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Titanium(IV) complexes with monocyclopentadienyl and phenoxy-alkoxo ligands: Synthesis, structures and catalytic properties for ethylene polymerization

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Abstract

Three monochlorotitanium complexes $Cp'Ti(2,4\text{-}^tBu_2\text{-}6\text{-}(CPh_2O)C_6H_2O)Cl$ [$Cp' = \eta^5\text{-}C_5H_5$ (**2**), $\eta^5\text{-}C_5(CH_3)_5$ (**3**), $\eta^5\text{-}C_5H_2Ph_2CH_3$ (**4**)] have been synthesized in high yields (>90%) by the reaction of corresponding $Cp'TiCl_3$ with the dilithium salt of ligand $2,4\text{-}^tBu_2\text{-}6\text{-}(CPh_2OH)C_6H_2OH$ (**1**). When activated by $[Ph_3C]^+[B(C_6F_5)_4]^-$ and Al^iBu_3, complexes **2**–**4** exhibit reasonable catalytic activity for ethylene polymerization, producing polyethylenes with moderate molecular weights and melting points. Addition of excess water to complex **2** gave the oxo-bridged complex $[Ti(\eta^5\text{-}C_5H_5)(2,4\text{-}^tBu_2\text{-}6\text{-}(CPh_2O)C_6H_2O)]_2O$ (**5**). Complexes **4** and **5** were characterized by single crystal X-ray diffraction.

Keywords: Titanium complexes; Ethylene polymerization; Homogeneous catalysis; Metallocene catalysts

1. Introduction

Polyolefins are the largest volume synthetic materials used in the world, and have been almost applied in every aspect of our daily lives and productions. One of the most active areas of polyolefins research over the past decades has been the discovery and development of Ziegler–Natta catalysis for polymerization of ethylene and α-olefins. Since Kaminsky et. al. discovered the highly active zirconocene dichloride/methylaluminoxane (MAO) catalytic system for olefin polymerization [1], intensive research work has been focused on developing new Group 4 metallocene catalysts for improving catalytic activities and polymer properties [2,3]. Most of Group 4 metallocene and related complexes for olefin polymerization typically have two or more alkyl (or halide) groups attached to the metal. Examples of precatalysts containing only one such group are scarce [4], although they are active for olefin polymerization and are also of potential interest in the context of single-site olefin polymerization catalysis. Therefore, our current focus is the development of this class of monochlorotitanium complexes, and investigation of the influence of different substituents at cyclopentadienyl (Cp) on their catalytic activity.

In this work, a new bidentate chelating ligand $2,4\text{-}^tBu_2\text{-}6\text{-}(CPh_2OH)C_6H_2OH$ (**1**) was firstly synthesized and introduced into the monochlorotitanium system, based on the following considerations: (i) the phenoxy-alkoxo bidentate ligand comprising the alkoxo group linked with the phenol group has two different active oxygen functionalities in the metalation reaction, therefore increasing the selectivity of forming the desired complexes in the synthetic reaction; (ii) recently, Doherty et al. have reported that introducing phenyl groups on the alkoxo ligand are able to increase catalytic activity of the precatalysts $[CpTi\{NC_5H_4(CR_2O)\text{-}2\}Cl_2]$ [5], so here we choose the alkoxo ligand containing phenyl groups. With the new ligand, we successfully obtained a series of monochlorotitanium complexes

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Cp′Ti(2,4-${}^{t}Bu_2$-6-(CPh_2O)C_6H_2O)Cl (Cp′ = η^5-C_5H_5 (**2**), η^5-$C_5(CH_3)_5$ (**3**), η^5-$C_5H_2Ph_2CH_3$ (**4**)) which have different substituents in cyclopentadienyl in high yield (>90%), and studied their application in ethylene polymerization and their hydrolysis reactions.

