Inorganic Chemistry Communications 61 (2015) 144–148

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Dinuclear group 4 alkoxides: Excellent initiators for ring-opening polymerization of cyclic esters

Jia-Xuan He, Yu-Lai Duan, Xin Kou, Yi-Zhou Zhang, Wei Wang, Ying Yang, Yong Huang *

Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, Gansu, PR China

ARTICLE INFO

Article history:
Received 25 August 2015
Received in revised form 4 September 2015
Accepted 15 September 2015
Available online 18 September 2015

Keywords:
Group 4 complex;
Cyclic ester
Ring-opening polymerization
Initiator

ABSTRACT

Three new dinuclear group 4 metal alkoxides $[Ti_2(\mu\text{-}O^iPr)(O^iPr)_4L]$ (**1**), $[Zr_2(\mu\text{-}O^iPr)(O^iPr)_4L]$ (**2**) and $[Hf_2(\mu\text{-}O^iPr)(O^iPr)_4L]$ (**3**) have been prepared in good yields from the reaction of N, N-di(salicylidene)-2-hydroxyphenylmethanediamine (L-H_3) and two equiv. $[M(O^iPr)_4(HO^iPr)_n]$, respectively. Complexes **1**–**3** have been characterized by ^1H NMR, ^{13}C NMR, elemental analyses and X-ray diffraction analyses. The molecular structures of complexes **1** and **3** reveal dinuclear species in which the metal centers are hexa-coordinated to one oxygen atom and one nitrogen atom of the ligand, to two oxygen atoms of two isopropoxy groups, and to two bridging oxygen atoms of one phenolate group of ligand and one isopropoxy group. Complexes **1**–**3** are excellent catalysts/initiators for ring-opening polymerization of ε-caprolactone and L- and *rac*-lactide to give the corresponding polyesters.

Contents

Acknowledgments . . . 147
Appendix A. Supplementary material . . . 147
References . . . 147

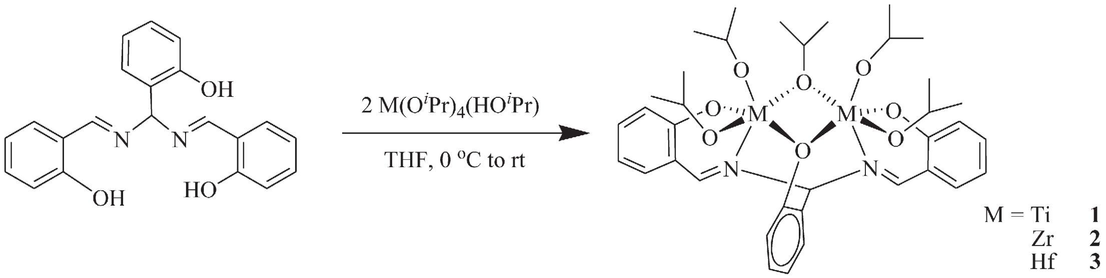
Because of their excellent biocompatible and biodegradable capability, polylactide (PLA), poly(ε-caprolactone) (PCL) and their copolymers have numerous applications in the biomedical and pharmaceutical fields [1]. The ring-opening polymerization (ROP) of cyclic esters with metal complexes as catalysts/initiators is the most common way to prepare these corresponding polymers [2]. In the past few decades, multiple metal complexes, such as Sn, Zn, Mg, Ca, Ti, Zr, Hf, Al, In, alkali metal and rare-earth metal complexes supported by a vast variety of ligands, have been reported as catalysts/initiators for the ROP of lactides and ε-caprolactone [3]. Structurally-defined group 4 complexes have been proven to be competent in the ROP of cyclic esters because they have the added advantage of being easy to prepare, relatively moisture stable and industrial applications under melt conditions [4]. Many ligands have been used to synthesize a large variety of group 4 complexes which are widely used as catalysts/initiators in the ROP field. Mononuclear or dinuclear group 4 complexes bearing tetradentate salen, salan, and salalen-type bis(phenolate) ligands have been synthesized and shown to depend on the steric bulk of the phenoxy groups and the stoichometry [5]. Also the reactions of tri(phenolate) ligands with group 4 metal precursors generate mononuclear, dinuclear, or polynuclear aggregates in high yields [6]. Among those ligands, Shiff-base ligands have attracted widespread attention over the past decades [7]. Nevertheless group 4 complexes bearing tris(phenolate) Shiff-base ligands are little explored as the initiators in the ROP of cyclic esters [3i]. In this paper, we describe the synthesis of Ti, Zr, Hf complexes supported by one tris(phenolate) Shiff-base ligand N, N-di(salicylidene)-2-hydroxyphenylmethanediamine and their application in the ROP of lactides and ε-caprolactone.

