

Titanium(IV) complexes with monocyclopentadienyl and phenoxy-alkoxo ligands: Synthesis, structures and catalytic properties for ethylene polymerization

Tie-Qi Xu, Wei Gao, Ying Mu *, Ling Ye

Key Laboratory for Supramolecular Structure and Materials of Ministry of Education, School of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, People's Republic of China

Received 11 December 2006; accepted 8 March 2007
Available online 15 March 2007

Abstract

Three monochlorotitanium complexes $\text{Cp}'\text{Ti}(2,4\text{-}i\text{Bu}_2\text{-6-(CPh}_2\text{O)C}_6\text{H}_2\text{O})\text{Cl}$ [$\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$ (**2**), $\eta^5\text{-C}_5(\text{CH}_3)_5$ (**3**), $\eta^5\text{-C}_5\text{H}_2\text{Ph}_2\text{CH}_3$ (**4**)] have been synthesized in high yields (>90%) by the reaction of corresponding $\text{Cp}'\text{TiCl}_3$ with the dilithium salt of ligand 2,4-*i*Bu₂-6-(CPh₂OH)C₆H₂OH (**1**). When activated by $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and $\text{Al}'\text{Bu}_3$, complexes **2–4** exhibit reasonable catalytic activity for ethylene polymerization, producing polyethylenes with moderate molecular weights and melting points. Addition of excess water to complex **2** gave the oxo-bridged complex $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)(2,4\text{-}i\text{Bu}_2\text{-6-(CPh}_2\text{O)C}_6\text{H}_2\text{O})_2\text{O}]_2$ (**5**). Complexes **4** and **5** were characterized by single crystal X-ray diffraction.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Titanium complexes; Ethylene polymerization; Homogeneous catalysis; Metallocene catalysts

1. Introduction

Polyolefins are the largest volume synthetic materials used in the world, and have been almost applied in every aspect of our daily lives and productions. One of the most active areas of polyolefins research over the past decades has been the discovery and development of Ziegler–Natta catalysis for polymerization of ethylene and α -olefins. Since Kaminsky et al. discovered the highly active zirconocene dichloride/methylaluminumoxane (MAO) catalytic system for olefin polymerization [1], intensive research work has been focused on developing new Group 4 metallocene catalysts for improving catalytic activities and polymer properties [2,3]. Most of Group 4 metallocene and related complexes for olefin polymerization typically have two or more alkyl (or halide) groups attached to the metal. Examples of precatalysts containing only one such group are

scarce [4], although they are active for olefin polymerization and are also of potential interest in the context of single-site olefin polymerization catalysis. Therefore, our current focus is the development of this class of monochlorotitanium complexes, and investigation of the influence of different substituents at cyclopentadienyl (Cp) on their catalytic activity.

In this work, a new bidentate chelating ligand 2,4-*i*Bu₂-6-(CPh₂OH)C₆H₂OH (**1**) was firstly synthesized and introduced into the monochlorotitanium system, based on the following considerations: (i) the phenoxy-alkoxo bidentate ligand comprising the alkoxo group linked with the phenol group has two different active oxygen functionalities in the metalation reaction, therefore increasing the selectivity of forming the desired complexes in the synthetic reaction; (ii) recently, Doherty et al. have reported that introducing phenyl groups on the alkoxo ligand are able to increase catalytic activity of the precatalysts $[\text{CpTi}\{\text{NC}_5\text{H}_4(\text{CR}_2\text{O})_2\}\text{Cl}_2]$ [5], so here we choose the alkoxo ligand containing phenyl groups. With the new ligand, we successfully obtained a series of monochlorotitanium complexes

* Corresponding author. Tel.: +86 431 85168472; fax: +86 431 85193421.

E-mail address: ymu@mail.jlu.edu.cn (Y. Mu).

$\text{Cp}'\text{Ti}(2,4\text{-}^t\text{Bu}_2\text{-6-(CPh}_2\text{O)C}_6\text{H}_2\text{O})\text{Cl}$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$ (**2**), $\eta^5\text{-C}_5(\text{CH}_3)_5$ (**3**), $\eta^5\text{-C}_5\text{H}_2\text{Ph}_2\text{CH}_3$ (**4**)) which have different substituents in cyclopentadienyl in high yield (>90%), and studied their application in ethylene polymerization and their hydrolysis reactions.

