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Synthesis, structures, and catalytic properties of dimeric constrained geometry diphenylcyclopentadienyl-phenoxyoxochlorotitanium(IV) complexes

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Abstract

High-yield synthesis (>90%) of two dimeric diphenyl cyclopentadienyl-phenoxyoxochlorotitanium(IV) complexes **3**, and **4** has been achieved by hydrolysis of the monomeric 2-(3,4-diphenyl-cyclopentadienyl)-4,6-di-*tert*-butyl phenoxytitanium dichloride (**1**) and 2-(3,4-diphenyl-cyclopentadienyl)-6-*tert*-butyl phenoxytitanium dichloride (**2**). The molecular structure of **3** has been determined by single-crystal X-ray analysis. Both complexes have been characterized by ¹H and ¹³C NMR spectroscopy. When activated with ^{*i*}Bu₃Al and Ph₃C⁺B(C₆F₅)₄⁻, complexes **3** and **4** exhibit reasonable catalytic activity for ethene polymerization, producing polyethylenes with moderate molecular weights and melting temperatures. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Constrained geometry catalysts; Ethylene polymerization; Metallocenes; Titanium

1. Introduction

Group 4 constrained geometry metallocene catalysts which have an appended chelating heteroatom donor group on the cyclopentadienyl ligand have received extensive attention in recent years [1,2]. Especially the constrained geometry catalysts with a pendant nitrogen donor on the cyclopentadienyl ligand have been widely studied in industry [3–8] as well as academic institutions [9–18]. In comparison, the constrained geometry catalysts with a pendant oxygen donor on the cyclo-

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pentadienyl ligand received less attention although a number of catalysts of this type have also been reported [19–27]. Recently, we have reported a series of new constrained geometry cyclopentadienyl–phenoxytitanium dichloride complexes [28] by modifying the ligand of Marks catalyst [29]. During the course of study on the stability of these new complexes, it was found these complexes can be easily hydrolysized to produce dimeric oxo-bridged complexes in solution. While they are stable to air and moisture in solid state and can be left in air for several days without obvious decomposition. Here, we report the synthesis and characterization of the dimeric oxo-bridged complexes, as well as their catalytic performance in ethene polymerization.

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2. Experimental

2.1. General comments

All non-hydrolytic procedures were carried out under a nitrogen atmosphere (ultra-high purity) using standard schlenk techniques [30]. Solvents were dried and distilled prior to use [31]. Polymerization grade ethene was further purified by passage through columns of 10 A molecular sieves and MnO. Al(^{*i*}Bu)₃, ^{*n*}BuLi and TiCl₄ were purchased from Aldrich. 2-(3, 4-diphenyl cyclopentadienyl)-4, 6-di-*tert*-butyl phenoxytitanium dichloride (1), 2-(3, 4-diphenyl cyclopentadienyl)-6*tert*-butyl phenoxytitanium dichloride (2) [28], and Ph₃C⁺B(C₆F₅)⁻ [32–34] were prepared according to literature procedures. NMR spectra were measured using a Varian Unity-400 or Varian Mercury-300 NMR spectrometer. Hydrolysis reactions were carried out in air using commercial solvents without purification.

2.2. Preparation of $\{[\eta^5; \eta^1-2-(3,4-Ph_2Cp)-4,6-di-^tBu-C_6H_2O]TiCl\}_2O(3)$

Complex 1 (100 mg, 0.185 mmol) was dissolved in CH_2Cl_2 (20 mL), the color of the solution changed slowly from red to yellow (Scheme 1). After 24 h, the solvent was removed to leave a yellow solid. Recrystallization from CH_2Cl_2 :hexane (1:3) gave pure 3 as orange yellow crystals (88.3 mg, 93.0%). Anal. Calc. for C₆₂H₆₄Cl₂O₃Ti₂ (1023.81): C, 72.73; H, 6.30. Found: C, 72.67; H, 6.25%. ESI-MS, m/z: 927.6 $[M - {}^{t}Bu - 3CH_2 + 2H]^+$, 814.4 $[M - 2{}^{t}Bu - 2CI]$ $- 2CH_2 + 3H^{\dagger}$, 701.4 $[M - 2^tBu - 2CO - 6CH_2 2Cl + 2H^{+};$ MALDI-MS, m/z: 842.7 [M - 2CO - $4CH_2 - 2Cl + 2H$], 422.7 [ligand]⁺. ¹H NMR (CDCl₃, 300 MHz; 298 K) & 6.73-7.58 (m, 24H, Ph), 6.81 (d, ${}^{4}J_{H-H} = 3$ Hz, 2H, Cp), 4.49 (d, ${}^{4}J_{H-H} = 3$ Hz, 2H, Cp), 1.40 (s, 18H, Ph-^tBu), 1.30 (s, 18H, Ph-^tBu). ¹³C NMR (CDCl₃, 75 MHz; 298 K) δ 171.8, 145.7, 143.8, 134.9, 133.4, 132.8, 131.3, 130.4, 130.3, 129.8, 129.6, 129.5, 128.5, 128.3, 128.2, 128.0, 126.6, 124.0, 122.8, 35.3, 35.1, 32.1, 29.9 ppm.

