–Cp(cent)–C(1)	87.5
C(6)–C(1)–Cp(cent)	169.5	C(1)–C(6)–C(7)	112.7(4)
C(6)–C(7)–O(1)	114.4(4)	C(7)–O(1)–Ti(1)	128.9(3)
	Complex **10**		
Ti(1)–O(1)	1.834(3)	Ti(1)–C(1)	2.307(4)
Ti(1)–C(2)	2.326(5)	Ti(1)–C(3)	2.385(6)
Ti(1)–C(4)	2.388(6)	Ti(1)–C(5)	2.323(5)
Ti(1)–Cl(1)	2.2446(16)	Ti(1)–Cl(2)	2.2554(17)
O(1)–C(7)	1.390 (4)	Cp(cent)–Ti(1)	2.005
C(1)–C(6)	1.489(6)	O(1)–Ti(1)–Cl(1)	105.87(11)
O(1)–Ti(1)–Cl(2)	103.77(12)	Cl(1)–Ti(1)–Cl(2)	104.47(6)
Cp(cent)–Ti(1)–O(1)	107.1	Ti(1)–Cp(cent)–C(1)	87.6
C(6)–C(1)–Cp(cent)	168.9	C(1)–C(6)–C(7)	113.0(5)
C(6)–C(7)–O(1)	114.5(5)	C(7)–O(1)–Ti(1)	128.8(4)
	Complex **11**		
Ti(1)–O(1)	1.837(2)	Ti(1)–C(1)	2.294(3)
Ti(1)–C(2)	2.321(3)	Ti(1)–C(3)	2.375(3)
Ti(1)–C(4)	2.384(3)	Ti(1)–C(5)	2.350(3)
Ti(1)–Cl(1)	2.2518(10)	Ti(1)–Cl(2)	2.2590(11)
O(1)–C(7)	1.377(3)	Cp(cent)–Ti(1)	2.011
C(1)–C(6)	1.485(4)	O(1)–Ti(1)–Cl(1)	105.67(7)
O(1)–Ti(1)–Cl(2)	103.85(8)	Cl(1)–Ti(1)–Cl(2)	104.76(4)
Cp(cent)–Ti(1)–O(1)	107.3	Ti(1)–Cp(cent)–C(1)	87.2
C(6)–C(1)–Cp(cent)	168.8	C(1)–C(6)–C(7)	114.0(3)
C(6)–C(7)–O(1)	113.9(3)	C(7)–O(1)–Ti(1)	128.34(18)

Table 2. Summary of Ethylene Polymerization Catalyzed by Complexes 9–12 (activated by $Ph_3C^+[B(C_6F_5)_4]^-$)[a]

no.	catalyst	Al:Ti	yield (g)	activity[b] × 10^{-6}	M_η[c] × 10^{-4}	T_m (°C)[d]
1	**9**	50	4.42	3.92	7.2	129.3
2	**9**	75	5.85	5.19	11	131.8
3	**9**	100	3.74	3.32	7.3	129.7
4[e]	**9**	75	3.91	6.93	7.6	132.2
5	**10**	50	3.83	2.96	5.9	130.6
6	**10**	75	5.01	3.88	9.4	131.7
7	**10**	100	3.22	2.49	6.7	131.8
8	**11**	50	1.54	1.25	3.8	131.3
9	**11**	75	1.98	1.61	3.7	131.4
10	**11**	100	0.91	0.74	3.5	130.5
11	**12**	50	1.47	1.01	3.9	131.0
12	**12**	75	2.14	1.48	4.5	130.9
13	**12**	100	1.18	0.81	4.3	131.2

[a] Polymerization conditions: solvent 100 mL of toluene, temperature 80 °C, catalyst 1 mg, B/Ti ratio 1.5, time 30 min, ethylene pressure 5 bar. [b] g PE (mol Ti)$^{-1}$ h^{-1}. [c] Measured in decahydronaphthalene at 135 °C. [d] Determined by DSC at a heating rate of 10 °C min^{-1}. [e] Catalyst 0.5 mg.

