

Note

# Facile synthesis and X-ray structures of $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OAr}^{\text{F}})_3$ ( $\text{OAr}^{\text{F}} = \text{OC}_6\text{F}_5$ , $\text{OCH}_2\text{C}_6\text{F}_5$ , and $\text{OCH}_2\text{C}_6\text{F}_2\text{H}_3$ )

Junseong Lee <sup>a</sup>, Youngkyu Do <sup>a,\*</sup>, Youngjo Kim <sup>b,\*</sup>

<sup>a</sup> Department of Chemistry, School of Molecular Science BK21, Center for Molecular Design and Synthesis, KAIST, Daejeon 305-701, Republic of Korea

<sup>b</sup> Department of Chemistry, Chungbuk National University, Cheongju, Chungbuk 361-763, Republic of Korea

Received 28 March 2007; received in revised form 26 April 2007; accepted 1 May 2007

Available online 10 May 2007

## Abstract

New half-sandwich titanocene complexes  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OC}_6\text{F}_5)_3$  (**1**),  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OCH}_2\text{C}_6\text{F}_5)_3$  (**2**), and  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OCH}_2\text{C}_6\text{F}_2\text{H}_3)_3$  (**3**) were synthesized via the displacement of methoxide ligands in  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OMe})_3$  by the corresponding aryloxy or benzyloxy ligands. These compounds have been fully characterized by various spectroscopic methods including X-ray crystallography. Compound **1** has a distorted three-legged piano stool structure. However, complexes **2** and **3** have the chariot-like structure, where chariot means a two-wheeled horse-drawn vehicle. The  $\pi$  electron donation of oxygen atom to Ti center in complexes **1–3** is considerable.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Titanium; Half-sandwich metallocene; X-ray structure; Pentafluorophenol; Pentafluorobenzylalcohol; 2,5-Difluorobenzylalcohol; Pentamethylcyclopentadienyl;  $\pi$ - $\pi$  Interaction

## 1. Introduction

Since the discovery of the Ziegler–Natta catalyst systems in early 1950s [1], tremendous advances in the design and application of organometallic complexes as  $\alpha$ -olefin polymerization catalysts have been achieved [2]. Of the extensive previous work, most has focused on the development of catalytic systems based on cyclopentadienyl group 4 compounds suitable for the polymerization of monomers such as ethylene, propylene, and styrene. However, there are only few reports for the polymerization catalysis using non-bridged  $\text{Cp}'\text{TiX}_3$  complexes, which contain both one pentahapto ligand and three monodentate ligands, though the syntheses of these complexes have been known for several decades [3]. The examples include  $(\eta^5\text{-C}_5\text{R}_5)\text{TiCl}_3$  [4] and  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OR}')_3$  ( $\text{R} = \text{H}$  and  $\text{Me}$ ;  $\text{R}' = \text{Me}$ ,  $\text{Et}$ ,

$\text{Bu}$ , and so on) [5,6]. Several types of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OR}')_3$  have been synthesized by a two-step reaction in which  $\text{LiOR}'$  is made from  $\text{R}'\text{OH}$  and  $n\text{-BuLi}$ , followed by reaction with a third equivalent of  $(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_3$  [5,6]. However, yields were somewhat low and some by-product could be obtained. Other synthetic route to  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OR}')_3$  is an amine or methane displacement with alkoxide ligand using  $(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_3$  or  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{NR}'_2)_3$  [7], which is commercially unavailable and difficult to purify. In addition, complexes of the type  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OR}')_3$  complexes can be prepared by reacting  $\text{Cp}'\text{TiCl}_3$  with  $\text{R}'\text{OH}$  in the presence of  $\text{NEt}_3$  [8] in spite of the high dependence of yield on  $\text{R}'$  group. In this regard, we are interested in the facile one-pot and quantitative synthetic route to  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OR}')_3$  using commercially available starting materials. Herein we report the simple one-pot and quantitative synthesis, characterization, and X-ray structures of complexes  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OC}_6\text{F}_5)_3$  (**1**),  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OCH}_2\text{C}_6\text{F}_5)_3$  (**2**), and  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OCH}_2\text{C}_6\text{F}_2\text{H}_3)_3$  (**3**) from the reaction between commercially available  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OMe})_3$  and corresponding aryloxy or benzyloxy ligand.

\* Corresponding authors. Tel./fax: +82 42 869 2829 (Y. Do), Tel.: +82 43 261 3395; fax: +82 43 267 2279 (Y. Kim).

E-mail addresses: [ykdo@kaist.ac.kr](mailto:ykdo@kaist.ac.kr) (Y. Do), [ykim@cnu.ac.kr](mailto:ykim@cnu.ac.kr) (Y. Kim).

## 2. Experimental

### 2.1. General procedures

All reactions were carried out under dinitrogen atmosphere using standard Schlenk and glove box techniques [9]. Dinitrogen was deoxygenated with activated Cu catalyst and dried with drierite. All chemicals were purchased from Aldrich and were used as supplied unless otherwise indicated. Cp\*Ti(OMe)<sub>3</sub> were purchased from Strem Co. All solvents (Aldrich anhydrous grade) were dried by distilling from sodium–potassium alloy (*n*-hexane) or CaH<sub>2</sub> (dichloromethane) under a dinitrogen atmosphere and stored over the activated molecular sieves 3A [10]. CDCl<sub>3</sub> was dried over activated molecular sieves (4A) and were used after vacuum transfer to a Schlenk tube equipped with J. Young valve. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>19</sup>F NMR spectra were recorded at ambient temperature on a Bruker AM300 spectrometer using standard parameters. The chemical shifts are referenced to the peaks of residual CDCl<sub>3</sub> (δ 7.24 in <sup>1</sup>H NMR). Elemental analyses were performed by EA 1110-FISONS(CE).