N,N-di(salicylidene)-2-hydroxyphenylmethanediamine (L-H_3) were synthesized and characterized according to the literature procedures [8]. As shown in Scheme 1, the dinuclear group 4 complexes $[Ti_2(\mu\text{-}O^iPr)(O^iPr)_4L]$ (**1**), $[Zr_2(\mu\text{-}O^iPr)(O^iPr)_4L]$ (**2**), and $[Hf_2(\mu\text{-}O^iPr)(O^iPr)_4L]$ (**3**), containing a deprotonated ligand, can be prepared by the reaction of L-H_3 with two equiv. of $M(O^iPr)_4(HO^iPr)_n$ ($M = Ti$, $n = 0$; $M = Zr$ or Hf, $n = 1$) in good yields [9]. In the ^1H NMR spectra, the formations of excepted complexes **1**–**3** were demonstrated by the appearance of three septet signals for methine protons of five isopropyl groups with an integration ratio of 1:2:2. Complexes **2** and **3** have the similar NMR spectra which indicate that they have similar structures due to the

---

* Corresponding author.
E-mail address: huangyong@lzu.edu.cn (Y. Huang).

http://dx.doi.org/10.1016/j.inoche.2015.09.012
1387-7003/



Scheme 1. The synthesis of complexes 1–3.

similar ionic radius of the metal centers. But in the complex **1**, the methine resonances of the isopropoxy groups shift to the lower field (4.82, 5.25, 3.43 ppm for **1** *versus* 4.56, 4.48, 3.02 ppm for **2**; 4.69, 4.58, 3.09 ppm for **3**, respectively) because of the smaller ionic radius and the higher electronegativity of titanium. The complexes **1**–**3** have all been characterized by NMR spectroscopy as well as elemental analysis.

The reactions of L-H$_3$ with different equiv. of M(O^{i}Pr)$_4$(HO^{i}Pr) could yield different stoichiometric products. Complex [Zr(L-H)$_2$], containing two di-deprotonated ligand, was synthesized through the reaction of L-H$_3$ with half equiv. of Zr(O^{i}Pr)$_4$(HO^{i}Pr) [8b]. It was worth noting that the reaction between the ligand L-H$_3$ and M(O^{i}Pr)$_4$(HO^{i}Pr) with a 1:1 reactant ratio did not form a 1:1 metalto-ligand stoichiometry mononuclear complex [M(O^{i}Pr)L] or dinuclear complex [M$_2$(O^{i}Pr)$_2$L$_2$] even though the reaction of complex [M$_2$(μ-O^{i}Pr)(O^{i}Pr)$_4$L] with one equiv. of L-H$_3$ was carried out.

The structures of complexes **1** and **3** were further verified by X-ray single crystal diffraction [10]. Crystals of the complexes **1** and **3** were obtained from a slow concentrated toluene solution. The Oak Ridge Thermal Ellipsoid Plot (ORTEP) representations of the molecular structures of **1** and **3** in solid state were shown in Figs. 1 and 2, respectively. The X-ray structures of complexes **1** and **3** revealed dinuclear species in which the metal centers were hexa-coordinated to one oxygen atom and one nitrogen atom of the ligand, to two oxygen atoms of two terminal isopropoxy groups, and to two bridging oxygen atoms of one phenolate group of ligand and one isopropoxy group. Each Ti or Hf center adopted a distorted octahedral geometry.

Ring-opening polymerization of lactides employing complexes **1**–**3** as initiators has been systematically studied as shown in Table 1 [11]. Experimental results indicate that these dinuclear complexes are active initiators for the polymerization of L-lactide and *rac*-lactide under solution or melt conditions. The reactivity in the order of **2**(Zr) ≈ **3**(Hf) > > **1**(Ti), just same with the ionic radius order, reflects that complexes **2** and **3** have much higher activities than their titanium analog because of the more open spheres than that of titanium complex. Complex **2** is the most excellent initiator for the ROP of L-lactide in toluene at 100 °C. The conversion can reach over 90% within an hour in a variety of monomer-initiator ratios ranging from 125 to 500 (Table 1, entries 2–5). The linear relationship between M_n *versus* [L–LA]$_0$/[**2**] and narrow molecular weight distribution (PDI < 1.30) indicate a well controlled process and quality of living polymerization (Fig. 3). Based on the ^{1}H NMR spectrum of PLLA, the polymer chain is believed to be capped with an isopropyl ester group on one end and a hydroxyl group on the other end (Fig. 4), suggesting that the polymerization procedures agree with the "coordination–insertion" process found in other group 4 metal alkoxides. Also complex **2** exhibits similar excellent catalytic activity for the polymerization of *rac*-lactide under solution conditions (Table 1, entry 8). Complex **3** shows similar activity to that of complex **2** in the polymerization of L-lactide and *rac*-lactide under solution or melt conditions due to the similar ionic radius and structure. It is worth noting that complexes **2** and **3** show very high reactivity in the solvent-free bulk polymerization of *rac*-LA with the conversion reach over 80% in 2–5 min. The resulting polylactides have highly controlled