shorter than those in **II** (2.36(1) Å) and complexes **1** (2.365 Å) and **2** (2.362 Å). The distances of Ti–C3 and Ti–C4 in **9**, **10**, and **11** are obviously longer than those of the remaining Ti–C_{ring} bonds and the Ti–Cp(cent)–C1 angles of **9** (87.5°), **10** (87.6°), and **11** (87.2°) are less than 90°, which is characteristic for constrained geometry metallocene catalysts.[2–5] The phenolate plane–Cp plane dihedral angle is 89.3° for **9**, 87.0° for **10**, and 85.3° for **11** and the (phenolate)C–C(ring) vector is bent 9.9° in **9**, 10.8° in **10**, and 11.3° in **11** from the Cp ring plane, which are similar to those for complexes **1** (89.7° and 9.4°) and **2** (86.5° and 9.4°). The corresponding data in **II** are 81(1)° and 15(1)°, reflecting less steric strain in **1**, **2**, **9**, **10**, and **11** than in **II** in the solid state. The Ti–O bond lengths of 1.832(3) Å in **9**, 1.834(3) Å in **10**, and 1.837(2) Å in **11** are shorter than that in **II** (1.851(7) Å) but longer than those in **1** (1.813(4) Å) and **2** (1.818(4) Å), while the Ti–O–C angles of 128.9(3)° in **9**, 128.8(4)° in **10**, and 128.34(18)° in **11** are larger than the one in **II** (126.6(6)°) and smaller than those in **1** (129.1(4)°) and **2** (129.8(4)°). These results indicate the Ti–O double-bond character[5,14] in **9**, **10**, and **11** is intermediate compared with that in **1**, **2**, and **II**. It should be pointed out that the differences in solid state structures of **9**, **10**, **11**, and **II** probably result from packing force since there is no other reasonable explanation for them. One more thing that should be mentioned is that all Me groups of the ^{t}Bu group at the *para* position of the phenolate in complex **9** are disordered owing to the free rotation of the ^{t}Bu group.

Ethylene Polymerization Studies. Complexes **9**–**12** are studied as ethylene polymerization catalysts, and the results are summarized in Table 2. Upon alkylation and activation with $Al(^iBu)_3$ and $Ph_3C^+B(C_6F_5)_4^-$, complexes **9**–**12** show good catalytic activity for ethylene polymerization, producing polyethylenes with moderate molecular weights and melting points. The order of catalytic activity for ethylene polymerization under similar conditions (see runs 2, 6, 9, and 12 in Table 2) is **9** > **10** > **11** ≈ **12**, which could be attributed to the nature of the substituents on the phenolate. As seen

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from the structures of these catalysts, the electronic effect of the R group at the *para* position of the phenolate might play a significant role in the catalytic activity when the R_1 group at the *ortho* position is kept the same (comparing **9** and **10**), while both steric and electronic effects of the R_1 group at the *ortho* position seem to be important in determining the order of the catalytic activity when the R group at the *para* position is unchanged (comparing **10**, **11**, and **12**).[9] For all complexes, the catalytic activity increases with the increase in Al/Ti ratio and reaches the highest catalytic activities with the Al/Ti ratio about 75. Further increasing in the Al/Ti ratio results in a decrease in the catalytic activity. It is possible that excessive $Al(^iBu)_3$ would consume so much $Ph_3C^+B(C_6F_5)_4^-$ that the catalyst could not be efficiently activated.[15] Compared with the catalytic activity of complexes **1**−**4** ((0.5−3.4) × 10^6 g polymer/mol cat.), complexes **9**−**12** show higher catalytic activity ((0.7−6.9) × 10^6 g polymer/mol cat.) for ethylene polymerization, which is expected since the four electron-donating Me groups on the Cp ring of **9**−**12** would increase their catalytic activity.[9] Similar to **1**−**4**, the catalytic activity of complexes **9**−**12** is low at room temperature and increases at elevated temperatures due probably to tight interaction between the catalyst cation and the cocatalyst anion in the constrained geometry catalyst systems.[12c] ^{13}C NMR analysis of typical polymer samples reveals that the polyethylenes contain a small amount of ethyl branches.[16] The degree of ethyl branching is 1−2 branches per 1000 C atoms for samples obtained with **11** and **12**, while the degree of ethyl branching for samples obtained with **9** and **10** is lower than 1 branch per 1000 C atoms.

