

Preliminary communication

# Siloxy-substituted tetramethylcyclopentadienyl and indenyl trichlorotitanium complexes for syndiospecific polymerization of styrene

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## Abstract

( $\eta^5$ -trimethylsiloxytetramethylcyclopentadienyl)- and ( $\eta^5$ -2-trimethylsiloxyindenyl)trichloro titanium have been synthesized and characterized. Their catalytic behavior for the polymerization of styrene was studied in the presence of methylaluminoxane (MAO) as a cocatalyst. They show only low activity for styrene polymerization. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Titanium; Polymerization; Syndiotactic polystyrene; Catalysts

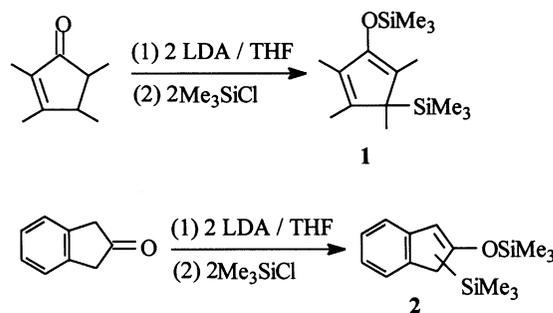
## 1. Introduction

Ishihara and coworkers discovered that syndiotactic polystyrene (s-PS) could be produced with high stereoregularity and yield under conventional conditions using  $\text{CpTiCl}_3$  activated with methylaluminoxane (MAO) [1,2]. Since the initial discovery, several studies on the effect of ligand substitution on polymerization behavior have been reported [3–7]. In addition to the well-known alkyl and aryl derivatives, mono-cyclopentadienyltrichloride and trialkoxide derivatives of titanium that contain functional ring substituents, such as diphenylphosphinyl, *N,N*-dimethylamino and methylthio, have also been prepared and investigated as catalysts for styrene polymerization [3,6,8].

We now report on the synthesis of trimethylsiloxy substituted (tetramethylcyclopentadienyl)- and (indenyl)trichlorotitanium, and their catalytic activities toward the polymerization of styrene with MAO as a cocatalyst.

## 2. Results and discussion

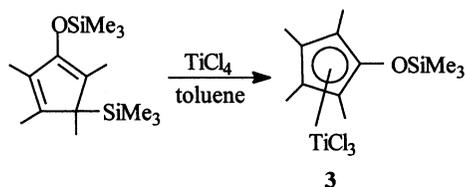
2,3,4,5-tetramethylcyclopent-2-enone was treated with two equivalents of lithium diisopropylamide (LDA), then reacted with two equivalents of trimethylchlorosilane to afford 2-trimethylsiloxy-5-trimethylsilyl-1,3,4,5-tetramethylcyclopentadiene (**1**) in 76% yield. 2-trimethylsiloxy substituted trimethylsilyl indene (**2**) was prepared similarly from 2-indanone in moderate yield.



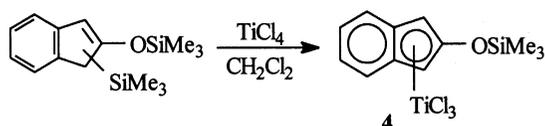
The reaction between **1** and  $\text{TiCl}_4$  was carried out at both  $-78$  and  $0^\circ\text{C}$  in toluene. Both attempts gave a

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dark solid, which was insoluble in most solvents (e.g.  $\text{CHCl}_3$ , THF and acetone). When **1** was added in one portion to  $\text{TiCl}_4$  in toluene at elevated temperature, the corresponding titanium complex (**3**) was isolated in 33% yield.



(2-trimethylsiloxyindenyl)trichlorotitanium (**4**) was prepared in a similar manner to the procedure for **3** except using  $\text{CH}_2\text{Cl}_2$  as solvent. An attempt to synthesize **4** by the reaction of 2-trimethylsiloxyindene, after treated with *n*-butyl lithium, with  $\text{TiCl}_4 \cdot \text{THF}$  failed to produce **4**.



The preparation of **3** and **4** is remarkable for it represents a simple route to monocyclopentadienyltitanium trichloride with an oxygen atom directly bonded to the  $\text{C}_5$  ring, although the yield is not very satisfactory. In general, the reaction of an appropriate substituted trimethylsilylcyclopentadiene and titanium tetrachloride is an efficient route to  $\text{CpTiCl}_3$  and substituted derivatives [9,10], and the yield is usually excellent. The low yield of these two syntheses may be attributed to the interaction of  $\text{TiCl}_4$  with the silyl enol ether to yield  $\text{Me}_3\text{SiCl}$  and a trichlorotitanium enol ether [11].

