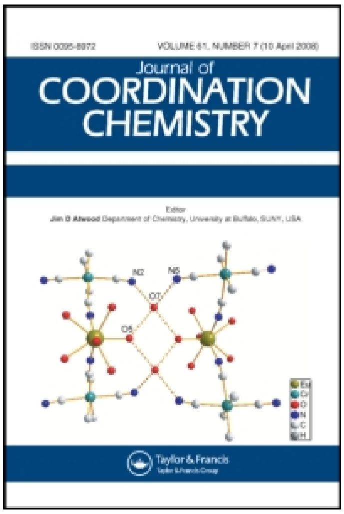

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New binuclear half-titanocene derivatives with aryl-substituted cyclopentadienyl ligands: synthesis, structures, and catalytic properties

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New binuclear half-titanocene derivatives with aryl-substituted cyclopentadienyl ligands: synthesis, structures, and catalytic properties

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Two binuclear oxo-bridged half-titanocene complexes, μ-oxo-bis[(1-aryl-2,3,4,5-tetramethylcyclopentadienyl)dichlorotitanium] [$(ArMe_4CpTiCl_2)_2O$, Ar = 4-$^iPrC_6H_4$ (**3**), 4-$^tBuC_6H_4$ (**4**)], have been prepared by the treatment of 1-aryl-2,3,4,5-tetramethylcyclopentadienyltitanium trichloride [$ArMe_4CpTiCl_3$, Ar = 4-$^iPrC_6H_4$ (**1**), 4-$^tBuC_6H_4$ (**2**)] with 0.5 equiv of H_2O. Complexes **3** and **4** have been characterized by elemental analysis and ^1H- and ^{13}C-NMR (nuclear magnetic resonance; NMR) spectroscopies, and their molecular structures have been determined by X-ray crystallography. When activated with $^iBu_3Al$ and $Ph_3CB(C_6F_5)_4$, complexes **3** and **4** both exhibit reasonable catalytic activity for ethylene polymerization (90×10^3 to 280×10^3 kg PE (mol Ti)$^{-1}$ bar^{-1} h^{-1}), producing polyethylenes with moderate molecular weight.

Keywords: Binuclear complexes; Ethylene polymerization; Metallocene catalysts; Polyethylene; Titanium complexes

1. Introduction

Group 4 metallocene-based complexes have attracted extensive attention due to their application as catalyst precursors for homogeneous olefin polymerization and copolymerization [1–3]. Many studies focused on the development of homogeneous metallocene catalysts for producing a variety of high-performance polyolefins and establishing new strategy with control over catalyst activity and selectivity with regard to polymer chain composition and architecture [4–8]. Mononuclear metallocene complexes have been extensively investigated as homogeneous catalysts for ethylene polymerization and copolymerization with α-olefins [9], cycloolefins [10], dienes [11], and polar monomers [12]. However, only limited research on the development of binuclear metallocene catalysts have been reported [13]. The most interesting thing for developing the binuclear catalyst systems is that these systems offer the opportunity of

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cooperative effects exerted by two adjacent metal centers [14]. In this regard, binuclear metallocene catalysts linked by different bridging units have been explored to investigate both their structural features and catalytic properties [15]. This research is focused on substituted monocyclopentadienyl titanium derivatives with special electronic and steric properties. Such titanium complexes are sensitive to H_2O and can be easily converted to corresponding oxo-bridged binuclear complexes in solution. Herein we report the synthesis and structural characterization of two binuclear oxo-bridged half-titanocene complexes, μ-oxo-bis[(1-aryl-2,3,4,5-tetramethylcyclopentadienyl)dichlorotitanium] [$(ArMe_4CpTiCl_2)_2O$, Ar = 4-^{i}PrC_6H_4 (**3**), 4-^{t}BuC_6H_4 (**4**)], as well as their catalytic performance for ethylene polymerization.