Conclusions

The constrained geometry tetramethylcyclopentadienyl-phenoxytitanium dichlorides **9**−**12** can be synthesized with modified ligands **5**−**8** by the template lithium salt elimination reaction of corresponding ligand and $TiCl_4$ with 2 equiv of ^nBuLi. Complexes **9**−**12** are relatively stable to air and moisture and can be left in air for several days without obvious decomposition. They also show good thermostability and can be heated to about 200 °C without decomposition. ^1H and ^{13}C NMR spectra and X-ray crystallography indicate that **9**−**12** have C_s-symmetric structures. The Cp(cent)−Ti−O angle is about 107° for these complexes, which is characteristic of constrained geometry metallocene catalysts. Upon alkylation and activation with $Al(^iBu)_3$ and $Ph_3C^+B(C_6F_5)_4^-$, **9**−**12** exhibit good catalytic activity for ethylene polymerization. The catalytic activity of these complexes is obviously relative to the nature of the substituents at the phenoxy group, and the order of the catalytic activity under similar conditions is **9** > **10** > **11** ≈ **12**.

Experimental Section

General Comments. Reactions with organometallic reagents were carried out under a nitrogen atmosphere (ultra-high purity) using standard Schlenk techniques.[17] Solvents were dried and distilled prior to use.[18] Polymerization grade ethylene was further purified by passage through columns of 10 Å molecular sieves and MnO. $Al(^iBu)_3$, ^nBuLi, and $TiCl_4$ were purchased from Aldrich. 2-Bromophenol,[8] 2,3,4,5-tetramethyl-2-cyclopentenone,[19] and $Ph_3C^+B(C_6F_5)_4^-$ [20] were prepared according to literature procedures. NMR spectra were recorded on either a Varian Unity-400 or a Varian Mercury-300 NMR spectrometer.

Preparation of 2-(Tetramethylcyclopentadienyl)-4,6-di-*tert*-butylphenol (5). A solution of 2-bromo-4,6-di-*tert*-butylphenol (5.0 g, 17.5 mmol) in Et_2O (80 mL) was added dropwise to a solution of ^nBuLi (36.8 mmol) in Et_2O (20 mL) at −15 °C. The mixture was slowly warmed to room temperature and stirred overnight. To this solution was slowly added 2,3,4,5-tetramethyl-2-cyclopentenone (2.64 mL, 17.5 mmol) in Et_2O over 1 h. The resulting solution was then allowed to warm to room temperature and stirred overnight. The reaction mixture was hydrolyzed with 20 mL of saturated NH_4Cl(aq). The organic layer was separated and treated three times with 20 mL of concentrated HCl, then washed three times with water (50 mL), dried over $MgSO_4$, filtered, and evaporated to dryness, affording a brown oil. Pure product (2.9 g, 50.7%) was obtained by column chromatography over silica (hexanes/CH_2Cl_2, 9:1) as a yellow crystalline material. Anal. Calcd for $C_{23}H_{34}O$ (326.52): C, 84.60; H, 10.50. Found: C, 84.57; H, 10.49. ^1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.09 (s, 1H, Ph), 7.03 (s, 1H, Ph), 3.12 (s, 1H, OH), 2.63 (q, 1H, CpH), 1.64 (s, 3H, C_5Me_4), 1.56 (s, 3H, C_5Me_4), 1.56 (s, 3H, C_5Me_4), 1.35 (s, 9H, ^tBu), 1.30 (s, 9H, ^tBu), 1.21 (d, 3H, C_5Me_4). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 153.91, 142.37, 138.25, 132.63, 132.44, 131.87, 122.26, 119.34, 100.68, 57.85, 51.16, 34.60, 32.15, 31.88, 29.59, 25.11, 20.64, 12.76, 9.68 ppm.