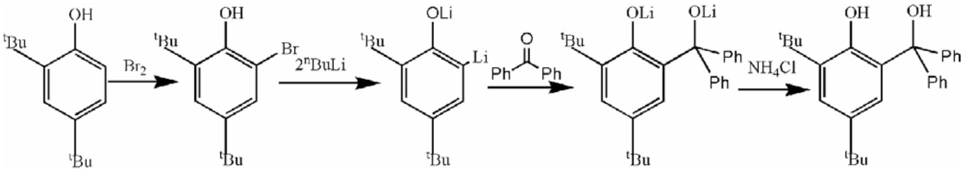
2. Results and discussion

2.1. Synthesis and characterization

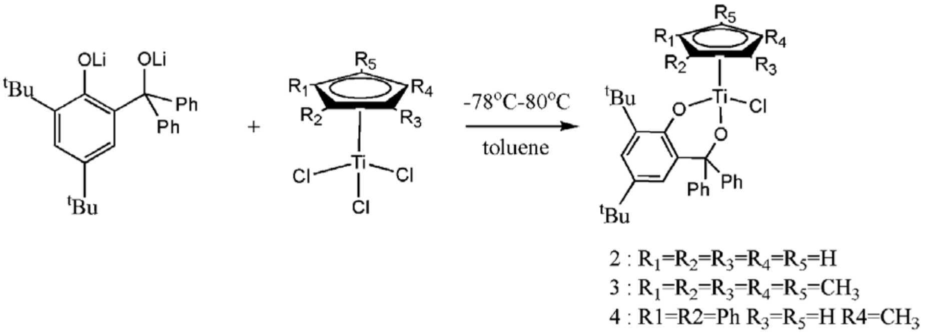
The new bidentate ligand **1** was synthesized with 2,4-di-*tert*-butylphenol as the starting material. 2-Bromo-4,6-di-*tert*-butylphenol was easily prepared from the reaction of Br_2 with 2,4-di-*tert*-butylphenol in $CHCl_3/CCl_4$ at 0 °C. The reaction of dilithium phenoxide, obtained by treating 2-bromo-4,6-di-*tert*-butylphenol with 2 equiv. of ^{n}BuLi, with benzophenone in Et_2O at −15 °C, followed by hydrolysis with saturated NH_4Cl produced the ligand **1** in a moderate yield (Scheme 1). The monochlorotitanium complexes **2**–**4** were prepared by reaction of Cp′$TiCl_3$ (Cp′ = η^5-C_5H_5, η^5-$C_5(CH_3)_5$, η^5-$C_5H_2Ph_2CH_3$) with equimolar amount of dilithium salt of 2,4-${}^{t}Bu_2$-6-(CPh_2OH)C_6H_2OH in toluene in high yields (Scheme 2). These complexes were found to be easily hydrolyzed. Addition of excess water to toluene solution of complex **2** gave the oxo-bridged complex [Ti(η^5-C_5H_5)(2,4-${}^{t}Bu_2$-6-(CPh_2O)C_6H_2O)]$_2$O (**5**) (Scheme 3). However, the same reaction with complexes **3** and **4** caused complete decomposition of both complexes to a mixture of unknown composition in which no organometallic complexes were isolated. All complexes were characterized by elemental analysis and NMR spectroscopy. Complexes **4** and **5** were characterized by single crystal X-ray diffraction.

2.2. Crystal Structures of 4 and 5

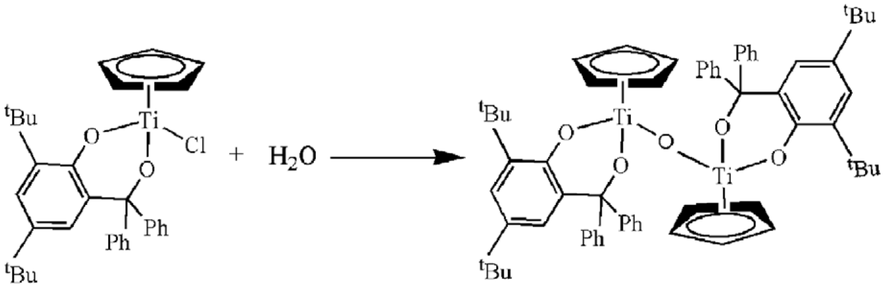
Crystals of complexes **4** and **5** suitable for single-crystal X-ray diffraction study were grown by cooling the saturated solutions of **4** and **5** in mixed CH_2Cl_2/hexane. The ORTEP drawings of the molecule structures are shown in Figs. 1 and 2. The selected bond lengths and angles are summarized in Table 1. The geometry around titanium in **4** can be described as a pseudo-tetrahedral coordination environment, which is defined by a substituted Cp ring



Scheme 1. Synthetic procedure of ligand **1**.