2. Results and discussion

2.1. *Synthesis of 3 and 4*

The binuclear oxo-bridged half-titanocene complexes, **3** and **4**, were readily synthesized by the treatment of 1-aryl-2,3,4,5-tetramethylcyclopentadienyltitanium trichloride [$ArMe_4CpTiCl_3$, Ar = 4-^{i}PrC_6H_4 (**1**), 4-^{t}BuC_6H_4 (**2**)] with 0.5 equiv of H_2O in diethyl ether according to the modified literature procedure [16]. Complexes **1** and **2** were prepared similar to a published procedure [17] in high yields as red solids. Both **1** and **2** are relatively stable to air and moisture in the solid state, while very sensitive to H_2O in solution, and can be easily converted to the oxo-bridged complexes **3** and **4** by hydrolysis. Analytically pure **3** and **4** could be obtained by recrystallization from methylene chloride/hexane as red crystalline solids. Both complexes are soluble in methylene chloride, diethyl ether, toluene and benzene, while slightly soluble in *n*-hexane and *n*-pentane. Similar to **1** and **2**, complexes **3** and **4** are also sensitive to H_2O and moisture, and have to be stored under an inert atmosphere. These titanium complexes were all characterized by ^{1}H- and ^{13}C-NMR spectroscopies along with elemental analysis. ^{1}H-NMR spectra of **3** and **4** show two characteristic signals at 2.30–2.40 ppm for $CpCH_3$, similar to those of their parent complexes **1** and **2**. In ^{13}C-NMR spectra, both **3** and **4** give all 11 signals for their C_5Me_4Ar ligands with the $CpCH_3$ carbons shifted about 0.9–1.2 ppm upfield in comparison to the corresponding signals in **1** and **2**. These data are in good agreement with their structures.

2.2. *Crystal structures of 3 and 4*

The molecular structures of **3** and **4** were determined by single crystal X-ray diffraction analysis. Oak Ridge thermal ellipsoid plot program (ORTEP) drawings of the molecular structures are shown in figures 1 and 2, respectively; selected bond lengths and angles are summarized in table 1. For both complexes, the two Ti ions are symmetrically linked by μ-O which resides on a crystallographic twofold rotation axis. The coordination geometry around titanium can be described as a pseudo-octahedron, consisting of a substituted cyclopentadienyl ring, two chlorides, and one oxygen. The Ti–C distances in **3** and **4** are in the range of 2.341(4)–2.413(3) Å, similar to the values observed previously for similar complexes [16, 18]. The Ti–O bond lengths (1.8108(7) Å for **3** and 1.8056(8) Å for **4**) are slightly shorter than the average Ti–O distance (1.8120 Å) reported for related

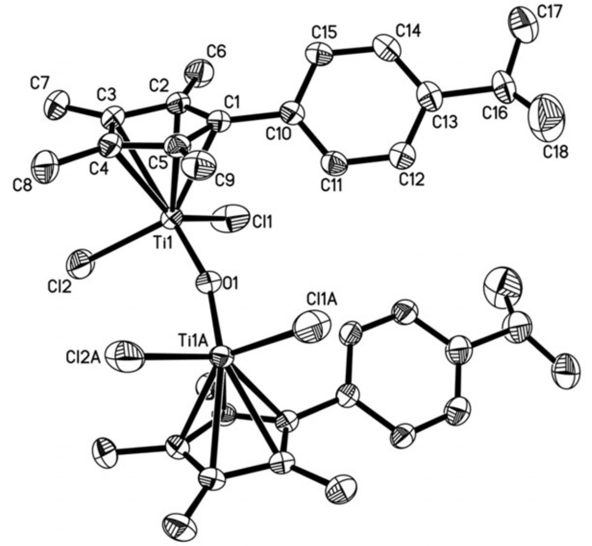

Figure 1. The molecular structure of **3**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogens have been omitted for clarity.

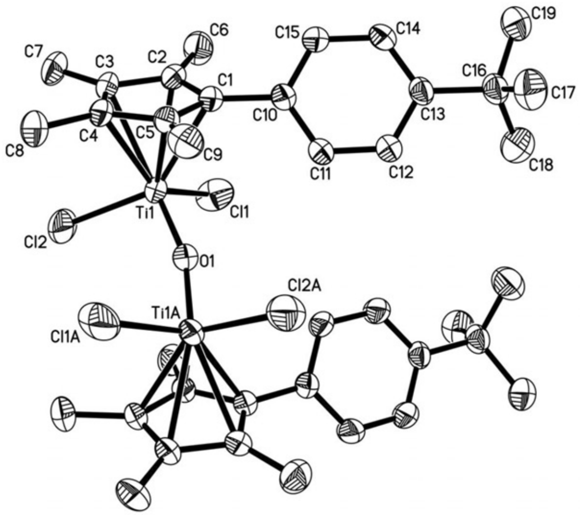

Figure 2. The molecular structure of **4**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogens have been omitted for clarity.

oxo-bridged titanium complexes [18–20]. The Ti–O–Ti angles in **3** and **4** (163.03(16)° and 163.67(19)°, respectively) are in the normal range (150–180°) observed for oxo-bridged titanocene analogues [21, 22]. The two cyclopentadienyl rings are nearly parallel, with an angle of 1.70(6)° for **3** and 1.41(2)° for **4**. The angle between the Cp ring and the adjacent phenyl ring for **3** [44.01(5)°] is smaller than that for **4** [53.80(7)°]. The 4-*iso*-propylphenyl in **3** shows rotational disorder with site occupancy factors of 0.618/0.382 for two

Table 1. Selected bond lengths and angles for **3** and **4**.

