Journal of Organometallic Chemistry 783 (2015) 105–115

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Synthesis and characterization of zinc complexes supported by NHC-based CNN- and CNP-tridentate ligands and their catalysis in the ring-opening polymerization of *rac*-lactide and ε-caprolactone

Xiang-Xin Zheng [a, b], Cheng Zhang [a, c], Zhong-Xia Wang [a, b, *]

[a] Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China
[b] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China
[c] School of Engineering Technology, Beijing Normal University at Zhuhai, Guangdong 519087, China

ARTICLE INFO

Article history:
Received 1 December 2014
Received in revised form
5 February 2015
Accepted 10 February 2015
Available online 19 February 2015

Keywords:
Zinc complex
Synthesis
Catalysis
rac-Lactide
ε-Caprolactone
Polymerization

ABSTRACT

A series of zinc complexes bearing NHC-based C,N,N- or C,N,P-tridentate ligands were synthesized and characterized and the catalysis of the complexes toward the ring-opening polymerization of *rac*-lactide was evaluated. The ligand precursors $[2\text{-}(\overline{\mathrm{CHN(R)(CH)_2N}})\mathrm{C_6H_4N{=}P(Ph)_2CH_2Py}]^+\,\mathrm{I}^-$ (**2a**, R = Me; **2b**, R = *i*Pr) prepared from $[2\text{-}\mathrm{N_3C_6H_4}(\overline{\mathrm{N(CH)_2N(R)CH}})]^+\,\mathrm{I}^-$ (R = Me or *i*Pr) and Ph_2PCH_2Py were successively treated with *n*BuLi and $ZnEt_2$ to afford corresponding zinc complexes $[\mathrm{Zn(Et)}\{2\text{-}(\overline{\mathrm{CN(R)(CH)_2N}})\mathrm{C_6H_4NP(Ph)_2{=}CHPy}\}]$ (**3a**, R = Me; **3b**, R = *i*Pr). Similar treatment of $[2\text{-}(\overline{\mathrm{CHN(Me)(CH)_2N}})\mathrm{C_6H_4N{=}P(Ph)_2CH_2PPh_2}]^+\,\mathrm{I}^-$ (**4a**) (prepared from $[2\text{-}\mathrm{N_3C_6H_4}(\overline{\mathrm{N(CH)_2N(Me)CH}})]^+\,\mathrm{I}^-$ and $Ph_2PCH_2PPh_2$) with *n*BuLi and then $ZnEt_2$ gave $[\mathrm{Zn(Et)}\{2\text{-}(\overline{\mathrm{CN(Me)(CH)_2N}})\mathrm{C_6H_4NP(Ph)_2{=}CHPPh_2}\}]$ (**5**). Treatment of $[2\text{-}(\overline{\mathrm{CHN(R)(CH)_2N}})\mathrm{C_6H_4N{=}P(Ph)_2CH_2PPh_2}]^+\,\mathrm{X}^-$ (**4a**, R = Me, X = I; **4b**, R = Bn, X = Br; **4c**, R = *i*Pr, X = I) with *p*-$MeC_6H_4N_3$ resulted in $[2\text{-}(\overline{\mathrm{CHN(R)(CH)_2N}})\mathrm{C_6H_4N{=}P(Ph)_2CH_2P(Ph)_2{=}N(\textit{p}\text{-}MeC_6H_4)}]^+\,\mathrm{X}^-$ (**6a**, R = Me, X = I; **6b**, R = Bn, X = Br; **6c**, R = *i*Pr, X = I). The reaction of **6a** with *n*BuLi and $ZnEt_2$ in sequence produced $[\mathrm{Zn(Et)}\{2\text{-}(\overline{\mathrm{CN(Me)(CH)_2N}})\mathrm{C_6H_4NP(Ph)_2{=}CHP(Ph)_2{=}N(\textit{p}\text{-}MeC_6H_4)}\}]$ (**7**). Whereas the reaction of **6a**–**c** with an equimolar amount of $ZnEt_2$ gave $[\mathrm{Zn(X)}\{2\text{-}(\overline{\mathrm{CN(R)(CH)_2N}})\mathrm{C_6H_4NP(Ph)_2{=}CHP(Ph)_2{=}N(\textit{p}\text{-}MeC_6H_4)}\}]$ (**8a**, R = Me, X = I; **8b**, R = Bn, X = Br; **8c**, R = *i*Pr, X = I). All new compounds were characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy and elemental analyses. The structures of complexes **3a**, **5** and **8b** were additionally characterized by single crystal X-ray diffraction. In the presence of BnOH complexes **3a**, **3b**, **5** and **7** catalyze the ring-opening polymerization of *rac*-lactide at room temperature and **3a**, **3b**, and **5** exhibited high activity. Complexes **8a**–**c** are inactive under the same conditions. Complexes **3a** and **5** were also tested for the catalysis in the ROP of ε-caprolactone and both showed good catalytic activity.