Scheme 2. Synthetic procedure of complexes **2**–**4**.



Scheme 3. Synthetic procedure of complex **5**.

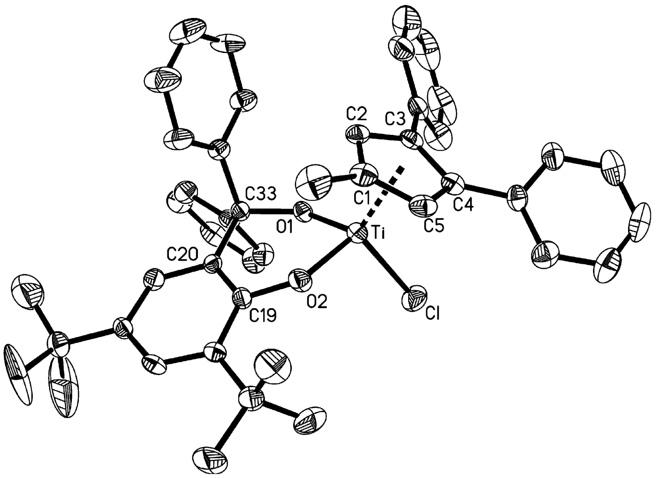


Fig. 1. Molecular structure of complex **4**.

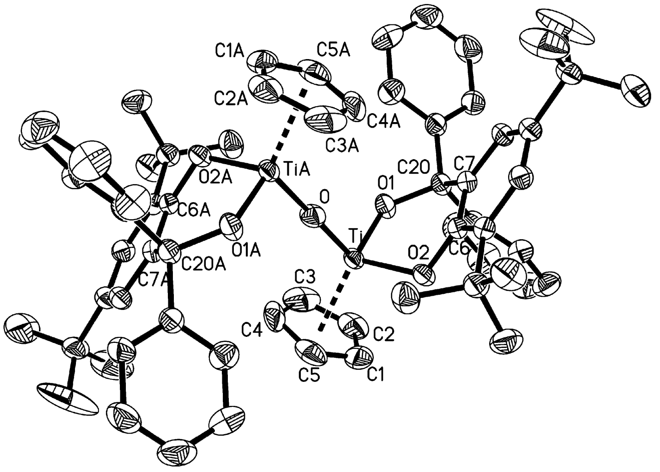


Fig. 2. Molecular structure of complex **5**.

(assuming Cp to occupy one coordination site), a chlorine atom, and two oxygen atoms from the phenol-alkoxo ligand. The phenol-alkoxo ligand adopts a puckered chelate disposition with the typical *boat* conformation. The Ti–C bond lengths range from 2.336 to 2.445 Å, and Ti–C4 (2.445 Å) are longer than those of known Ti–C (Cp ring carbon) bond lengths in similar monochlorotitanium complexes [4]. The C–C bond lengths in the substituted Cp ring range from 1.408 to 1.447 Å, and the C3–C4 (1.447 Å) bond length is the longest among these values, which could be explained by the steric and conjugate effects of the two phenyl groups on the Cp-ring.

The molecular structure of complex **5** consists of two [Ti(η^5-C_5H_5)(2,4-^{t}Bu$_2$-6-(CPh_2O)C_6H_2O)] units linked by Ti–O–Ti bridge. Each titanium is coordinated in a pseudo-tetrahedral geometry by a Cp ring, and three oxygen atoms (one from the oxo-bridge, and the other two from the phenoxy-alkoxo ligand). The C–C bond lengths in the Cp ring are close to the ones observed in know Ti–Cp ring carbon distances. The conformation of the phenol-alkoxo ligand 2,4-^{t}Bu$_2$-6-(CPh_2O)C_6H_2O in **5** is similar to complex **4**, showing a *boat* structure. The Ti–O (alkoxo) bond lengths of 1.778 Å in **4** and 1.803 Å in **5** are shorter than Ti–O (phenoxy) bond lengths of 1.831 Å in **4** and 1.848 Å in **5**, respectively, which may reflect O(pπ)–Ti(dπ) donation of alkoxo groups to the metal [5].

