Journal of Organometallic Chemistry 758 (2014) 65–72

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Synthesis, structure, and catalytic activity of organolanthanide complexes with chiral biaryl Schiff-base ligands

Wenshan Ren [a,b], Liang Chen [b], Ning Zhao [b], Qiuwen Wang [b], Guohua Hou [b], Guofu Zi [b,*]

[a] College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China
[b] Department of Chemistry, Beijing Normal University, Beijing 100875, China

ARTICLE INFO

Article history:
Received 21 December 2013
Received in revised form
10 February 2014
Accepted 13 February 2014

Keywords:
Chiral NO_2 ligand
Organolanthanide complex
Lactide
Polymerization

ABSTRACT

A new series of organolanthanide complexes have been prepared by silylamine elimination in good yields from $Ln[N(SiMe_3)_2]_3$ and chiral biaryl Schiff-base NO_2 ligands, **1**H_2–**4**H_2, which are derived from (*S*)-2-amino-2′-hydroxy-1,1′-binaphthyl or (*S*)-2-amino-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl, respectively. However, the formation of the organolanthanide complexes is strongly influenced by the solvent used in the synthesis. For example, treatment of ligand **1**H_2 or **2**H_2 with 1 equiv of $Ln[N(SiMe_3)_2]_3$ in DME or THF gives the mononuclear complexes (**1**)$Ln[N(SiMe_3)_2](DME)$ (Sm (**5**), Y (**6**), Yb (**7**)) and (**2**)$Y[N(SiMe_3)_2](THF)_2$ (**8**), respectively. While reaction of **2**H_2, **3**H_2 or **4**H_2 with 1 equiv of $Ln[N(SiMe_3)_2]_3$ in toluene gives the binuclear complexes $\{(\mathbf{2})Ln[N(SiMe_3)_2]\}_2$ (Ln = Sm (**9**), Yb (**10**)), $\{(\mathbf{3})Yb[N(SiMe_3)_2]\}_2$ (**11**) and $\{(\mathbf{4})Ln[N(SiMe_3)_2]\}_2$ (Ln = Y (**12**), Yb (**13**)), respectively. Complexes **5**–**13** have been characterized by various spectroscopic techniques, elemental analyses, and X-ray diffraction analyses. The complexes **5**–**13** are active catalysts for the polymerization of *rac*-lactide, leading to the isotactic-rich polylactides.

1. Introduction

Chiral organolanthanide complexes based on non-Cp multidentate ligands have received growing attention in the past two decades [1–14]. One of driving forces in this field is the growing interest in the development of catalysts for lactide polymerization [15–22], since polylactides are increasingly used as a commodity polymer due to its biodegradability and the possibility of deriving the monomer from renewable resources [23,24]. The physical and mechanical properties of polylactides, as well as the rate of degradation, are highly dependent on the chain stereochemistry [25–27]. For example, a stereocomplex polymer formed by an equivalent mixture of poly(L-lactide) and poly(D-lactide) has many advantages such as higher melting temperature (230 °C) comparing with the enantiopure polylactide (180 °C) [28,29]. Therefore, the polymerization of *rac*-lactide via stereoselective catalysts represents a significant challenge, but it is also an opportunity for chemists. To date, the catalyst systems based on metals such as magnesium, zinc, calcium, aluminum, lanthanides, tin, group 4 metals, germanium, indium and iron, for the ring-opening polymerization (ROP) of cyclic esters have been covered in numerous reviews [3,30–33]. Among these, the organolanthanide catalysts have been shown to be promising for this transformation [15–22,34–36], however, compared to other metals, structurally well-characterized chiral organolanthanide complexes that initiate controlled ring-opening polymerization of lactides are rather scarce [3,30–33]. Thus, the development of new chiral organolanthanide catalysts for polymerization of *rac*-lactide is still a desirable and challenging goal.

In recent years, we have developed a series of chiral multidentate ligands, and their Ta(IV), Ti(IV), Zr(IV), Zn(II), Al(III) and lanthanide complexes that are useful catalysts for a range of transformations [37–65]. Furthermore we demonstrated that the chiral biaryl-based lanthanide, zinc and aluminum complexes are effective catalysts for the polymerization of *rac*-lactide, in which the isotactic or heterotactic rich polylactides have been obtained [42,45,47,54,56,59,63–65]. In our ongoing research, we are now focusing on the preparation of lanthanide catalysts coordinated by chiral biaryl-based C_1-symmetric tridentate ligands, and to our knowledge, few lanthanide catalysts based on chiral binaphtholamine or biphenolamine have been reported [1–14]. More recently, we have reported a series of titanium and aluminum complexes with the chiral tridentate Schiff-base NO_2-ligands, **1**H_2–**4**H_2, which are derived from (*S*)-2-amino-2′-hydroxy-1,1′-binaphthyl and