Preparation of 2-(Tetramethylcyclopentadienyl)-6-*tert*-butylphenol (6). Compound **6** was prepared in the same manner as **5** with 2-bromo-6-*tert*-butylphenol (5.0 g, 21.8 mmol) as starting material. Pure product (2.7 g, 45.8%) was obtained as a yellow oil. Anal. Calcd for $C_{19}H_{26}O$ (270.41): C, 84.39; H, 9.69. Found: C, 84.34; H, 9.65. ^1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.06 (d, 1H, Ph), 7.03 (d, 1H, Ph), 6.78 (t, 1H, Ph), 3.15 (s, 1H, OH), 2.63 (q, 1H, CpH), 1.67 (s, 3H, C_5Me_4), 1.59 (s, 3H, C_5Me_4), 1.57 (s, 3H, C_5Me_4), 1.36 (s, 9H, ^tBu), 1.22 (d, 3H, C_5Me_4). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 156.26, 138.42, 133.09, 133.08, 132.51, 125.04, 122.57, 119.71, 100.66, 57.60, 51.24, 34.39, 29.49, 25.00, 20.57, 12.71, 9.66 ppm.

Preparation of 2-(Tetramethylcyclopentadienyl)-6-phenylphenol (7). Compound **7** was prepared in the same manner as **5** with 2-bromo-6-phenylphenol (5.0 g, 20.1 mmol) as starting material. Pure product (2.3 g, 39.4%) was obtained as a yellow oil. Anal. Calcd for $C_{21}H_{22}O$ (290.40): C, 86.85; H, 7.64. Found: C, 86.81; H, 7.62. ^1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.74−7.80 (m, 2H, Ph), 7.41−7.47 (m, 2H, Cp), 7.33−7.35 (m, 1H, Ph), 7.31 (d, 1H, Ph), 7.17 (d, 1H, Ph), 6.95 (t, 1H, Ph), 3.25 (s, 1H, OH), 2.72 (q, 1H, CpH), 1.74 (s, 3H, C_5Me_4), 1.63 (s, 3H, C_5Me_4), 1.63 (s, 3H, C_5Me_4), 1.28 (d, 3H, C_5Me_4). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 155.75, 138.91, 137.97, 133.73, 132.50, 128.62, 128.54, 128.45, 127.01, 123.94, 123.67, 120.64, 101.62, 57.89, 51.51, 25.03, 20.63, 12.73, 9.81 ppm.

Preparation of 2-(Tetramethylcyclopentadienyl)-6-methylphenol (8). Compound **8** was prepared in the same manner as **5** with 2-bromo-6-methylphenol (5.0 g, 26.7 mmol)

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Table 3. Crystal Data and Structural Refinements Details for 9, 10, and 11

	9	10	11
mol formula	$C_{23}H_{32}Cl_2OTi$	$C_{19}H_{24}Cl_2OTi$	$C_{21}H_{20}Cl_2OTi$
mol wt	443.29	387.18	407.17
cryst syst	monoclinic	tetragonal	orthorhombic
space group	*P*2(1)/*c*	*P*4(3)2(1)2	*Pna*2(1)
a/Å	9.3320(19)	10.197(3)	19.691(2)
b/Å	13.693(3)	10.197(3)	11.4221(13)
c/Å	18.994(4)	38.678(18)	8.9263(10)
α/deg	90	90	90
β/deg	101.47(3)	90	90
γ/deg	90	90	90
V/Å^3	2425.5(8)	4022(2)	2007.7(4)
Z	4	8	4
D_c/g cm^{-3}	1.214	1.279	1.347
F(000)	936	1616	840
abs coeff/mm^{-1}	0.583	0.693	0.698
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
collect range/deg	$3.64 \leq 2\theta \leq 50.06$	$4.14 \leq 2\theta \leq 49.96$	$4.12 \leq 2\theta \leq 46.58$
no. of reflns	5748	5281	9220
no. of indep reflns	4268	3527	2866
R_{int}	0.0238	0.0314	0.0398
no. of data/restraints/ params	4268/3/260	3527/0/215	2866/1/226
R	0.0523	0.0387	0.0302
R_w	0.1491	0.0308	0.0798
goodness of fit	0.959	0.606	1.019
largest diff peak and hole/e Å^{-3}	0.606 −0.257	0.164 −0.178	0.299 −0.150