Table 1
Selected bond lengths and angles

Complex ***4***			
Ti–O(1)	1.778(3)	Ti–O(2)	1.831(4)
Ti–Cl	2.268(7)	Ti–C(1)	2.409(6)
Ti–C(2)	2.336(6)	Ti–C(3)	2.374(6)
Ti–C(4)	2.445(6)	Ti–C(5)	2.423(6)
O(1)–C(33)	1.428(6)	O(2)–C(19)	1.380(6)
C(1)–C(2)	1.420(8)	C(2)–C(3)	1.421(8)
C(3)–C(4)	1.447(7)	C(4)–C(5)	1.408(8)
C(1)–C(5)	1.408(7)	Cp(cent)–Ti	2.071
Cp(cent)–Ti–O(1)	121.5	Cp(cent)–Ti–O(2)	113.7
O(1)–Ti–O(2)	90.7(2)	O(1)–Ti–Cl	104.0(1)
O(2)–Ti–Cl	105.0(1)	Cp(cent)–Ti–Cl	117.7
Complex ***5***			
Ti–O(1)	1.803(2)	Ti–O	1.812(1)
Ti–O(2)	1.848(2)	Ti–C(1)	2.402(4)
Ti–C(2)	2.366(3)	Ti–C(3)	2.341(4)
Ti–C(4)	2.373(3)	Ti–C(5)	2.403(4)
O(2)–C(6)	1.377(3)	O(1)–C(20)	1.435(3)
C(1)–C(2)	1.348(7)	C(2)–C(3)	1.413(7)
C(3)–C(4)	1.408(7)	C(4)–C(5)	1.367(7)
C(1)–C(5)	1.345(6)	Cp(cent)–Ti	2.069
Cp(cent)–Ti–O(1)	119.5	Cp(cent)–Ti–O(2)	111.3
Cp(cent)–Ti–O	120.7	O(1)–Ti–O(2)	93.1(9)
O(1)–Ti–O	103.9(8)	O(2)–Ti–O	104.0(7)

2.3. Ethylene polymerization studies

The experimental results of ethylene polymerization with complexes **2**–**4** as precatalysts were summarized in Table 2. Upon activation with Al^{i}Bu$_3$ and $[Ph_3C]^+$-$[B(C_6F_5)_4]^-$, complexes **2**–**4** show good catalytic activity for ethylene polymerization, producing polyethylenes with moderate molecular weights and melting points. For complexes **2**–**4** the catalytic activity increases with the increase of Al/Ti ratio, and reaches the highest catalytic activity with the ratio Al/Ti of 150, while further increasing the Al/Ti ratio results in a decrease in catalytic activity. It is possible that excessive Al^{i}Bu$_3$ would consume so much $[Ph_3C]^+[B(C_6F_5)_4]^-$ that catalysts could not be efficiently activated [6]. The catalytic activity of all complexes increases with the increase of polymerization temperature, and reaches the highest value at 80 °C. Further increase in the polymerization temperature results in a decrease in the catalytic activity. The order of catalytic activity for ethylene polymerization under similar conditions (see run 2, 7 and 12 in Table 2) is **3** > **4** > **2**, which implies that both the electronic and steric factors of substituents on the cyclopentadienyl group play roles in determining catalytic activity of these complexes.

Table 2
Results of ethylene polymerization using procatalysts **2**–**4**[a]

Number	Catalyst	Al:Ti	T (°C)	Activity[b] × 10^{-5}	Mη[c] × 10^{-5}	T_m^d (°C)
1	2	100	80	0.64	2.12	134.7
2	2	150	80	1.32	2.32	135.2
3	2	200	80	1.16	1.98	134.2
4	2	150	60	0.44	1.86	134.0
5	2	150	100	0.92	1.71	134.5
6	3	100	80	2.88	2.89	134.6
7	3	150	80	7.22	3.11	136.3
8	3	200	80	5.16	3.37	135.8
9	3	150	60	4.04	2.74	134.9
10	3	150	100	5.12	2.88	135.1
11	4	100	80	1.82	3.67	133.7
12	4	150	80	2.52	3.01	134.2
13	4	200	80	1.76	2.76	134.1
14	4	150	60	1.52	2.52	133.6
15	4	150	100	1.74	2.34	133.3

[a] Polymerization conditions: solvent, 60 ml of toluene; catalyst, 2 μmol; B/Ti ratio, 1.3; time, 5 min.

[b] g PE (mol Ti)$^{-1}$ h^{-1} bar^{-1}.

[c] Measured in decahydronaphthalene at 135 °C.