* Corresponding author. Tel.: +86 10 5880 6051; fax: +86 10 5880 2075.
E-mail addresses: gzi@bnu.edu.cn, ziguofu@hotmail.com (G. Zi).

http://dx.doi.org/10.1016/j.jorganchem.2014.02.005
0022-328X/

(*S*)-2-amino-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl, respectively [62,65]. These complexes are efficient chiral catalysts for the asymmetric hydrophosphonylation of aldehydes and polymerization of *rac*-lactide, respectively, in which good enantioselectivities or stereoselectivities have been obtained [62,65]. In our efforts to further explore the coordination chemistry of the chiral ligands **1**H_2–**4**H_2, we have recently extended our research interests to organolanthanide chemistry. Herein, we report on the reaction of ligands **1**H_2–**4**H_2 with Ln[N(SiMe$_3$)$_2$]$_3$, and the use of the resulting complexes as catalysts in the polymerization of *rac*-lactide.

2. Experimental section

2.1. General methods

Organolanthande complexes and catalytic reactions were performed under an atmosphere of dry dinitrogen with rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Racemic lactide was recrystallized twice from dry toluene and then sublimed under vacuum prior to use. **1**H_2–**4**H_2 [62,65] and Ln[N(SiMe$_3$)$_2$]$_3$ [66] were prepared according to the literature procedures. All chemicals were purchased from Aldrich Chemical Co. and Beijing Chemical Co. used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets on an Avatar 360 Fourier transform spectrometer. Molecular weights of the polymer were estimated by gel permeation chromatography (GPC) using a PL-GPC 50 apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 500 spectrometer at 500 and 125 MHz, respectively. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents for proton and carbon chemical shifts. Melting points were measured on an X-6 melting point apparatus and were uncorrected. Elemental analyses were performed on a Vario EL elemental analyzer.

2.2. Preparation of (*1*)Sm[N(SiMe$_3$)$_2$](DME) (*5*)

A DME (10 mL) of **1**H_2 (0.19 g, 0.5 mmol) was slowly added to a DME (10 mL) of Sm[N(SiMe$_3$)$_2$]$_3$ (0.32 g, 0.5 mmol) with stirring at room temperature. The resulting solution was refluxed overnight to give a yellow solution. The solution was filtered, and the filtrate was concentrated to about 2 mL. Complex **5** was isolated as yellow crystals after this solution stood at room temperature for one week. Yield: 0.30 g (77%). M.p.: 220–222 °C (dec.). ^{1}H NMR (C_6D_6): δ 8.67 (d, J = 7.6 Hz, 1H aryl), 8.04 (s, 1H, C*H*=N), 7.94 (d, J = 6.2 Hz, 1H, aryl), 7.36 (t, J = 7.7 Hz, 1H, aryl), 7.26 (d, J = 7.6 Hz, 1H, aryl), 6.18 (d, J = 7.6 Hz, 1H, aryl), 5.60 (d, J = 7.5 Hz, 1H, aryl), 4.85 (t, J = 7.5 Hz, 1H, aryl), 4.40 (d, J = 7.6 Hz, 1H, aryl), 3.40 (s, 4H, DME), 3.13 (s, 6H, DME), 2.19 (d, J = 7.3 Hz, 1H, aryl), 1.31 (s, 3H, C*H*$_3$), 1.09 (s, 3H, C*H*$_3$), −0.86 (br s, 18H, SiC*H*$_3$), −1.64 (s, 9H, C*H*$_3$). ^{13}C NMR (C_6D_6): 180.0, 175.4, 171.5, 140.0, 139.2, 138.6, 136.5, 134.6, 132.9, 129.3, 128.5, 126.0, 125.6, 124.3, 120.2, 117.8, 117.1, 115.7, 115.4, 67.9, 60.2, 33.2, 31.9, 19.5, 19.1, 2.6. IR (KBr, cm^{-1}): ν 2961 (s), 1598 (m), 1536 (m), 1414 (m), 1260 (s), 1089 (s), 1018 (s), 798 (s). Anal. Calcd for $C_{35}H_{53}N_2O_4Si_2Sm$: C, 54.43; H, 6.92; N, 3.63. Found: C, 54.36; H, 6.83; N, 3.68%.