### 2.2. Synthesis of (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ti(OC<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (1)

To a dichloromethane solution of (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ti(OMe)<sub>3</sub> (0.55 g, 2 mmol) was added dropwise at –78 °C a solution of pentafluorophenol (1.14 g, 6.2 mmol) in 30 mL of dichloromethane. The reaction mixture was warmed to room temperature and stirred for 12 h. The residue, obtained by removing the solvent under vacuum, was washed with 20 ml of *n*-hexane several times. The desired product **1** was isolated as orange crystals after recrystallization from the dichloromethane/*n*-hexane solution at –20 °C in a refrigerator for overnight (1.43 g, 98%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.133 MHz): δ = 2.18 (s, 15H, C<sub>5</sub>-Me<sub>5</sub>).

<sup>19</sup>F NMR (CDCl<sub>3</sub>, 282.376 MHz): δ = –168.74 (t, 3H, *J* = 22.0 Hz), –165.47 (dd, 6H, *J* = 21.5 and 18.6 Hz), –160.60 (m, 6H).

Anal. Calc. for C<sub>28</sub>H<sub>15</sub>F<sub>15</sub>O<sub>3</sub>Ti: C, 45.93; H, 2.06. Found: C, 46.04; H, 2.20%.

### 2.3. Synthesis of (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ti(OCH<sub>2</sub>C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (2)

The desired product **2** as yellow crystals was prepared in an isolated yield of 95 % (1.49 g) in a manner analogous to the procedure for **1** using pentafluorobenzylalcohol (1.23 g, 6.2 mmol) and (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ti(OMe)<sub>3</sub> (0.55 g, 2 mmol).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.133 MHz): δ = 5.17 (s, 6H, OCH<sub>2</sub>PhF<sub>5</sub>), 1.96 (s, 15H, C<sub>5</sub>Me<sub>5</sub>).

<sup>19</sup>F NMR (CDCl<sub>3</sub>, 282.376 MHz): δ = –163.13 (m, 6H), –155.95 (t, 3H, *J* = 20.3 Hz), –145.50 (dd, 6H, *J* = 13.3 and 8.75 Hz).

Anal. Calc. for C<sub>31</sub>H<sub>21</sub>F<sub>15</sub>O<sub>3</sub>Ti: C, 48.08; H, 2.73. Found: C, 48.43; H, 2.62%.

### 2.4. Synthesis of (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ti(OCH<sub>2</sub>C<sub>6</sub>F<sub>2</sub>H<sub>3</sub>)<sub>3</sub> (3)

The desired product **3** as yellow crystals was prepared in an isolated yield of 96% (1.18 g) in a manner analogous to the procedure for **1** using 2,5-difluorobenzylalcohol (0.89 g, 6.2 mmol) and (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ti(OMe)<sub>3</sub> (0.55 g, 2 mmol).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.133 MHz): δ = 7.1–6.6 (m, 9H, OCH<sub>2</sub>C<sub>6</sub>F<sub>2</sub>H<sub>3</sub>), 5.25 (s, 6H, OCH<sub>2</sub>C<sub>6</sub>F<sub>2</sub>H<sub>3</sub>), 2.02 (s, 15H, C<sub>5</sub>Me<sub>5</sub>).

<sup>19</sup>F NMR (CDCl<sub>3</sub>, 282.376 MHz): δ = –119.73 (d, 3H, *J* = 18.4 Hz), –126.74 (d, 3H, *J* = 18.4 Hz).

Anal. Calc. for C<sub>31</sub>H<sub>30</sub>F<sub>6</sub>O<sub>3</sub>Ti: C, 60.80; H, 4.94. Found: C, 60.80; H, 5.03%.

### 2.5. X-ray structural determination

The crystals were coated with paraton oil. The diffraction data for **1** were collected on a Bruker 1K SMART CCD-based diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). The hemisphere of reflection data were collected as ω scan frames with 0.3°/frame and an exposure time of 5 s/frame. Cell parameters were determined and refined by the SMART program [11]. Data reduction were performed using SAINT software [12]. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program [13]. The diffraction data of complexes **2** and **3** were measured at 193 K with synchrotron radiation (λ = 0.75000 Å) on a 4AMXW ADSC Quantum-210 detector with a silicon double crystal monochromator at the Pohang Accelerator Laboratory, Korea. The HKL2000 (Ver.0.98.689) [14] was used for data collection, cell refinement, reduction, and absorption correction. The structures of the compounds were solved by direct methods and refined by full matrix least-squares methods using the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms [15]. Further details are listed in Tables 1 and 2.

## 3. Results and discussion

Complexes **1–3** could be prepared via the displacement of methoxide ligands in (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ti(OMe)<sub>3</sub> by the corresponding fluorine-substituted aryloxy or benzyloxy ligands. The treatment of commercially available (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ti(OMe)<sub>3</sub> with three equivalents of pentafluorophenol, pentafluorobenzylalcohol, or 2,5-difluorobenzylalcohol ligand in dichloromethane gave, after workup, the new half-sandwich titanocene **1–3** as orange or yellow crystals in more than 95% isolated yield. Unlike the previous reported literature [4–8], attempted reaction between (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)TiCl<sub>3</sub> and corresponding lithiated aryloxy or benzyloxy species in toluene or THF was not successful and a mixture of the desired product with non-separable impurities was obtained. In addition, the same result was observed in the reaction between (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)TiCl<sub>3</sub> and corresponding species in the presence of NEt<sub>3</sub>. These suggest that the reaction

Download English Version:

<https://daneshyari.com/en/article/1326608>

Download Persian Version:

<https://daneshyari.com/article/1326608>

[Daneshyari.com](https://daneshyari.com)