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Preliminary communication

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

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Abstract

(η^5-trimethylsiloxytetramethylcyclopentadienyl)- and (η^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

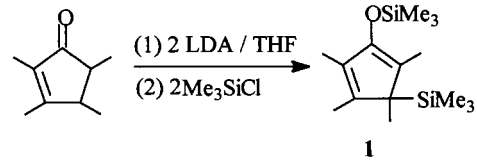
1. Introduction

Ishihara and coworkers discovered that syndiotactic polystyrene (s-PS) could be produced with high stereoregularity and yield under conventional conditions using $CpTiCl_3$ 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].

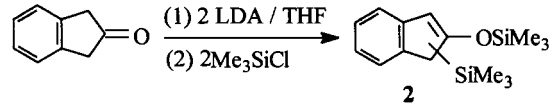
We now report on the synthesis of trimethylsiloxy substituted (tetramethylcyclopentadienyl)- and (indenyl)trichlorotitanium, and their catalytic activities toward the polymerization of styrene with MAO as a cocatalyst.

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.



1



2

The reaction between **1** and $TiCl_4$ was carried out at both −78 and 0°C in toluene. Both attempts gave a

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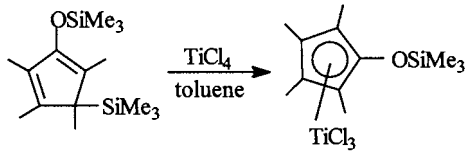
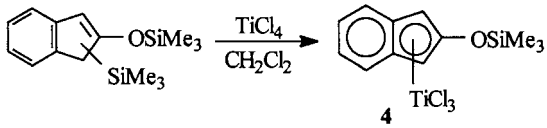
dark solid, which was insoluble in most solvents (e.g. $CHCl_3$, THF and acetone). When **1** was added in one portion to $TiCl_4$ in toluene at elevated temperature, the corresponding titanium complex (**3**) was isolated in 33% yield.



3

(2-trimethylsiloxyindenyl)trichlorotitanium (**4**) was prepared in a similar manner to the procedure for **3** except using CH_2Cl_2 as solvent. An attempt to synthesize **4** by the reaction of 2-trimethylsiloxyindene, after treated with *n*-butyl lithium, with $TiC_4 \cdot THF$ failed to produce **4**.



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 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 $CpTiCl_3$ and substituted derivatives [9,10], and the yield is usually excellent. The low yield of these two synthese may be attributed to the interaction of $TiCl_4$ with the sily enol ether to yield Me_3SiCl and a trichlorotitanium enol ether [11].

3 and **4** are stable in the solid state when stored at -20°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 (0.11×10^7 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, $IndTiCl_3$ and $C_5Me_4HTiCl_3$, exhibited high activities (3.2×10^7 and 0.37×10^7 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 trimethylsiloxy 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 P_2O_5. Diisopropylamine was distilled from CaH_2. THF, hexane and toluene were distilled under argon from sodium-diphenyl Ketone. $TiCl_4$ and Me_3SiCl were distilled prior to use. ^1H 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], $IndTiCl_3$ [4], $(C_5Me_4H)TiCl_3$ [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°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°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°C, and 62 ml of Me_3SiCl (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 72–78°C/0.3 mmHg gave 35.0 g of **1** (76%) as a yellow oil, which was reasonably pure by ^1H NMR and was used without further purification. ^1H NMR ($CDCl_3$): δ 1.76 (s, 3H, CH_3), 1.71 (s, 6H, CH_3), 1.10 (s, 3H, CH_3), 0.18 (s, $OSiMe_3$), -0.12 (s, 9H, $SiMe_3$).

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_3SiCl (0.236 mol) to afford **2** (7.2 g, 37%) as a yellow oil. b.p. 76–82°C/1 mmHg. ^1H NMR ($CDCl_3$): δ 7.4–7.0 (m, 4H, arom), 5.75 (s, 1H, sp^2, 2-position), 3.23 (s, 1H, sp^3, 1-position), 0.30 (s, 9H, $OSiMe_3$), −0.05 (s, 9H, $SiMe_3$).

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 $TiCl_4$ (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_2Cl_2 = 1:1. The extracts was filtered, concentrated under reduced pressure and cooled to −20°C, affording red needle crystals of **3** (5.4 g, 33%). ^1H NMR ($CDCl_3$): δ 2.34 (s, 6H, CH_3), 2.28 (s, 6H, CH_3), 0.30 (s, 9H, $SiMe_3$). MS (*m*/*e*, % intensity), 209 (100, M-3Cl-Ti^+), 73 (53, $SiMe_3^+$). Anal. Found: C, 39.41; H, 5.21. $C_{12}H_2Cl_3OSiTi$. 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_2Cl_2 was added in one portion to a solution of $TiCl_4$ (1.4 ml, 12.6 mmol) in 20 ml of CH_2Cl_2 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_2Cl_2 = 1:1, passed through a Celite plug, concentrated and stored at −20°C, affording dark red needle crystals of **4** (1.25 g, 28%). ^1H NMR ($CDCl_3$) δ 7.64 (m, 2H, arom), 7.42 (m, 2H, arom), 6.50 (s, 2H, 1- and 3-positions), 0.42 (s, 9H, $OSiMe_3$). MS (*m*/*e*, % intensity) 229 (100, M-3Cl-Ti^+), 73 (20, $SiMe_3$). Anal. Found: C, 40.17; H, 4.28. $C_{12}H_2Cl_3OSiTi$. 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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