Complex **3**			
Ti(1)–C(1)	2.353(2)	Ti(1)–Cl(1)	2.2524(10)
Ti(1)–C(2)	2.410(2)	Ti(1)–Cl(2)	2.2563(10)
Ti(1)–C(3)	2.394(3)	Ti(1)–O(1)	1.8108(7)
Ti(1)–C(4)	2.346(3)	Ti(1)–Cp(cent)	2.041(3)
Ti(1)–C(5)	2.357(3)		
O(1)–Ti(1)–Cl(1)	103.31(7)	Ti(1)–O(1)–Ti(2)	163.03(16)
O(1)–Ti(1)–Cl(2)	102.01(8)	O(1)–Ti(1)–C(1)	102.92(8)
Cl(1)–Ti(1)–Cl(2)	103.40(5)	O(1)–Ti(1)–C(2)	137.71(9)
Cp(cent)–Ti(1)–O(1)	118.60(2)	O(1)–Ti(1)–C(3)	143.25(8)
Cp(cent)–Ti(1)–Cl(1)	113.51(7)	O(1)–Ti(1)–C(4)	108.64(9)
Cp(cent)–Ti(1)–Cl(2)	114.20(5)	O(1)–Ti(1)–C(5)	87.77(7)
Complex **4**			
Ti(1)–C(1)	2.359(3)	Ti(1)–Cl(1)	2.2442(13)
Ti(1)–C(2)	2.413(3)	Ti(1)–Cl(2)	2.2506(13)
Ti(1)–C(3)	2.386(3)	Ti(1)–O(1)	1.8056(8)
Ti(1)–C(4)	2.341(4)	Ti(1)–Cp(cent)	2.043(1)
Ti(1)–C(5)	2.362(4)		
O(1)–Ti(1)–Cl(1)	103.11(8)	Ti(1)–O(1)–Ti(2)	163.67(19)
O(1)–Ti(1)–Cl(2)	102.14(9)	O(1)–Ti(1)–C(1)	102.99(10)
Cl(1)–Ti(1)–Cl(2)	103.43(7)	O(1)–Ti(1)–C(2)	137.52(11)
Cp(cent)–Ti(1)–O(1)	118.70(3)	O(1)–Ti(1)–C(3)	143.44(12)
Cp(cent)–Ti(1)–Cl(1)	113.31(6)	O(1)–Ti(1)–C(4)	108.96(12)
Cp(cent)–Ti(1)–Cl(2)	114.30(8)	O(1)–Ti(1)–C(5)	88.03(10)

different positions, caused by rotation around the C10–C13 axis by approximately 16.5°. Similarly, the 4-*tert*-butylphenyl group in **4** also exhibits rotational disorder, which results in each of the terminal methyl carbons having two positions with site occupancy factors of 0.507/0.493.

2.3. *Ethylene polymerization*

Ethylene polymerizations were carried out using **3** and **4** as precatalysts under different conditions, and the results are summarized in table 2. Upon activation with $Al(^{i}Bu)_3$ and $Ph_3CB(C_6F_5)_4$, **3** and **4** exhibit reasonable catalytic activity for ethylene polymerization, producing polyethylenes with moderate molecular weight ($M\eta = 3.1 \times 10^4$ to $4.4 \times 10^4\,g\,mol^{-1}$). Under the same conditions, the binuclear **3** and **4** show similar catalytic activities to that observed for the mononuclear **1** and **2** (entries 9, 10 in table 2); the molecular weight of the polyethylenes produced by **3** and **4** are close to that obtained with **1** and **2**. These results imply that the catalytic active species formed in these catalyst systems might be the same. The Ti–O–Ti bond in **3** and **4** may be cleaved during the activation reaction with $Al(^{i}Bu)_3$ and $Ph_3CB(C_6F_5)_4$. Similar results have been reported for other binuclear oxo-bridged titanium catalyst systems, $[Me_2Si(C_5Me_4)$(3-*tert*-butyl-5-methyl-2-phenoxy)$TiCl]_2(\mu\text{-O})$ and $(Cp^{N\cdot HCl}CpTiCl)_2(\mu\text{-O})$ ($Cp^{N\cdot HCl} = C_5H_4CH_2CH_2NMe_2\cdot HCl$) [23].