as starting material. Pure product (2.2 g, 36.0%) was obtained as a pale yellow oil. Anal. Calcd for $C_{16}H_{20}O$ (228.33): C, 84.16; H, 8.83. Found: C, 84.11; H, 8.80. ^{1}H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.01 (d, 1H, Ph), 6.96 (d, 1H, CpH), 6.76 (t, 1H, Ph), 3.20 (s, 1H, OH), 2.64 (q, 1H, CpH), 2.21 (s, 3H, Ph-Me), 1.70 (s, 3H, C_5Me_4), 1.61 (s, 3H, C_5Me_4), 1.59 (s, 3H, C_5Me_4), 1.24 (d, 3H, C_5Me_4). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 156.94, 138.74, 132.46, 132.03, 131.87, 129.55, 122.12, 119.95, 101.09, 58.31, 51.31, 25.02, 20.59, 15.67, 12.71, 9.63 ppm.

Template Synthesis of (TCDBP)TiCl$_2$ (9). A solution of **5** (1.0 g, 3.1 mmol) in toluene (20 mL) was added dropwise to a solution of $TiCl_4$ (3.1 mmol) in toluene (40 mL), and the reaction mixture was stirred at room temperature for 1 h. A solution of ^{n}BuLi (6.2 mmol) was slowly added at −78 °C, and the reaction mixture was then allowed to warm to room temperature and stirred overnight. The precipitate was filtered off and the solvent was removed to leave a red residue. Recrystallization from CH_2Cl_2/hexane (1:5) gave pure product **9** as red crystals (0.56 g, 41.2%). Anal. Calcd for $C_{23}H_{32}Cl_2OTi$ (443.27): C, 62.32; H, 7.28. Found: C, 62.25; H, 7.23. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.33 (s, 1H, Ph), 7.12 (s, 1H, Ph), 2.42 (s, 6H, C_5Me_4), 2.04 (s, 6H, C_5Me_4), 1.354 (s, 9H, ^{t}Bu), 1.347 (s, 9H, ^{t}Bu). ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K): δ 171.60, 146.87, 145.72, 143.59, 134.82, 130.14, 128.88, 123.40, 123.11, 35.02, 34.76, 31.72, 29.52, 13.49, 13.00 ppm.

Template Synthesis of (TCBP)TiCl$_2$ (10). Reaction of the ligand **6** (3.5 mmol) and $TiCl_4$ (3.5 mmol) with ^{n}BuLi (7.0 mmol) in toluene (70 mL) was carried out in the same way as described above for the synthesis of **9**. Pure **10** (0.54 g, 39.8%) was obtained as red crystals. Anal. Calcd for $C_{19}H_{24}Cl_2OTi$ (387.17): C, 58.94; H, 6.25. Found: C, 58.88; H, 6.20. ^{1}H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.33−7.36 (m, 1H, Cp), 7.11−7.13 (m, 2H, Ph), 2.43 (s, 6H, C_5Me_4), 2.04 (s, 6H, C_5Me_4), 1.35 (s, 9H, ^{t}Bu). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 174.18, 146.05, 143.43, 136.53, 130.62, 129.47, 126.93, 126.79, 123.97, 35.14, 29.68, 13.73, 13.31 ppm.