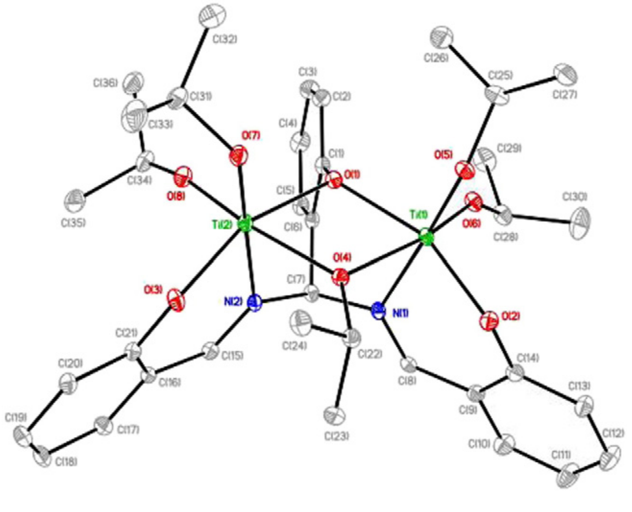


Fig. 1. ORTEP representation of the molecular solid-state structure of [Ti$_2$(μ-O^{i}Pr)(O^{i}Pr)$_4$L](1). Thermal ellipsoids are drawn at the 20% probability level and H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ti(1)–O(6) 1.7946(18), Ti(1)–O(5) 1.823(2), Ti(1)–O(2) 1.9097(19), Ti(1)–O(1) 2.0529(19), Ti(1)–O(4)2.0563(19), Ti(1)–N(1) 2.279(2), Ti(2)–O(8) 1.789(2), Ti(2)–O(7) 1.814(2), Ti(2)–O(3) 1.9117(18), Ti(2)–O(4) 2.0377(19), Ti(2)–O(1) 2.0696(19), Ti(2)–N(2) 2.294(2), Ti(1) Ti(2) 3.2967(15); O(2)–Ti(1)–O(1) 158.62(8), O(6)–Ti(1)–O(4) 162.89(9), O(5)–Ti(1)–N(1) 177.89(8), Ti(1)–O(1)–Ti(2) 106.20(8), Ti(2)–O(4)–Ti(1) 107.27(8).

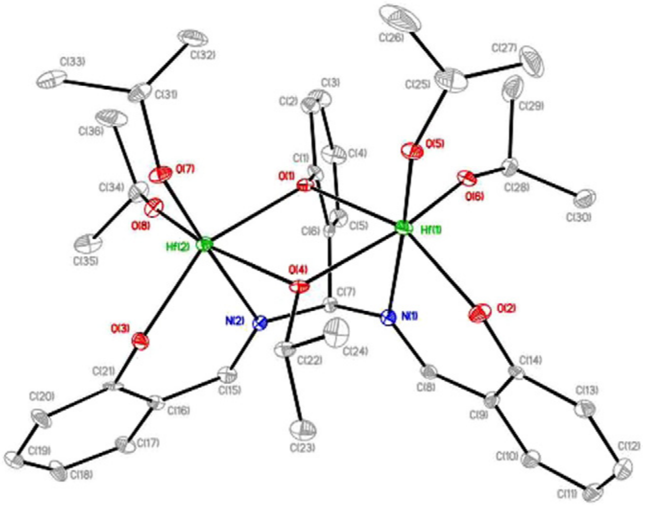


Fig. 2. ORTEP representation of the molecular solid-state structure of [Hf$_2$(μ-O^{i}Pr)(O^{i}Pr)$_4$L] (**3**). Thermal ellipsoids were drawn at the 20% probability level and H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Hf(1)–O(6) 1.920(4), Hf(1)–O(5) 1.948(4), Hf(1)–O(2) 2.029(4), Hf(1)–O(4) 2.160(4), Hf(1)–O(1) 2.197(4), Hf(1)–N(1) 2.420(5), Hf(2)–O(8) 1.934(4), Hf(2)–O(7) 1.954(4), Hf(2)–O(3) 2.046(4), Hf(2)–O(4) 2.165(4), Hf(2)–O(1) 2.164(4), Hf(2)–N(2) 2.398(5), Hf(1)···Hf(2) 3.5279(7); O(2)–Hf(1)–O(1) 154.53(16), O(6)–Hf(1)–O(4) 157.91(16) O(5)–Hf(1)–N(1) 176.27(17), Hf(2)–O(1)–Hf(1) 107.97(17), Hf(1)–O(4)-Hf(2) 109.33(17).