

Synthesis, structures and catalytic properties of stable oxo-bridged half-sandwich titanium complexes

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Abstract

Hydrolysis of 1,2-diphenyl-4-R-cyclopentadienyl titanium trichloride (R = Me (**1**), *n*-Bu (**2**)) affords the corresponding oxo-bridged monocyclopentadienyl titanium compounds (1,2-Ph₂-4-R-CpTiCl₂)₂(μ-O) (R = Me (**3**), *n*-Bu (**4**)), new dinuclear species. The molecular structures of complexes **3** and **4** have been confirmed by single-crystal X-ray diffraction. Both complexes have been characterized by elemental analysis, ¹H and ¹³C NMR spectroscopy. When activated with Al(^tBu)₃ and Ph₃C⁺B(C₆F₅)₄⁻, complexes **3** and **4** show reasonable catalytic activity for ethylene polymerization, producing polyethylenes with moderate molecular weights, and upon activation with methylaluminoxane (MAO), complexes **3** and **4** exhibit high catalytic activity and syndiospecificity for the polymerization of styrene. © 2007 Elsevier Ltd. All rights reserved.

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1. Introduction

Group 4 metallocene catalysts have attracted extensive interest due to their applications in the fields of organometallic chemistry, catalysis and polymer science [1–3]. In particular titanium catalysts based on the cyclopentadienyl ligand have been widely studied as active catalysts employed in industry and academic institutions [4–15]. It is well known that even minor modification of the ligands can result in remarkable changes in catalytic activity, as well as polymer properties, such as molecular weight, comonomer incorporation and stereoregularity [16–20]. Thus, it is of great significance to develop new homogeneous catalysts producing a number of high performance polyolefins. Recently we have reported a series of diphenyl substituted cyclopentadienyl titanium trichloride complexes as precatalysts for styrene polymerization [21]. Fur-

ther study on these titanium systems found that these complexes could be readily hydrolyzed to produce corresponding dimeric compounds in solution. In previous instances, dinuclear complexes bearing a cyclopentadienyl ligand play a significant role in some catalytic processes, because a cooperative effect of two close reactive metal centers is generated to accomplish unusual coordination modes [22]. Herein we report the synthesis and structural characterization of the oxo-bridged binuclear complexes, as well as their catalytic performance in ethylene and styrene polymerization.

2. Experimental

2.1. General comments

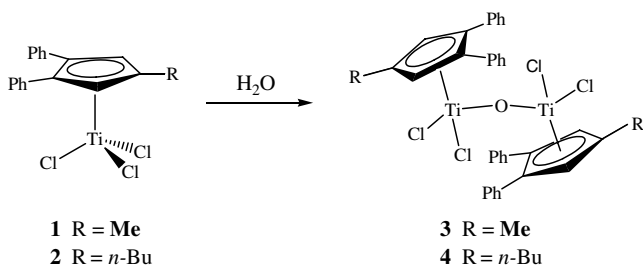
All manipulations involving air and moisture sensitive compounds were carried out under a nitrogen atmosphere (ultra-high purity) using either standard Schlenk techniques or glovebox techniques. Et₂O and toluene were

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dried over sodium/benzophenone under nitrogen and were freshly distilled prior to use. CH_2Cl_2 and *n*-hexane were refluxed under nitrogen over calcium hydride and distilled before use. Methylaluminoxane (MAO, 10 wt.% solution in toluene, $M = 800 \text{ g mol}^{-1}$, $\text{Al} = 5.3 \text{ wt.}\%$) was purchased from Wtico. $\text{Al}(\text{t-Bu})_3$, methyl lithium, *n*-butyl lithium and titanium tetrachloride were purchased from Aldrich. 1,2-Diphenyl-4-methyl-cyclopentadienyl titanium trichloride (**1**), 1,2-diphenyl-4-*n*-butyl-cyclopentadienyl titanium trichloride (**2**) [21] and $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)^-$ [23–25] were prepared according to the literature procedures. The crystal structure was determined with a CCD diffraction apparatus. NMR spectra were measured using a Varian Mercury-300 NMR spectrometer. Elemental analyses were performed on a Perkin–Elmer 240c element analyzer. Viscosity-average molecular weights of the polyethylenes were determined in decahydronaphthalene at 135°C using a Schott Gerate Mod. AVS/T2 Ubbelohde viscosimeter. Viscosity-average molecular weights of the polystyrenes were determined in *o*-dichlorobenzene at 135°C using a Schott Gerate Mod. AVS/T2 Ubbelohde viscosimeter. Melting transition temperatures (T_m) of the polyethylenes and polystyrenes were determined by DSC (Du Pont 910 differential scanning calorimeter) at a heating rate of $10^\circ\text{C min}^{-1}$.