2.3. Preparation of $\{[\eta^5; \eta^1-2-(3, 4-Ph_2Cp)-6^{-t}Bu-C_6H_3O]TiCl\}_2O$ (4)

Complex 4 (100 mg, 0.207 mmol) was prepared in the same way as described above for the synthesis of **3** (Scheme 1). Pure **4** (86 mg, 91.2% was obtained as yellow solid); *Anal.* Calc. for $C_{54}H_{48}Cl_2O_3Ti_2$ (911.60): C, 71.15; H, 5.31. Found: C, 71.09; H, 5.27%. ESI-MS, *m/z*: 814.4 [M - 2Cl - 2CH₂ + 1H]⁺, 701.4 [M - 2CO - 4CH₂ - 2Cl - 2Me + 2H]⁺; MALDI-MS, *m/z*: 730.8 [M - 2CO - 4CH₂ - 2Cl + 2H]⁺; MALDI-MS, *m/z*: 730.8 [M - 2CO - 4CH₂ - 2Cl + 2H]⁺; 366.7 [ligand]⁺. ¹H NMR (CDCl₃, 300 MHz; 298 K) δ 6.77-7.59 (m, 26H, Ph and 2H, Cp), 4.60 (d, ⁴J_{H-H} = 3 Hz, 2H, Cp), 1.29 (s, 18H, Ph-^{*t*}Bu). ¹³C NMR (CDCl₃, 75 MHz; 298 K) δ 174.0, 143.7, 136.1, 134.4, 132.3, 131.5, 130.4, 130.1, 129.9, 129.8, 129.6, 128.7, 128.4, 128.3, 128.0, 127.0, 126.5, 125.9, 122.3, 35.0, 29.7 ppm.

2.4. X-ray structure determinations of 3

Single crystals of **3** suitable for X-ray structural analysis were obtained from solution of CH₂Cl₂:hexane (V/ V = 1/3). Diffraction data were collected at 293 K on a Bruker SMART-CCD diffractometer (graphite-monochromated Mo K α -radiation: $\lambda = 0.71073$ Å). Details of the crystal data, data collections, and structure refinements are summarized in Table 1. The structure was solved by direct method [35] 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 [36] crystallographic software packages.

2.5. Polymerization reactions

A dry 250 mL steel autoclave was charged with 70 mL of toluene, thermostated at desired temperature and saturated with ethene (1.0 bar). The polymerization reaction was started by injection of a mixture of catalyst and $Al({}^{i}Bu)_{3}$ in toluene (5 mL) and a solution of $Ph_{3}C^{+}B(C_{6}F_{5})_{4}^{-}$ in toluene (5 mL) at the same time.



Scheme 1. Synthetic procedure of complexes 3-4.

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 Table 1

 Crystal data and structural refinements details for 3

•	
Empirical formula	C ₃₁ H ₃₂ ClO _{1.50} Ti
Formula weight	511.92
Crystal system	monoclinic
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Space group	C2/c
a (Å)	24.863(5)
$b(\mathbf{A})$	9.902(2)
<i>c</i> (Å)	23.726(6)
β (°)	106.540(5)
Volume (Å ³)	5599(2)
Ζ	8
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.215
$F(0\ 0\ 0)$	2152
Absorption coefficient (mm ⁻¹)	0.423
Scan type	$\omega - 2\theta$
2θ Range (°)	$3.42 \leqslant 2\theta \leqslant 46.56$
Reflections collected	6354
Reflections unique (R_{int})	3983 (0.0381)
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	3983/7/312
Goodness-of-fit on F^2	0.917
Final <i>R</i> indices $[I \ge 2\sigma(I)]$	$R1 = 0.0522, wR_2 = 0.1155$
R indices (all data)	$R_1 = 0.1047, wR_2 = 0.1327$
Largest difference peak	0.355 and -0.281
and hole (e $Å^{-3}$)	

The vessel was repressurized to needed pressure with ethene immediately and the pressure was kept by continuously feeding monomer. After 30 min, the polymerization was quenched by injecting acidified methanol [HCl (3 M):methanol = 1:1]. The mixture was stirred overnight and the polymer was collected by filtration, washed with water, methanol, and dried in vacuo.