Introduction

Aliphatic polyesters such as poly(lactide) (PLA), poly(ε-caprolactone) (PCL), and poly(glycolide) (PGA) have found wide applications in many areas, e.g. agricultural and packaging materials, drug delivery, medical devices, and so on [1]. One of the most effective methods for the synthesis of the polymers is metal-complex-catalyzed ring-opening polymerization (ROP) of corresponding cyclic esters [2]. Among numerous catalysts studied, zinc complexes have been proven to be excellent for the polymerizations [2–13]. For example, β-diketiminato zinc complexes catalyze the polymerization of *rac*-LA in high activity and selectivity [3]; salicylaldiminato zinc complexes also exhibited excellent catalytic properties in the polymerization of cyclic esters [4]. Similarly, zinc anilido-imine and β-ketiminate complexes have also been studied as variants of the above systems [5]. In addition, some *N*,*N*,*N*- and *N*,*N*,*O*-chelate zinc complexes were also proven to be efficient

---

* Corresponding author. Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China. Tel.: +86 551 63603043; fax: +86 551 63601592.
E-mail address: zxwang@ustc.edu.cn (Z.-X. Wang).

http://dx.doi.org/10.1016/j.jorganchem.2015.02.013
0022-328X/© 2015 Elsevier B.V. All rights reserved.

catalysts for the ROP of lactides and ε-caprolactone [4a,6]. However, different catalysts can bring about different microstructures and physical and mechanical properties of the polymers. Hence the search for new catalysts is still an attractive topic. *N*-Heterocyclic carbenes have been proven to be excellent ligands in stabilizing metal ions and in catalytic chemistry [8]. In 2004 Tolman et al. found that (μ-BnO)$_2$[Zn(IMes)(OBn)]$_2$ (IMes = 1,3-dimesitylimidazol-2-ylidene) (**I** in Chart 1) catalyzed rapid polymerization of *rac*-lactide to heterotactic enriched poly(lactide) [9]. In 2005 the same group further evaluated NHC zinc alkoxide complexes and C,N-chelate zinc complexes (**II** and **III** in Chart 1) for catalyzing the polymerization of *rac*-lactide [10]. Arnold et al. reported the catalysis of C,O-chelate zinc or magnesium complexes (**IV** and **V** in Chart 1) for the polymerization of *rac*-lactide in 2009 [11]. The results showed that the C,N- or C,O-chelate zinc complexes have relatively low activity. They required either high polymerization temperature or a long reaction time to drive the reactions to completion. Recently several monodentate N-heterocyclic carbene-Zn complexes [12] or abnormal N-heterocyclic carbene-Zn/Al complexes [13] were further tested. The abnormal N-heterocyclic carbene–Zn complex (**VI** in Chart 1) exhibited good activity in catalyzing the controlled polymerization of *rac*-lactide. In view of above facts, we became interested in knowing how the catalysis of zinc complexes bearing NHC-based multidentate ligands is. For this purpose, we synthesized a series of zinc complexes supported by NHC-based tridentate chelate ligands and evaluated the catalysis of the complexes in the ROP of *rac*-lactide and ε-caprolactone. Herein we report the results.

Results and discussion

Synthesis and characterization of the zinc complexes

Synthetic routes of the ligand precursors and the complexes are summarized in Scheme 1. The imidazolium salts **1a**–**c**, **2a**, **4b**, **4c** and **6c** were reported by us previously [14]. **2b** was prepared similarly to **2a** by reaction of **1c** with Ph$_2$PCH$_2$Py in CH$_2$Cl$_2$. Respective treatment of **2a** and **2b** in THF with an equiv of *n*BuLi and then ZnEt$_2$ gave neutral zinc complexes **3a** and **3b** in 81% and 73% yields, respectively. **4a** was prepared through reaction of **1a** with CH$_2$(PPh$_2$)$_2$ in CH$_2$Cl$_2$ using the same procedure as for **4b** reported earlier. In this study, both **4b** and **4c** were not isolated after reaction of **1b** or **1c** with CH$_2$(PPh$_2$)$_2$ and used directly in following transformations. Reaction of **4a** with an equiv of *n*BuLi for 6 h and then ZnEt$_2$ for 12 h afforded complex **5** in 90% yield. **4a**–**c** were transformed to **6a**–**c** by their respective reaction with *p*-MeC$_6$H$_4$N$_3$ in CH$_2$Cl$_2$. Treatment of **6a** with an equiv of *n*BuLi and followed with ZnEt$_2$ yielded complex **7** in 81% yield. The respective reaction of **6a**–**c** with an equiv of ZnEt$_2$ in THF resulted in complexes **8a**–**c** in 63–66% yields. The ligand precursors **2b**, **4a**, **6a** and **6b** are white solids. They are almost insoluble in THF, toluene and Et$_2$O, and soluble in CH$_2$Cl$_2$ and CHCl$_3$. The zinc complexes are air sensitive and stable under nitrogen. Both **3a** and **3b** are yellow solids and the others are colorless crystals. They are soluble in THF, benzene and toluene, but **8a**–**c** showed a little lower solubility than the others. All new compounds were characterized by elemental analyses and ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The ^{1}H NMR spectra of the imidazolium salts showed characteristic signals at δ 9.81–10.53 ppm for the imidazolium CH. The signals disappeared when the imidazolium salts were transformed to the zinc complexes. In the ^{13}C NMR spectra of the zinc complexes the carbene carbon signals appeared at the range of δ 178.91–185.94 ppm. The other signals of the ^{1}H and ^{13}C NMR spectra are also consistent with their respective structure. The chemical shifts of the ^{31}P NMR spectra of the imidazolium salts appeared at lower frequencies than