Template Synthesis of (TCPP)TiCl$_2$ (11). Reaction of the ligand **7** (3.0 mmol) and $TiCl_4$ (3.0 mmol) with ^{n}BuLi (6.0 mmol) in toluene (60 mL) was carried out in the same way as described above for the synthesis of **9**. Pure **11** (0.43 g, 35.2%) was obtained as red crystals. Anal. Calcd for $C_{21}H_{20}Cl_2OTi$ (407.16): C, 61.95; H, 4.95. Found: C, 61.88; H, 4.90. ^{1}H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.24−7.64 (m, 8H, Ph), 2.44 (s, 6H, C_5Me_4), 2.11 (s, 6H, C_5Me_4). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 171.97, 145.85, 142.68, 136.44, 130.76, 130.24, 129.26, 129.01, 128.36, 127.81, 127.38, 126.61, 124.23, 13.60, 13.12 ppm.

Template Synthesis of (TCMP)TiCl$_2$ (12). Reaction of the ligand **8** (3.2 mmol) and $TiCl_4$ (3.2 mmol) with ^{n}BuLi (6.4 mmol) in toluene (65 mL) was carried out in the same way as described above for the synthesis of **9**. Pure **12** (0.29 g, 26.3%) was obtained as red crystals. Anal. Calcd for $C_{16}H_{18}Cl_2OTi$ (345.09): C, 55.69; H, 5.26. Found: C, 55.61; H, 5.21. ^{1}H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.19−7.23 (m, 1H, Ph), 7.03−7.12 (m, 2H, Ph), 2.43 (s, 6H, C_5Me_4), 2.18 (s, 3H, Ph-Me), 2.06 (s, 6H, C_5Me_4). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 173.65, 145.95, 143.16, 131.22, 130.55, 128.01, 126.20, 123.67, 123.55, 15.31, 13.53, 13.12 ppm.

X-ray Structure Determinations of 9, 10, and 11. Single crystals of **9**, **10**, and **11** suitable for X-ray structural analysis were obtained from the mixture of CH_2Cl_2/hexane (v/v 1:3). The data were collected at 293 K on the Siemens P4 four-circle diffractometer for **9** and **10** and the Bruker SMART-CCD diffractometer for **11** (graphite-monochromated Mo Kα radiation: $\lambda = 0.71073$ Å). Details of the crystal data, data collections, and structure refinements are summarized in Table 3. All structures were solved by direct methods[21] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealized positions. All calculations were performed using the SHELXTL[22] crystallographic software packages.

Ethylene Polymerization. A dry 250 mL steel autoclave was charged with 80 mL of toluene, thermostated at the desired temperature, and saturated with ethylene (1.0 bar). The polymerization reaction was started by injection of a mixture of catalyst and Al(^{i}Bu)$_3$ in toluene (10 mL) and a solution of $Ph_3C^+B(C_6F_5)_4^-$ in toluene (10 mL) at the same time. The vessel was repressurized to the needed pressure with ethylene immediately, and the pressure was maintained by continuously feeding ethylene. After 30 min, the polymerization was quenched by injecting acidified methanol [HCl (3 M)/

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(21) *SHELXTL*; PC Siemens Analytical X-ray Instruments: Madison WI, 1993.

(22) Sheldrick, G. M. *SHELXTL Structure Determination Programs*, Version 5.0; PC Siemens Analytical Systems: Madison, WI, 1994.

methanol, 1:1]. The mixture was stirred overnight, and the polymer was collected by filtration, washed with water and methanol, and dried at 60 °C in vacuo to a constant weight.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic positional parameters, bond lengths and angles, anisotropic temperature factors, and calculated hydrogen atom positions for **9**, **10**, and **11** and ^{1}H and ^{13}C NMR spectra for **5**−**12**. X-ray crystallographic files (CIF) for **9**, **10**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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