3. Results and discussions

3.1. Synthesis and analysis of complexes 3 and 4

It has been found that complexes 1 and 2 are stable to air and moisture in solid state and can be left in air for several days without obvious change [28]. They also exhibit good thermostability and could be heated to about 200 °C without decomposition. However, complexes 1 and 2 can be easily hydrolyzed in solution to produce corresponding dimeric oxo-bridged complexes 3 and 4, which can be obtained in high yields by dissolving 1 and 2 in wet solvent, such as CH_2Cl_2 , toluene, and hexanes. Similar hydrolysis reaction for titanocene type complexes has been reported previously [37-39]. In some instances, stable polynuclear oxo-bridged species containing dimer, trimer and tetramer had been produced by aerobic oxidation [40] or hydrolysis processes [41– 45]. In our case, only the dimeric hydrolytic product 3 or 4 has been obtained and no polynuclear oxo-bridged complex has been observed.

¹H and ¹³C NMR spectra of **3** and **4** are obviously complicated than those of 1 and 2, which could be attributed to that the dimeric oxo-bridged complexes 3 and 4 both adopt a chiral environment about Ti atom. For this reason, the two phenyl groups on the Cp ring and the two protons of the Cp group of 3 and 4 are inequivalent. As a result, the number of inequivalent C in ¹³C NMR spectra of 3 and 4 is six more than that of complexes 1 and 2, respectively. Due to steric repulsion between two units of the molecule, the ¹H NMR signal for one of the two protons shifts to high-field ($\delta = 4.49$ ppm for 3, $\delta = 4.60$ ppm for 4), while the signal for the other proton does not change very much compared to the Cp protons of complexes 1 and 2 [28] (6.81 ppm for 3, the signal for 6 is mixed with the signals of the Ph protons). The coupling constant $({}^{4}J_{H-H})$ of the two protons for 3 and 4 are both about 3 Hz.

3.2. Crystal structure of 3

The molecular structure of complex **3** was determined by single crystal diffraction analysis. The ORTEP drawing of the molecular structure is shown in Fig. 1. The selected bond lengths and angles are summarized in Table 2. The molecular structure consists of two $\{[\eta^5;\eta^1-2-(3,4-Ph_2Cp)-4,6-di-'Bu-buty]-C_6H_2O]TiCl\}$ units linked by Ti–O–Ti linkage. Selected bond lengths and angles for one unit will be used in subsequent discussions. The whole molecule adopts a C_2 -symmetric structure. The geometry around titanium can be described as pseudo-tetrahedral, which is defined by a substituted cyclopentadienyl ring, a chloride atom, and two oxygen atoms (one is from the oxo-bridge, the other is from the phenoxy). The Cp(cent)–Ti1–O2 angle of 105.9° is slightly smaller than the one in **2**



Fig. 1. Structure of complex 3. (Thermal ellipsoids are drawn at the 30% probability level.)

Table 2Selected bond lengths and angles for complex 3

Ti(1)–O(1)	1.8125(9)
Ti(1)-C(1)	2.332 (4)
Ti(1)–C(3)	2.470(4)
Ti(1)-C(5)	2.309(4)
O(2)–C(7)	1.377(4)
C(1)–C(6)	1.473(5)
C(4)–C(26)	1.483(5)
Ti(1)-H(5)	2.861
O(1)-Ti(1)-O(2)	104.16(10)
Cpl(cent)-Ti(1)-O(1)	119.1
Ti(1)-Cp1(cent)-C(1)	87.1
C(1)-C(6)-C(7)	113.7(4)
C(7)–O(2)–Ti(1)	128.9(3)
Ti(1)–O(2)	1.842(3)
Ti(1)-C(2)	2.385(4)
Ti(1)-C(4)	2.396(4)
Ti(1)-Cl(1)	2.2607(15)
Cp(cent)–Ti(1)	2.051
C(3)–C(20)	1.477(6)
Ti(1)-H(2)	2.957
O(2)-Ti(1)-Cl(1)	106.58(10)
O(1)-Ti(1)-Cl(1)	102.48(11)
Cp1(cent)-Ti(1)-O(2)	105.9
C(6)-C(1)-Cp(cent)	169.3
C(6)-C(7)-O(2)	114.5(4)