The effect of Al/Ti molar ratio on the catalytic activity of **3** and **4** was examined, with highest catalytic activity reached at an Al/Ti molar ratio about 150 for both catalyst systems. Further increase in the Al/Ti molar ratio would result in a decrease in catalytic activity. These results are in agreement with those observed for other half-titanocene catalyst systems [17]. It has been reported that excess $Al(^{i}Bu)_3$ would consume

Table 2. Summary of ethylene polymerizations catalyzed by **3** and **4** activated with $Al(^iBu)_3$ and $Ph_3CB(C_6F_5)_4$.[a]

Catalyst	Al : Ti	T (°C)	Yield (g)	Activity[b]	$M\eta^c \times 10^{-4}$	T_m (°C)[d]
3	100	70	0.62	186	4.09	130.5
3	150	70	0.86	258	3.53	126.8
3	200	70	0.70	210	3.18	124.0
3	150	50	0.32	96	4.25	131.0
4	100	70	0.65	195	3.89	130.4
4	150	70	0.91	273	3.63	126.5
4	200	70	0.75	225	3.15	125.1
4	150	50	0.36	108	4.39	131.6
1	150	70	0.71	213	3.57	126.7
2	150	70	0.76	228	3.68	127.0

[a] Polymerization conditions: solvent 60 mL of toluene, catalyst 1 μmol (2 μmol for **1** and **2**), B/Ti ratio 2.0, time 20 min, ethylene pressure 5 bar.
[b] Polymerization activity: 10^3 kg PE $(\text{mol Ti})^{-1}\,\text{bar}^{-1}\,\text{h}^{-1}$.
[c] Measured in decahydronaphthalene at 135°C.
[d] Determined by DSC at a heating rate of $10°\text{C min}^{-1}$.

$Ph_3CB(C_6F_5)_4$ and lead to the formation of $[Al^iBu_2]^+[B(C_6F_5)_4]^-$ [24]. The catalytic performance of these catalysts is also dependent on polymerization temperature, increasing for **3** and **4** with increase in polymerization temperature, and reaching the highest catalytic activity about 70°C. Differential scanning calorimetry (DSC) analysis on the obtained PE samples reveals a single melting point in the range of 124.0–132.0°C, which is typical for metallocene catalyzed polyethylene.

3. Experimental

3.1. *General comments*

All manipulations involving air- and moisture-sensitive compounds were carried out under argon (ultra-high purity) using either standard Schlenk techniques or glovebox techniques. Solvents were dried and distilled prior to use [25]. Polymerization grade ethylene was further purified by passage through columns of 5 Å molecular sieves and MnO. Complexes **1** and **2** [16], as well as $Ph_3CB(C_6F_5)_4$ [26] were prepared according to the literature procedures. NMR spectra were measured using a Varian Mercury-300 NMR spectrometer. Elemental analyses were performed on a Perkin Elmer 240c element analyzer. Melting transition temperatures (T_m) of the polyethylenes were determined by DSC (Du Pont 910 differential scanning calorimeter) at a heating rate of $10°\text{C min}^{-1}$. Viscosity-average molecular weights of the polyethenes were determined in decahydronaphthalene at 135°C using an Ubbelohde viscosimeter.

3.2. *Synthesis of 3*

A mixture of Et_2O (15 mL) and H_2O (9.0 μL, 0.50 mmol) was slowly added to a solution of **1** (393.6 mg, 1.00 mmol) in Et_2O (15 mL) at room temperature. After the reaction solution was stirred for an additional 48 h, the solvent was removed *in vacuo*, and the residue was extracted with CH_2Cl_2/*n*-hexane (1 : 3, 2 × 10 mL). The solution was concentrated to give a red solid (312.0 mg, 85.7%). Single crystals of **3** suitable for X-ray diffraction were obtained by recrystallization from a mixture of CH_2Cl_2 : *n*-hexane (1 : 5) at room temperature. Anal. Calcd for $C_{36}H_{46}Cl_4OTi_2$ (732.30) (%): C, 58.88; H, 6.59. Found (%): C, 58.70; and H, 6.37. ^{1}H-NMR ($CDCl_3$, 300 MHz, 298 K): 1.28 (d, 12H, $CH(CH_3)_2$), 2.34 (s, 12H, Cp-CH_3), 2.38 (s, 12H, Cp-CH_3), 2.92–2.97 (m, 2H, $CH(CH_3)_2$), and 7.25–7.33 (m, 8H, C_6H_5). ^{13}C-NMR ($CDCl_3$, 75 MHz, 298 K): 13.42, 14.67, 23.89, 30.27, 126.2, 130.4, 130.8, 133.3, 134.8, 138.7, and 148.5.