[d] Determined by DSC at a heating rate of 10 °C min^{-1}.

3. Experimental

3.1. General comments

Reactions with organometallic reagents were carried out under an argon atmosphere (ultra-high purity) using standard Schlenk techniques [7]. Solvents were dried and distilled prior to use [8]. Polymerization grade ethylene was further purified by passage through columns of 10 Å molecular sieves and MnO. Al^{i}Bu$_3$, ^{n}BuLi and TiCl$_4$ were purchased from Aldrich. [η^5-C$_5$H$_5$]TiCl$_3$ [9], [η^5-C$_5$(CH$_3$)$_5$]TiCl$_3$ [10], [η^5-C$_5$H$_2$Ph$_2$CH$_3$]TiCl$_3$ [11], and [Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ [12] were prepared according to the literature procedures. NMR spectra were measured using a Varian Mercury-300 NMR spectrometer.

3.2. Synthesis of 2,4-^{t}Bu$_2$-6-(CPh$_2$OH)C$_6$H$_2$OH (*1*)

A solution of Br$_2$ (5.2 ml, 95 mmol) in CHCl$_3$ (20 ml) was added dropwise to a solution of 2,4-Di-*tert*-butylphenol (19.6 g, 95 mmol) in CHCl$_3$ (20 ml) and CCl$_4$ (20 ml) over 2 h at 0 °C. The mixture was stirred for 1 h at this temperature. The organic phase was separated, and washed six times with water (50 ml), dried with MgSO$_4$. Pure product (24.4 g, 90%) was obtained by column chromatography over silica (hexanes) as white crystals. A solution of 2-bromo-4,6-di-*tert*-butylphenol (5.71 g, 20 mmol) in Et$_2$O (40 ml) was added dropwise to a solution of ^{n}BuLi (40 mmol) in Et$_2$O (40 ml) at −15 °C. The mixture was slowly warmed to room temperature and stirred overnight. The solution was cooled to −15 °C, and a solution of benzophenone (7.32 g, 40 mmol) in Et$_2$O (20 ml) was added dropwise. The reaction mixture was stirred overnight and then quenched with 60 ml of saturated NH$_4$Cl (aq). The organic layer was separated, dried over MgSO$_4$, filtered, and concentrated by distillation under reduced pressure. Pure product (4.90 g, 64%) was obtained by column chromatography over silica (hexanes) as white needles. *Anal.* Calc. for C$_{27}$H$_{32}$O$_2$ (388.54): C, 83.46; H, 8.30. Found: C, 83.38; H, 8.24%. ^{1}H NMR (CDCl$_3$, 300 MHz; 298 K): δ 8.27 (s, 1H, Ph–OH), 7.17–7.35 (m, 11H, Ph), 6.33 (d, 1H, Ph), 3.47 (s, 1H, OH), 1.39 (s, 9H, Ph–^{t}Bu), 1.11 (s, 9H, Ph–^{t}Bu). C^{13} NMR (CDCl$_3$, 75.4 MHz) δ, ppm: 153.4, 145.6, 140.2, 136.9, 129.4, 128.1, 127.8, 127.7, 125.4, 124.0, 85.5, 35.5, 34.5, 31.9, 30.3.

3.3. Synthesis of [Ti(η^5-C$_5$H$_5$)(2,4-^{t}Bu$_2$-6-(CPh$_2$O)C$_6$H$_2$O)Cl] (*2*)

A solution of ^{n}BuLi in n-hexane (1.6 M, 1.6 ml) was added to a solution of 2,4-^{t}Bu$_2$-6-(CPh$_2$OH)C$_6$H$_2$OH (1.00 g, 2.57 mmol) in toluene (10 ml) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 1 h to give a solution of 2,4-^{t}Bu$_2$-6-(CPh$_2$OLi)C$_6$H$_2$OLi. This reaction mixture was added to a solution of CpTiCl$_3$ (0.56 g, 2.57 mmol) in toluene (5 ml) at −78 °C, and the reaction mixture was warmed slowly to room temperature and then heated for another 6 h at 80 °C. After allowing the mixture to cool to room temperature, the mixture was filtered, the solution was evaporated in vacuo, and the resultant solid was extracted with *n*-hexane. The extract was concentrated and placed in the freezer. The pale yellow microcrystals were collected. Yield 91% (1.25 g, 2.34 mmol). *Anal.* Calc. for C$_{32}$H$_{35}$ClO$_2$Ti (534.94): C, 71.85; H, 6.59. Found: C, 71.91; H, 6.49%. ^{1}H NMR (CDCl$_3$, 300 MHz; 298 K): δ 7.11–7.39 (m, 11H, Ph), 6.52 (d, 1H, Ph), 6.35 (s, 5H, Cp), 1.36 (s, 9H, Ph–^{t}Bu), 1.18 (s, 9H, Ph–^{t}Bu). C^{13} NMR (CDCl$_3$, 75.4 MHz) δ, ppm: 158.1, 147.6, 146.2, 142.9, 128.6, 128.1, 127.2, 126.5 125.4, 123.3, 118.3, 99.9, 35.3, 34.6, 31.1, 30.7.