(106.7°) [28], indicating similar sterically open features for 3 to complexes 1 and 2 as catalyst precursors. The Til– C_{ring} (av.) distance of 2.378 Å is slightly longer than the one in 2 2.362 Å. The distances of Ti1-C2 2.384(5) Å and Ti1–C3 (2.470(4) Å) are longer than the one of Ti1-C5 (2.309(4)) and Ti1-C4 (2.396(4)), respectively, which could be obviously attributed to the sterical repulsion between the bulky ligands on the two Ti atoms. The phenolate plane – Cp plane dihedral angle is 86.0° and the (phenolate)C-C(ring) vector is bent 10.3° from the Cp ring plane. The corresponding data for 2 are 86.5° and 9.4°, reflecting more steric strain in 3 than in 2. The Ti-O2 bond lengths of 1.842(3) Å is shorter than that in 2 (1.818(4) Å) and the Ti-O-C7 angles of 128.9(3)° is larger than the one in 2 (129.8(4)°), indicating less Ti-O double-bond character in complex 3 [17,46-48].

3.3. Ethene polymerization studies

Complexes 3 and 4 were studied as ethene polymerization catalysts and the results were summarized in Table 3. Upon activation with Al(^{*i*}Bu)₃ and Ph₃C⁺B(C₆F₅)₄⁻, complexes 3 and 4 both show good catalytic activity for ethene polymerization, producing polyethylenes with moderate molecular weights and melting temperatures. The order of the catalytic activity for ethene polymerization under similar conditions (see run 2, 5 on Table 3) is 3 > 4, which could be attributed to the nature of the substituents on the phenolate. As seen from the structures of complexes 3 and 4, the electron-donating effect of the ^tBu group at the para position of the phenolate would increase the catalytic activity of complex 3. For both 3 and 4, the catalytic activity increases with the increase in Al/Ti ratio and reaches the highest catalytic activities with the Al/Ti ratio about 40. Further increasing in the Al/Ti ratio results in decrease in the catalytic activity. Under the same conditions the catalytic activities for ethene polymerization of complexes 3 $(1.8-3.1 \times 10^6 \text{ g})$ polymer/mol Ti) and 4 $(1.3-2.3 \times 10^6 \text{ g polymer/mol Ti})$ are roughly equal to those of their corresponding dichloride complexes 1 (1.9–3.2 \times 10⁶ g polymer/mol Ti) and 2 $(1.3-2.0 \times 10^6 \text{ g polymer/mol Ti})$ [28], which could be explained by that the catalytic active species produced during the polymerization from 1 and 2 should be the same as that produced from 3 and 4.

4. Conclusions

Two new dimeric oxo-bridged cyclopentadienyloxochlorotitanium(IV) complexes **3** and **4** have been synthesized by hydrolysis of the corresponding dichlorides **1** and **2**. Structures of **3** and **4** have been confirmed by ¹H and ¹³C NMR spectra and X-ray crystallography. When activated with ^{*i*}Bu₃Al and Ph₃C⁺B(C₆F₅)₄⁻, complexes **3** and **4** exhibit reasonable catalytic activity for ethylene polymerization, producing polyethylenes with moderate molecular weights and melting temperatures.

Table 3
ummary of ethene polymerization catalyzed by complexes 3 and 4 (activated by $Ph_3C^+[B(C_6F_{5)4}]^-)^a$

•		•	• •				
Run	Catalyst	Al:Ti	<i>T</i> (°C)	Amount of polymer (g)	Activity ^b	$M\eta^{\rm c} \times 10^{-4}$	$T_{\rm m} (^{\circ}{\rm C})^{\rm d}$
1	3	20	80	2.11	2160	4.5	122.7
2	3	40	80	3.07	3143	3.9	123.2
3	3	60	80	1.78	1822	4.7	124.1
4	4	20	80	1.44	1313	5.0	124.3
5	4	40	80	2.29	2088	4.3	125.4
6	4	60	80	1.31	1194	4.8	126.4

^a Polymerization conditions: solvent 80 mL of toluene, catalyst 1 mg, B/Ti ratio 1.5, time 30 min, ethene pressure 5 bar.

^b kg $PE (mol Ti)^{-1} h^{-1}$.

^c Measured in decahydro-naphthalene at 135 °C.

^d Determined by DSC at a heating rate of $10 \circ C \min^{-1}$.

5. Supplementary data

¹H and ¹³C NMR spectra for **3** and **4** are available in supplementary data. The Crystallographic data for **3** has been deposited with Cambridge Crystallographic Data Center as supplementary publication number CCDC: 225984. Copies of this information can be obtained free of charge via 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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