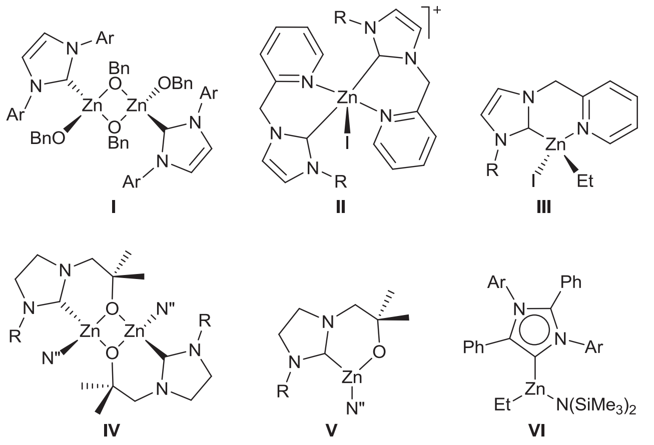
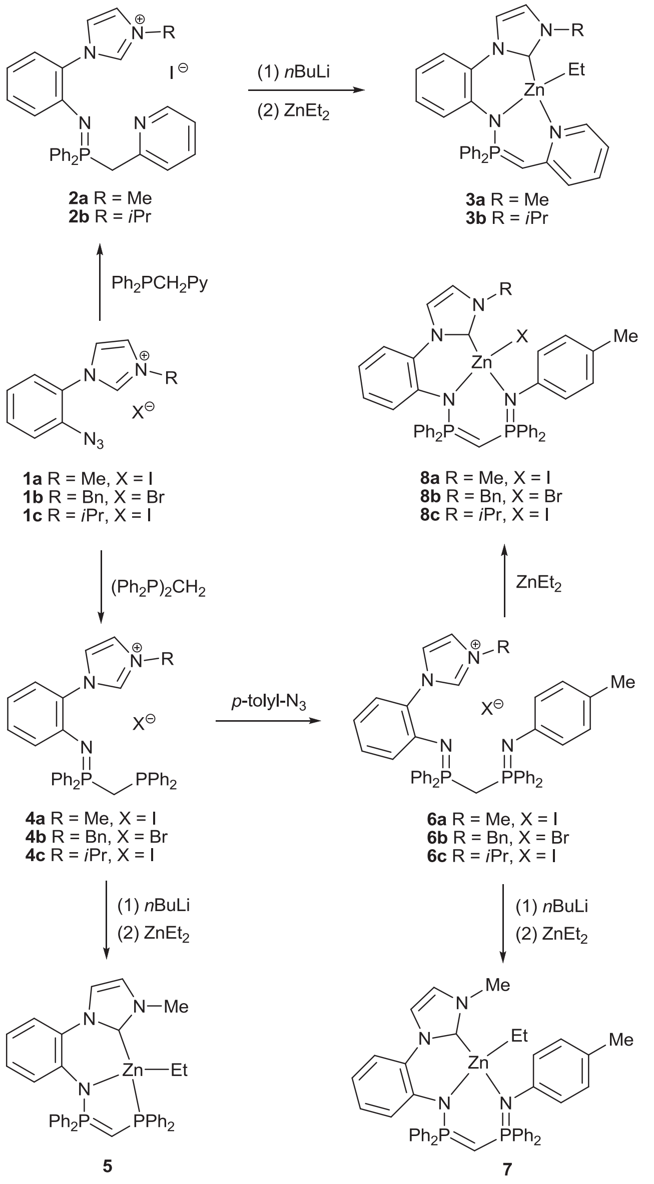


Chart 1. *N*-Heterocyclic carbene zinc complexes.



Scheme 1. Synthesis of C,N,N- and C,N,P-chelate zinc complexes.