2.2. Synthesis of (1,2-Ph₂-4-Me-CpTiCl₂)₂(μ-O) (**3**)

A mixture of Et_2O (20 mL) and distilled H_2O (9.0 μL, 0.50 mmol) was slowly added at -15°C to solid complex **1** (385.5 mg, 1.00 mmol), and the obtained solution was warmed to room temperature and stirred for 48 h (Scheme 1). The solvent was removed *in vacuo*, and the resulting residue was extracted with a mixed solvent of CH_2Cl_2 /*n*-hexane (1:3, $15 \times 2 \text{ mL}$). The solution was concentrated to give a red solid (317.3 mg, 88.6%). Red crystals of the complex suitable for X-ray diffraction were obtained by recrystallization from a mixture of CH_2Cl_2 /*n*-hexane (1:5) at room temperature. *Anal.* Calc. for $\text{C}_{36}\text{H}_{30}\text{Cl}_4\text{OTi}_2$ (716.20): C, 60.37; H, 4.22. Found: C, 60.31; H, 4.18%. $^1\text{H NMR}$ (CDCl_3 , 300 MHz, 298 K): δ 2.40 (s, 6H, CH_3), 6.87 (s, 4H, C_5H_2), 7.28–7.50 (m, 20H, C_6H_5). $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz, 298 K): δ 17.2 (CH_3), 128.9, 133.4, 137.9 (C_5H_2), 123.2, 128.4, 129.7, 136.3 (C_6H_5).



Scheme 1. Synthetic procedure of complexes **3–4**.

2.3. Synthesis of (1,2-Ph₂-4-*n*-Bu-CpTiCl₂)₂(μ-O) (**4**)

Compound **4** was prepared in the same manner as described above for the synthesis of **3** (Scheme 1), and isolated in 89.2% as a red crystalline solid. *Anal.* Calc. for $\text{C}_{42}\text{H}_{42}\text{Cl}_4\text{OTi}_2$ (800.36): C, 63.03; H, 5.29. Found: C, 63.05; H, 5.21%. $^1\text{H NMR}$ (CDCl_3 , 300 MHz, 298 K): δ 0.91 (t, $^3J_{\text{HH}} = 7.7 \text{ Hz}$, 6H, CH_3), 1.35 (m, $^3J_{\text{HH}} = 7.5 \text{ Hz}$, 4H, CH_2), 1.60 (m, $^3J_{\text{HH}} = 7.6 \text{ Hz}$, 4H, CH_2), 2.73 (t, $^3J_{\text{HH}} = 7.8 \text{ Hz}$, 4H, CH_2), 6.88 (s, 4H, C_5H_2), 7.27–7.50 (m, 20H, C_6H_5). $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz, 298 K): δ 14.1, 22.6, 31.4, 32.7 (C_4H_9), 128.9, 133.4, 143.3 (C_5H_2), 122.3, 128.4, 129.8, 136.1 (C_6H_5).

2.4. X-ray structure determination 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. Diffraction data were collected at 293 K on a Bruker SMART-CCD diffractometer using $\text{Mo K}\alpha$ radiation. The structures were solved using direct methods and refined by full-matrix least-squares procedures [26]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in ideal positions. All calculations were performed using the SHELXTL crystallographic software packages [27]. Relevant crystallographic data are summarized in Table 1.

2.5. Polymerization of ethylene

The ethylene polymerizations (runs 1–8) were carried out according to the following procedure: A dry 250 mL steel autoclave with a magnetic stirrer was charged with 70 mL of toluene, thermostated at the desired temperature and saturated with ethylene (1.5 bar). The polymerization reaction was initiated by addition of a mixture solution of precatalyst and $\text{Al}(\text{t-Bu})_3$ in toluene (5 mL) and a solution of $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ in toluene (5 mL) at the same time. The gaseous ethylene was then admitted into the reactor vessel through a gas purification column. The gas pressure was maintained at 6 bar throughout the polymerization period by means of a pressure manometer. After 15 min, the polymerization was quenched by addition of 120 mL of 1:1 (v/v) methanol and HCl solution. The white polymer was collected by filtration, washed several times with water, methanol, and dried to a constant weight under vacuum.

2.6. Polymerization of styrene

The styrene polymerizations (runs 1–10) with complexes **3** and **4** were carried out according to the following procedure: A 250 mL Schlenk flask with a magnetic stirrer was attached to high vacuum line and then sealed under a nitrogen atmosphere. Fifty milliliters of toluene, 5 mL of freshly distilled styrene and an appropriate amount of MAO were added to the flask which was placed in an oil bath at the

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