3.3. *Synthesis of 4*

Complex **4** was synthesized from **2** by the same procedures as described for **3**. Complex **4** was obtained in 83.6% yield as a red crystalline solid. Anal. Calcd for $C_{38}H_{50}Cl_4OTi_2$ (760.38) (%): C, 59.87; H, 6.82. Found (%): C, 59.52; and H, 6.58. ^{1}H-NMR ($CDCl_3$, 300 MHz, 298 K): 1.35 (s, 18H, $C(CH_3)_3$), 2.34 (s, 12H, Cp-CH_3), 2.37 (s, 12H, Cp-CH_3), and 7.29–7.42 (m, 8H, C_6H_5). ^{13}C-NMR ($CDCl_3$, 75 MHz, 298 K): 13.42, 14.67, 31.32, 34.65, 125.0, 130.1, 130.5, 133.3, 134.8, 138.6, and 150.7.

3.4. *X-ray structure determinations of 3 and 4*

Crystals of **3** and **4** suitable for X-ray structure determination were obtained from a saturated solution of CH_2Cl_2 : *n*-hexane (1 : 5, v/v) at room temperature. The data were collected at 293(K) on the Rigaku RAXIS-RAPID diffractometer using Mo-Kα radiation. The structures were solved by direct methods [27] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogens were included in idealized positions. All calculations were performed using the SHELXTL crystallographic software packages [28]. Details of the crystal data, data collections, and structure refinements are summarized in table 3.

3.5. *Polymerization reactions*

Ethylene polymerizations were carried out according to the following procedure: A dry 250 mL steel autoclave was charged with 50 mL of toluene, thermostated at the desired temperature and saturated with 1.0 bar of ethylene. The polymerization reaction was started by the addition of a mixture of catalyst and $Al(^iBu)_3$ in toluene (5 mL) and a solution of $Ph_3CB(C_6F_5)_4$ in toluene (5 mL) at the same time. The reaction mixture was stirred for 20 min under 5 bar of ethylene. The polymerization was then quenched by injecting 120 mL of acidified methanol [HCl (3 mol L^{-1})/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.

4. Conclusions

Two new binuclear oxo-bridged half-titanocene complexes, **3** and **4**, were synthesized by hydrolysis of the corresponding monocyclopentadienyl titanium complexes. The molecular structures of **3** and **4** were determined by X-ray crystallography.

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

	3	**4**
Empirical formula	$C_{36}H_{46}Cl_4OTi_2$	$C_{38}H_{50}Cl_4OTi_2$
Formula weight	732.33	760.38
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
Unit cell dimensions (Å, °)		
a	16.661(3)	16.763(3)
b	13.876(3)	13.851(3)
c	15.927(3)	16.976(3)
α	90	90
β	97.81(3)	99.55(3)
γ	90	90
Volume (Å^3), Z	3647.8(13), 4	3886.9(14), 4
Calculated density (g cm^{-3})	1.333	1.299
Absorption coefficient (mm^{-1})	0.757	0.713
$F(000)$	1528	1592
θ range for data collection (°)	3.08–27.48	3.16–27.48
Limiting indices	$-21 \le h \le 21$; $-17 \le k \le 18$; $-20 \le l \le 17$	$-21 \le h \le 21$; $-17 \le k \le 17$; $-19 \le l \le 22$
R(int)	0.0275	0.0630
Goodness-of–fit on F^2	1.083	1.062
Final R indices [$I > 2\sigma(I)$]	$R_1{}^a = 0.0508$, $wR_2{}^b = 0.1418$	$R_1 = 0.0633$, $wR_2 = 0.1513$
R indices (all data)	$R_1 = 0.0627$, $wR_2 = 0.1481$	$R_1 = 0.1098$, $wR_2 = 0.1725$
Largest difference peak and hole (e Å^{-3})	0.542 and -0.457	0.457 and -0.361

[a] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$.
[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

When activated with $Al(^iBu)_3$ and $Ph_3CB(C_6F_5)_4$, both **3** and **4** exhibit good catalytic activity for ethylene polymerization, producing polyethylene with moderate molecular weight.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers: 755767 (**3**); 755768 (**4**). Copies of this information may be obtained free of the charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccd.cam.ac.uk).

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