2. Results and discussion

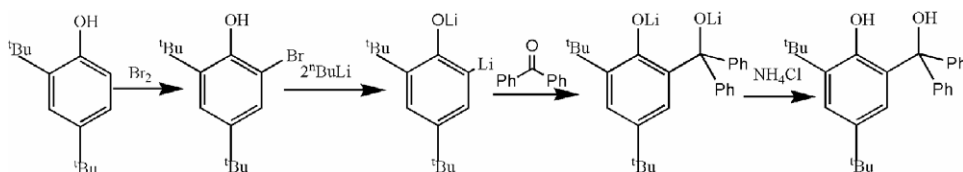
2.1. Synthesis and characterization

The new bidentate ligand **1** was synthesized with 2,4-di-*tert*-butylphenol as the starting material. 2-Bromo-4,6-di-*tert*-butylphenol was easily prepared from the reaction of Br_2 with 2,4-di-*tert*-butylphenol in $\text{CHCl}_3/\text{CCl}_4$ at 0°C . The reaction of dilithium phenoxide, obtained by treating 2-bromo-4,6-di-*tert*-butylphenol with 2 equiv. of $^t\text{BuLi}$, with benzophenone in Et_2O at -15°C , followed by hydrolysis with saturated NH_4Cl produced the ligand **1** in a moderate yield (Scheme 1). The monochlorotitanium complexes **2–4** were prepared by reaction of $\text{Cp}'\text{TiCl}_3$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$, $\eta^5\text{-C}_5(\text{CH}_3)_5$, $\eta^5\text{-C}_5\text{H}_2\text{Ph}_2\text{CH}_3$) with equimolar amount of dilithium salt of 2,4- $^t\text{Bu}_2\text{-6-(CPh}_2\text{OH)C}_6\text{H}_2\text{OH}$

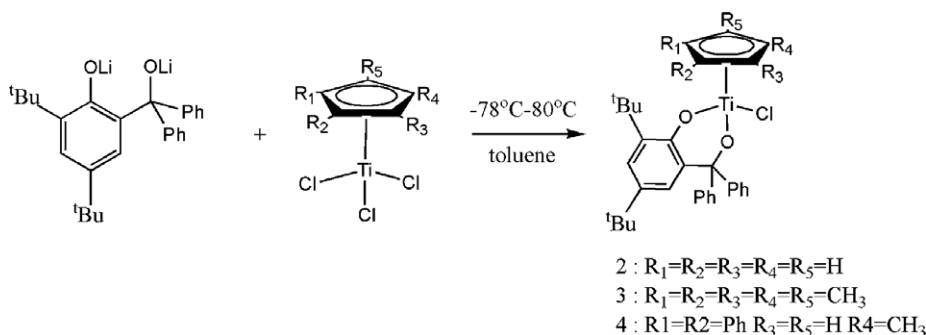
in toluene in high yields (Scheme 2). These complexes were found to be easily hydrolyzed. Addition of excess water to toluene solution of complex **2** gave the oxo-bridged complex $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)(2,4\text{-}^t\text{Bu}_2\text{-6-(CPh}_2\text{O)C}_6\text{H}_2\text{O})_2\text{O}$ (**5**) (Scheme 3). However, the same reaction with complexes **3** and **4** caused complete decomposition of both complexes to a mixture of unknown composition in which no organometallic complexes were isolated. All complexes were characterized by elemental analysis and NMR spectroscopy. Complexes **4** and **5** were characterized by single crystal X-ray diffraction.

2.2. Crystal Structures of **4** and **5**

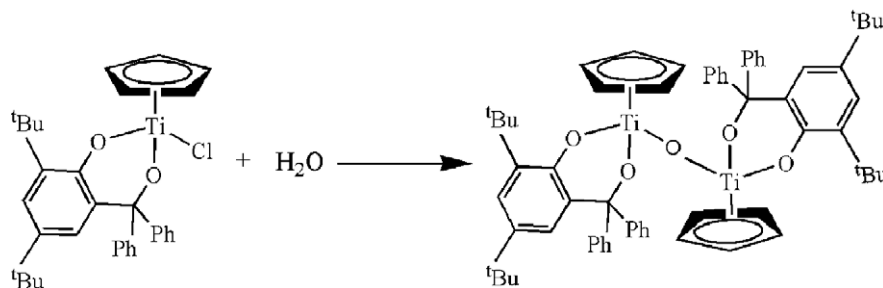
Crystals of complexes **4** and **5** suitable for single-crystal X-ray diffraction study were grown by cooling the saturated solutions of **4** and **5** in mixed $\text{CH}_2\text{Cl}_2/\text{hexane}$. The ORTEP drawings of the molecule structures are shown in Figs. 1 and 2. The selected bond lengths and angles are summarized in Table 1. The geometry around titanium in **4** can be described as a pseudo-tetrahedral coordination environment, which is defined by a substituted Cp ring



Scheme 1. Synthetic procedure of ligand **1**.



Scheme 2. Synthetic procedure of complexes **2–4**.



Scheme 3. Synthetic procedure of complex **5**.

Download English Version:

<https://daneshyari.com/en/article/1338508>

Download Persian Version:

<https://daneshyari.com/article/1338508>

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