3.4. Synthesis of [Ti(η^5-C$_5$(CH$_3$)$_5$)(2,4-^{t}Bu$_2$-6-(CPh$_2$O)C$_6$H$_2$O)Cl] (*3*)

Complex **3** was synthesized in the same way as described above for the synthesis of **2** with [η^5-C$_5$(CH$_3$)$_5$]TiCl$_3$ (0.74 g, 2.57 mmol) as the starting material. Pure complex **3** was obtained as yellow crystals. Yield 90% (1.40 g, 2.31 mmol). *Anal.* Calc. for C$_{37}$H$_{45}$ClO$_2$Ti (605.07): C, 73.45; H, 7.50. Found: C, 73.37; H, 7.42%. ^{1}H NMR (CDCl$_3$, 300 MHz; 298 K): δ 7.08–7.45 (m, 11H, Ph), 6.48 (d, 1H, Ph), 1.99 (s, 15H, Cp–Me), 1.39 (s, 9H, Ph–^{t}Bu), 1.03 (s, 9H, Ph–^{t}Bu). C^{13} NMR (CDCl$_3$, 75.4 MHz) δ, ppm: 156.1, 146.3, 145.2, 141.6, 128.8, 128.5, 127.4, 126.3, 125.4, 123.6, 118.8, 98.6, 35.3, 34.9, 31.8, 30.1, 12.6.

3.5. Synthesis of [Ti(η^5-C$_5$H$_2$Ph$_2$CH$_3$)(2,4-^{t}Bu$_2$-6-(CPh$_2$O)C$_6$H$_2$O)Cl] (*4*)

Complex **4** was synthesized in the same way as described above for the synthesis of **2** with [η^5-C$_5$H$_2$Ph$_2$CH$_3$] TiCl$_3$

(0.99 g, 2.57 mmol) as the starting material. Pure complex **4** was obtained as yellow crystals. Yield 95% (1.71 g, 2.44 mmol). *Anal.* Calc. for $C_{45}H_{45}ClO_2Ti$ (701.16): C, 77.08; H, 6.47. Found: C, 77.14; H, 7.54%. ^1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.06–7.46 (m, 21H, Ph), 6.51 (d, 1H, Ph), 6.32 (d, 1H, Cp), 6.19 (d, 1H, Cp), 1.98 (s, Cp–Me), 1.28 (s, 9H, Ph–^{t}Bu), 1.06 (s, 9H, Ph–^{t}Bu). C^{13} NMR ($CDCl_3$, 75.4 MHz) δ, ppm: 158.4, 148.2, 146.6, 143.2, 135.0, 134.2, 133.6, 132.8, 131.3, 129.7, 129.5, 129.4, 129.1, 128.8, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.4, 123.3, 118.9, 118.2, 99.5, 35.6, 34.5, 31.5, 30.5, 15.5.

