

# Diphenyl substituted cyclopentadienyl titanium trichloride derivatives: Synthesis, crystal structure and properties as catalysts for styrene polymerization

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## Abstract

New titanium complexes, 1,2-diphenyl-4-R-cyclopentadienyl titanium trichloride (R = Me (**4**), *n*-Bu (**5**), Ph (**6**)) have been synthesized. The crystal structure of complex **4** has been determined by X-ray diffraction analysis. All the titanium complexes were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. In the presence of methylaluminoxane (MAO), these complexes show high catalytic activity and syndiospecificity for the polymerization of styrene. The catalytic activity of the three complexes increases in the order of **6** < **5** < **4**.

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## 1. Introduction

In recent years, group IV metallocene complexes have been extensively studied as homogeneous catalysts for olefin polymerization in the fields of organometallic chemistry, catalysis and polymer science [1–5]. Stereospecific olefin polymerization catalyzed by metallocene catalysts can produce polymers with new microstructures and has thus attracted extensive attention in both academic and industrial communities [6]. Syndiotactic polystyrene (sPS) was first synthesized by Ishihara and coworkers with monocyclopentadienyl titanium catalysts activated with methylaluminoxane (MAO) [7]. Subsequently, a large number of monocyclopentadienyl titanium complexes were synthesized and studied to obtain better catalysts [8]. It has been known that even a minor modification of the cyclo-

pentadienyl ligand can result in a remarkable change in the catalytic properties of this type of catalysts, such as the catalytic activity, stereospecificity and polymer properties [9–18]. However, to our knowledge, few groups have studied the synthesis of monocyclopentadienyl titanium complexes with aromatic substituents on the cyclopentadienyl ring. In this paper, we wish to report the synthesis and characterization of three new 1,2-diphenyl-4-R-cyclopentadienyl titanium trichloride complexes (R = Me (**4**), *n*-Bu (**5**), Ph (**6**)), as well as their properties as catalysts for styrene polymerization.

## 2. Experimental

### 2.1. General procedures

All manipulations involving air and moisture sensitive compounds were carried out under a nitrogen (ultrahigh purity) atmosphere using standard Schlenk techniques. Tetrahydrofuran, diethyl ether and toluene were refluxed

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under nitrogen over Na\benzophenone and distilled before use. Methylene chloride, *n*-hexane and petroleum ether were refluxed under nitrogen over calcium hydride and distilled before use. Methylaluminoxane (MAO, 10 wt.% solution in toluene,  $M = 800 \text{ g mol}^{-1}$ , Al = 5.3 wt.%) was purchased from Wtico, *n*-butyl lithium, methyl lithium, phenyl lithium trimethylchlorosilane and titanium tetrachloride were purchased from Aldrich.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Mercury-300 NMR spectrometer with  $\text{CDCl}_3$  as solvent and TMS as an internal standard. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. Elemental analyses were performed on a Perkin–Elmer 240c element analyzer. The crystal structure was determined with a CCD diffraction apparatus. Viscosity-average molecular weights of the polystyrenes were determined in *o*-dichlorobenzene at  $135^\circ\text{C}$  using a Schott Gerate Mod. AVS/T2 Ubbelohde viscosimeter. Melting transition temperatures ( $T_m$ ) of the 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 ligands

1,2-Diphenyl-4-methylcyclopentadiene (**1**) and 1,2,4-triphenylcyclopentadiene (**3**) were synthesized according to the literature procedures [19,20]. Compound **1** was obtained as a white crystalline material after purification by column chromatography through silica (methylene chloride/petroleum ether, 1:4 in v/v). Yield: 68%. ESI-MS,  $m/z$ : 232.4  $[\text{M}]^+$ , 178.1  $[\text{M}-\text{CH}_3-\text{C}_3\text{H}_3]^+$ .  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  16.4 ( $\text{CH}_3$ ), 49.1, 132.3, 137.6, 141.6, 144.3 ( $\text{C}_5\text{H}_3$ ), 126.2, 127.1, 127.9, 128.4, 128.6, 137.6, 137.8 ( $\text{C}_6\text{H}_5$ ).

Compound **3** was purified by column chromatography through silica (methylene chloride/petroleum ether, 1:5 in v/v) as a white solid. Yield: 61%. ESI-MS,  $m/z$ : 294.3  $[\text{M}]^+$ , 178.2  $[\text{M}-\text{C}_6\text{H}_5-\text{C}_3\text{H}_3]^+$ .  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  45.2, 132.1, 137.1, 142.3, 145.3 ( $\text{C}_5\text{H}_3$ ), 125.2, 126.8, 127.2, 127.4, 128.0, 128.5, 128.7, 128.8, 129.0, 136.0, 137.4, 139.6 ( $\text{C}_6\text{H}_5$ ).