**3** and **4** are stable in the solid state when stored at  $-20^\circ\text{C}$  in an argon atmosphere, but they decompose gradually on standing at room temperature.

When **4**-MAO was used to polymerize styrene, it exhibited low activities ( $0.11 \times 10^7$  gPS/(molTi mol styrene h)) and low stereoselectivity (ca. 70%). The catalyst **3**-MAO had almost no activity for styrene polymerization. It did not produce a sufficient amount of polymer for characterization. In comparison, their unsubstituted analogues,  $\text{IndTiCl}_3$  and  $\text{C}_5\text{Me}_4\text{HTiCl}_3$ , exhibited high activities ( $3.2 \times 10^7$  and  $0.37 \times 10^7$  gPS/(molTi mol styrene h) respectively) and high stereoselectivity (> 91%).

Zambelli and coworkers considered that the syndiotactic-specific polymerization of styrene might be an 'electrophilic' polyinsertion reaction at the metal center, suggesting that titanium compounds with metal centers rich in electron density would be more effective catalysts [12,13]. Although trimethylsiloxy substituent has electron-releasing properties, the addition of trimethyl-

siloxy group only caused decrease in activity for **3** and **4** compared with their unsubstituted analogues. Oxygen–aluminum coordination may be responsible for the low activity. It should be kept in mind that these complexes act as 'pre-catalyst' and become active species after treated with cocatalyst. The cocatalyst MAO, as a Lewis-acid, may coordinate with oxygen atom of siloxy group. The coordination suppresses the resonance effect and enhances the inductive effect of the siloxy group. As a result **3** and **4** show only low activity. A similar result was observed previously when some metallocene catalysts with functionally substituted ligands were used for olefin polymerization [3,5,14].

### 3. Experimental section

Reactions were carried out under an argon atmosphere using standard schlenk techniques. Methylene chloride was distilled under argon from  $\text{P}_2\text{O}_5$ . Diisopropylamine was distilled from  $\text{CaH}_2$ . THF, hexane and toluene were distilled under argon from sodium-diphenyl Ketone.  $\text{TiCl}_4$  and  $\text{Me}_3\text{SiCl}$  were distilled prior to use.  $^1\text{H}$  NMR spectra were recorded on a Bruker AC-200. Electron impact mass spectra were obtained on a VG-7070EHF. 2,3,4,5-tetramethylcyclopent-2-enone [15], 2-indanone [16],  $\text{IndTiCl}_3$  [4],  $(\text{C}_5\text{Me}_4\text{H})\text{TiCl}_3$  [17] were prepared by literature procedures.

#### 3.1. Synthesis of 2-trimethylsiloxy-5-trimethylsilyl-1,3,4,5-tetramethylcyclopentadiene (**1**)

To a solution of 48.8 ml of diisopropylamine (0.345 mol) in 120 ml of THF was added 208 ml of *n*-BuLi (0.342 mol, 1.64 N in hexane). This solution was stirred for 0.5 h at  $0^\circ\text{C}$ . To this solution was added 22.8 g of 2,3,4,5-tetramethylcyclopent-2-enone (0.164 mol) in 30 ml of THF at  $0^\circ\text{C}$ . The reaction mixture was then refluxed for 20 h. Then diisopropylamine and solvent were removed under vacuum, leaving an orange semi-solid. THF (200 ml) was added, the resulting suspension was cooled to  $0^\circ\text{C}$ , and 62 ml of  $\text{Me}_3\text{SiCl}$  (0.490 mol) was quickly added. The resulting suspension was allowed to warm to room temperature and stirred for 3 h, then refluxed for 3 h. The resulting suspension was filtered and washed with two portions of ether. The solvent of filtrate was removed to produce a sticky red oil. Distillation at  $72\text{--}78^\circ\text{C}/0.3$  mmHg gave 35.0 g of **1** (76%) as a yellow oil, which was reasonably pure by  $^1\text{H}$  NMR and was used without further purification.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.76 (s, 3H,  $\text{CH}_3$ ), 1.71 (s, 6H,  $\text{CH}_3$ ), 1.10 (s, 3H,  $\text{CH}_3$ ), 0.18 (s,  $\text{OSiMe}_3$ ),  $-0.12$  (s, 9H,  $\text{SiMe}_3$ ).