3.6. Synthesis of $[Ti(\eta^5\text{-}C_5H_5)(2,4\text{-}^tBu_2\text{-}6\text{-}(CPh_2O)C_6H_2O)]_2O$ (**5**)

To a solution of complex **2** (0.60 g, 1.12 mmol) in toluene (20 ml) was added H_2O (0.04 g, 2 mmol) at room temperature. The reaction mixture was stirred for 12 h at room temperature, and the solvent was removed under vacuum. The residue was extracted with **n**-hexane. The extract was concentrated and placed in the freezer. The yellow microcrystals were collected. $[Ti(\eta^5\text{-}C_5H_5)(2,4\text{-}^tBu_2\text{-}6\text{-}(CPh_2O)\text{-}C_6H_2O)]_2O$ (**5**): Yield 80% (0.91 g, 0.90 mmol). *Anal.* Calc. for $C_{64}H_{70}O_5Ti_2$ (1014.97): C, 75.73 H, 6.95. Found: C, 75.66; H, 7.01%. ^1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.06–7.46 (m, 22 H, Ph), 6.51 (d, 2H, Ph), 5.91 (s, 10H, Cp), 1.36 (s, 18H, Ph–^{t}Bu), 1.07 (s, 18H, Ph–^{t}Bu). C^{13} NMR ($CDCl_3$, 75.4 MHz) δ, ppm: 158.8, 148.1, 146.7, 142.1, 129.1, 128.5, 127.7, 126.1, 125.0, 123.1, 118.9, 107.6, 35.1, 34.2, 31.9, 30.2.

3.7. X-ray structure determinations of **4** and **5**

Single crystals of complexes **4** and **5** suitable for X-ray structural analysis were obtained from the mixture of CH_2Cl_2/hexane. The data were collected at 293 K on Rigaku R-AXIS RAPID IP diffractometer for complexes **4** and **5** with Mo Kα ($\lambda = 0.71073$ Å). Details of the crystal data, data collections, and structure refinements are summarized in Table 3. Both structures were solved by direct methods [13] 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 position. All calculations were performed using the SHELXTL [14] crystallographic software packages.

3.8. Ethylene polymerization

A dry 250 ml steel autoclave was charged with 50 ml of toluene, thermostated at desired temperature and saturated with ethylene (1.0 bar). The polymerization reaction was started by injection of a mixture of catalyst and Al^iBu_3 in toluene (5 ml) and a solution of $[Ph_3C]^+[B(C_6F_5)_4]^-$ in toluene (5 ml) at the same time. The vessel was repressurized to needed pressure with ethylene immediately and the pressure was kept by continuously feeding of ethylene. After 5 min, the polymerization was quenched by injecting acidified methanol [HCl (3M)/methanol = 1:1], and the polymer was collected by filtration, washed with water, methanol, and dried at 60 °C in vacuo to a constant weight.

Table 3
Crystal data and structural refinements details for **4** and **5**

	4	**5**
Molecular formula	$C_{45}H_{45}ClO_2Ti$	$C_{64}H_{70}O_5Ti_2$
Molecular weight	701.16	1015.00
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.174(4)	10.721(8)
b (Å)	10.511(0)	11.192(8)
c (Å)	22.379(3)	13.145(7)
α (°)	77.27(7)	103.86(7)
β (°)	82.02(0)	102.81(5)
γ (°)	68.98(0)	104.76(5)
V (Å^3)	1960.8(3)	1412.1(8)
Z	2	1
D_{calc} (g cm^{-3})	1.188	1.194
$F(000)$	740	538
Absorption coefficient (mm^{-1})	0.321	0.330
Collect range (°)	$0.93 \leqslant \theta \leqslant 25$	$1.67 \leqslant \theta \leqslant 27.48$
Number of independent reflections	6058	6274
R_{int}	0.0238	0.0599
Number of data/restraints/parameters	6058/0/449	6274/0/328
$R_1(I > 2\sigma)$	0.0617	0.0720
$wR_2(I > 2\sigma)$	0.1538	0.1800
Goodness-of-fit	0.997	0.958
Largest difference in peak and hole (e Å^{-3})	0.384 and −0.380	0.786 and −0.558

4. Conclusions

We have synthesized and characterized three new monochlorotitanium complexes based on mono-Cp and phenoxy-alkoxo mixed ligands. These complexes were found to be stable in air, but can be easily hydrolyzed. The reaction of complex **2** with excess water gave the oxo-bridged complex **5**. When activated with $[Ph_3C]^+[B(C_6F_5)_4]^-$ and Al^iBu_3, these monochlorotitanium complexes exhibit good catalytic activity for ethylene polymerization and produce moderate molecular weight polyethylene. These new catalysts represent a valuable addition to the limited list of monochlorotitanium ethylene polymerization catalysts.

5. Supplementary material

CCDC 623912 and 623913 contain the supplementary crystallographic data for **4** and **5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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