1,2-Diphenyl-4-*n*-butylcyclopentadiene (**2**) was synthesized by a similar procedure as follows: To a solution of butyl lithium (27.7 mmol) in THF (20 mL) was slowly added a solution of 3,4-diphenyl-2-cyclopentenone (7.03 g, 30 mmol) in THF (40 mL) under nitrogen with stirring at  $0^\circ\text{C}$ . The resulting solution was allowed to warm to room temperature slowly and stirred overnight. The reaction mixture was quenched with ice-water (60 mL), treated with concentrated hydrochloric acid (9 mL) and the organic layer was separated. The aqueous layer was extracted with diethyl ether ( $3 \times 20 \text{ mL}$ ). The combined organic layers were washed with 80 mL of saturated aqueous solution of sodium chloride, dried over anhydrous  $\text{MgSO}_4$ , filtered and evaporated under reduced pressure. The pure product (5.15 g, 62.5%) was obtained by column chromatography through silica (methylene chloride/petroleum ether, 1:4 in

v/v) as a yellowish oil. ESI-MS,  $m/z$ : 274.4  $[\text{M}]^+$ , 232.3  $[\text{M}-\text{C}_3\text{H}_6]^+$ , 178.2  $[\text{M}-\text{CH}_3-\text{C}_3\text{H}_3]^+$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  0.96 (s, 3H,  $\text{CH}_3$ ), 1.41 (q, 2H,  $\text{CH}_2$ ), 1.52 (q, 2H,  $\text{CH}_2$ ), 2.47 (t, 2H,  $\text{CH}_2$ ), 3.46 (s, 2H,  $\text{C}_5\text{H}_3$ ), 6.34 (s, 1H,  $\text{C}_5\text{H}_3$ ), 7.10–7.41 (m, 10H,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  14.2, 22.8, 30.7, 31.9 (*n*-Bu), 47.5, 131.2, 137.6, 141.4, 149.4 ( $\text{C}_5\text{H}_3$ ), 126.2, 127.1, 127.9, 128.4, 128.6, 128.6, 137.6, 137.8 ( $\text{C}_6\text{H}_5$ ).

## 2.3. Synthesis of 1,2-diphenyl-4-methyl-cyclopentadienyltitanium trichloride (**4**)

To a solution of 1,2-diphenyl-4-methyl-cyclopentadiene (1.16 g, 5.0 mmol) in diethyl ether (40 mL) was slowly added a solution of *n*-BuLi (5.1 mmol) in *n*-hexane (20 mL) at  $-78^\circ\text{C}$  with stirring. After 1 h, the reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed under vacuum and the residue was washed with dry *n*-hexane ( $3 \times 20 \text{ mL}$ ). The obtained white powder was dissolved in THF (30 mL), and  $\text{Me}_3\text{SiCl}$  (5.1 mmol) was slowly added at  $-78^\circ\text{C}$ . The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The solvent and excess  $\text{Me}_3\text{SiCl}$  were removed under reduced pressure. The residue was extracted with toluene (20 mL) and slowly added to a solution of  $\text{TiCl}_4$  (4.75 mmol) in 30 mL of toluene at  $-78^\circ\text{C}$ . The reaction mixture was allowed to warm to room temperature and stirred for 24 h. The precipitate was filtered off and the solvent was removed to leave a red solid. Recrystallization from methylene chloride/*n*-hexane (1:3 in v/v) gave pure **4** (1.30 g, 68.2%). *Anal. Calc.* for  $\text{C}_{18}\text{H}_{16}\text{Cl}_3\text{Ti}$  (385.54): C, 56.08; H, 3.92. Found: C, 56.00; H, 3.98%. IR (KBr,  $\text{cm}^{-1}$ ): 3100w, 2957w, 2925m, 2850w, 1491m, 1453w, 1424m, 1163w, 1079w, 1050w, 1022w, 889m, 769vs, 706vs, 676m, 663m.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  2.59 (s, 3H,  $\text{CH}_3$ ), 7.12 (s, 2H,  $\text{C}_5\text{H}_2$ ), 7.56–7.35 (m, 10H,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  18.4 ( $\text{CH}_3$ ), 129.4, 132.8, 140.5 ( $\text{C}_5\text{H}_2$ ), 124.3, 128.4, 129.4, 138.4 ( $\text{C}_6\text{H}_5$ ).

## 2.4. Synthesis of 1,2-diphenyl-4-*n*-butyl-cyclopentadienyltitanium trichloride (**5**)

Complex **5** was synthesized in almost the same manner as complex **4** except that 1,2-diphenyl-4-*n*-butyl-cyclopentadiene (1.37 g, 5.0 mmol) was used as the starting material and its deprotonation reaction was carried out in *n*-hexane. Pure **5** (1.32 g, 61.5%) was obtained as red crystals by recrystallization from methylene chloride/*n*-hexane (1:4 in v/v). *Anal. Calc.* for  $\text{C}_{21}\text{H}_{21}\text{Cl}_3\text{Ti}$  (427.62): C, 58.98; H, 4.95. Found: C, 59.05; H, 4.89. IR (KBr,  $\text{cm}^{-1}$ ): 3086w, 2960m, 2932m, 2875w, 1494m, 1452w, 1427m, 1156w, 1079w, 1030w, 923w, 885m, 853m, 796s, 772vs, 757vs, 729m, 698s, 670m, 606m.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  0.98 (t,  $^3J_{\text{HH}} = 7.5 \text{ Hz}$ , 3H,  $\text{CH}_3$ ), 1.47 (m,  $^3J_{\text{HH}} = 7.4 \text{ Hz}$ , 2H,  $\text{CH}_2$ ), 1.73 (m,  $^3J_{\text{HH}} = 7.3 \text{ Hz}$ , 2H,  $\text{CH}_2$ ), 2.93 (t,  $^3J_{\text{HH}} = 7.5 \text{ Hz}$ , 2H,  $\text{CH}_2$ ), 7.13 (s, 2H,  $\text{C}_5\text{H}_2$ ), 7.36–7.57

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