### 3.2. Synthesis of 1-trimethylsilyl-2-trimethylsiloxyindene (**2**)

**2** was prepared in a manner analogous to the procedure for **1**. 2-indanone (10.0 g, 0.075 mol) was treated with LDA (0.165 mol), then reacted with Me<sub>3</sub>SiCl (0.236 mol) to afford **2** (7.2 g, 37%) as a yellow oil. b.p. 76–82°C/1 mmHg. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.4–7.0 (m, 4H, arom), 5.75 (s, 1H, sp<sup>2</sup>, 2-position), 3.23 (s, 1H, sp<sup>3</sup>, 1-position), 0.30 (s, 9H, OSiMe<sub>3</sub>), –0.05 (s, 9H, SiMe<sub>3</sub>).

### 3.3. Synthesis of (1-trimethylsiloxy-2,3,4,5-tetramethylcyclopentadienyl)trichlorotitanium (**3**)

A solution of **1** (12.9 g, 45.6 mmol) in 20 ml of toluene was added in one portion to a solution of TiCl<sub>4</sub> (5.0 ml, 45.6 mmol) in 100 ml of toluene at 40°C. The reaction mixture was allowed to cool to room temperature and stirred overnight. The resulting suspension was passed through a Celite plug. After removal of the solvent under vacuum, the dark red residue was extracted with 50 ml of hexane/CH<sub>2</sub>Cl<sub>2</sub> = 1:1. The extracts were filtered, concentrated under reduced pressure and cooled to –20°C, affording red needle crystals of **3** (5.4 g, 33%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.34 (s, 6H, CH<sub>3</sub>), 2.28 (s, 6H, CH<sub>3</sub>), 0.30 (s, 9H, SiMe<sub>3</sub>). MS (*m/e*, % intensity), 209 (100, M-3Cl-Ti<sup>+</sup>), 73 (53, SiMe<sub>3</sub><sup>+</sup>). Anal. Found: C, 39.41; H, 5.21. C<sub>12</sub>H<sub>2</sub>Cl<sub>3</sub>OSiTi. Calc.: C, 39.64; H, 5.82%.

### 3.4. Synthesis of (2-trimethylsiloxyindenyl)trichlorotitanium (**4**)

A solution of **2** (3.5 g, 12.6 mmol) in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> was added in one portion to a solution of TiCl<sub>4</sub> (1.4 ml, 12.6 mmol) in 20 ml of CH<sub>2</sub>Cl<sub>2</sub> at 40°C. The reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum. The residue was extracted in 40 ml of hexane/CH<sub>2</sub>Cl<sub>2</sub> = 1:1, passed through a Celite plug, concentrated and stored at –20°C, affording dark red needle crystals of **4** (1.25 g, 28%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.64 (m, 2H, arom), 7.42 (m, 2H, arom), 6.50 (s, 2H, 1- and 3-positions), 0.42 (s, 9H, OSiMe<sub>3</sub>). MS (*m/e*, % intensity) 229 (100, M-3Cl-Ti<sup>+</sup>), 73 (20, SiMe<sub>3</sub><sup>+</sup>). Anal. Found: C, 40.17; H, 4.28. C<sub>12</sub>H<sub>2</sub>Cl<sub>3</sub>OSiTi. Calc.: C, 40.31; H, 4.23%.

### 3.5. Polymerization studies

Styrene polymerizations were carried out in 250 ml schlenk flask with magnetic stirring and using toluene

as the solvent. Styrene was distilled from calcium hydride and stored at –20°C under argon in darkness. Toluene (50 ml), styrene (5.00 ml, 4.54 g, 43.6 mmol) and MAO (6.6 ml, 10 wt.% in toluene from Aldrich), and the catalysts (25 μmol, 1 ml of a 2.5 mM solution) were injected into the flask. The polymerizations were performed at 50°C for 30 min periods. After this time the polymerizations were terminated by the addition of 100 ml of 10% HCl in methanol. The precipitated polymer was washed three times each with 50 ml of methanol, and dried in vacuum to a constant weight. The polymer was extracted with refluxing 2-butanone for 12 h in order to determine the S-PS portion of the obtained polymer.

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