2.3. Preparation of (*1*)Y[N(SiMe$_3$)$_2$](DME) (*6*)

This compound was prepared as colorless crystals from the reaction of **1**H_2 (0.19 g, 0.5 mmol) with Y[N(SiMe$_3$)$_2$]$_3$ (0.28 g, 0.5 mmol) in DME (20 mL) and recrystallization from a DME solution by a similar procedure as in the synthesis of **5**. Yield: 0.23 g (65%). M.p.: 236–238 °C (dec.). ^{1}H NMR (C_6D_6): δ 8.14 (s, 1H, N=C*H*), 7.38 (m, 2H, aryl), 7.25 (m, 2H, aryl), 6.96 (d, J = 7.8 Hz, 1H, aryl), 6.70 (m, 2H, aryl), 6.54 (m, 2H, aryl), 3.11 (s, 4H, DME), 2.91 (s, 6H, DME), 2.09 (s, 3H, C*H*$_3$), 2.03 (s, 3H, C*H*$_3$), 1.49 (s, 9H, C*H*$_3$), 0.33 (s, 18H, SiC*H*$_3$). ^{13}C NMR (C_6D_6): δ 167.7, 161.1, 156.4, 151.1, 139.8, 138.8, 134.8, 134.2, 133.7, 132.3, 129.7, 128.7, 128.3, 123.2, 122.6, 117.7, 117.1, 116.6, 115.1, 69.9, 61.0, 35.0, 29.8, 20.2, 20.0, 5.1. IR (KBr, cm^{-1}): ν 2960 (s), 1607 (s), 1422 (s), 1388 (s), 1260 (s), 1091 (s), 1019 (s), 799 (s). Anal. Calcd for: $C_{35}H_{53}N_2O_4Si_2Y$: C, 59.13; H, 7.51; N, 3.94. Found: C, 59.26; H, 7.53; N, 3.88%.

2.4. Preparation of (*1*)Yb[N(SiMe$_3$)$_2$](DME) (*7*)

This compound was prepared as yellow crystals from the reaction of **1**H_2 (0.19 g, 0.5 mmol) with Yb[N(SiMe$_3$)$_2$]$_3$ (0.33 g, 0.5 mmol) in DME (20 mL) and recrystallization from a DME solution by a similar procedure as in the synthesis of **5**. Yield: 0.27 g (67%). M.p.: 212–214 °C (dec.). IR (KBr, cm^{-1}): ν 2962 (s), 1602 (s), 1384 (s), 1260 (s), 1092 (s), 1020 (s), 799 (s). Anal. Calcd for $C_{35}H_{53}N_2O_4Si_2Yb$: C, 52.88; H, 6.72; N, 3.52. Found: C, 52.86; H, 6.73; N, 3.48%.

2.5. Preparation of (*2*)Y[N(SiMe$_3$)$_2$](THF)$_2$ (*8*)

This compound was prepared as colorless microcrystals from the reaction of **2**H_2 (0.22 g, 0.5 mmol) with Y[N(SiMe$_3$)$_2$]$_3$ (0.28 g, 0.5 mmol) in THF (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **5**. Yield: 0.30 g (73%) M.p.: 190–192 °C (dec.). ^{1}H NMR (C_6D_6): δ 8.13 (d, J = 2.2 Hz, 1H, aryl), 7.76 (d, J = 8.0 Hz, 1H, aryl), 7.61 (d, J = 2.5 Hz, 1H, aryl), 7.59 (d, J = 2.5 Hz, 1H, aryl), 7.49 (d, J = 2.4 Hz, 1H, aryl), 7.33 (d, J = 7.6 Hz, 1H, aryl), 7.07 (m, 2H, aryl), 6.94 (m, 1H, aryl), 3.67 (s, 8H, THF), 1.97 (s, 3H, C*H*$_3$), 1.85 (s, 3H, C*H*$_3$), 1.48 (s, 9H, C*H*$_3$), 1.42 (s, 9H, C*H*$_3$), 1.36 (m, 8H, THF), 0.22 (s, 18H, SiC*H*$_3$). ^{13}C NMR (C_6D_6): δ 168.3, 167.8, 163.7, 161.1, 156.5, 148.1, 139.3, 138.2, 137.2, 131.7, 130.4, 130.1, 129.6, 128.6, 127.5, 122.7, 120.5, 118.8, 116.0, 68.3, 35.2, 33.7, 31.2, 31.1, 25.4, 20.3, 20.0, 4.6. IR (KBr, cm^{-1}): ν 2961 (s), 1535 (s), 1456 (s), 1388 (m), 1258 (s), 1090 (s), 1021 (s), 798 (s). Anal. Calc. for $C_{43}H_{67}N_2O_4Si_2Y$: C, 62.90; H, 8.22; N, 3.41. Found: C, 62.83; H, 8.23; N, 3.38%. A few colorless crystals suitable for X-ray diffraction analysis were selected.

2.6. Preparation of {(*2*)Sm[N(SiMe$_3$)$_2$]}$_2$ (*9*)

This compound was prepared as yellow microcrystals from the reaction of **2**H_2 (0.22 g, 0.5 mmol) with Sm[N(SiMe$_3$)$_2$]$_3$ (0.32 g, 0.5 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **5**. Yield: 0.22 g (60%). M.p.: 230–232 °C (dec.). ^{1}H NMR (C_6D_6): δ 8.79 (d, J = 2.2 Hz, 2H, aryl), 8.04 (s, 2H, C*H*=N), 7.57 (d, J = 2.2 Hz, 2H, aryl), 6.32 (d, J = 7.6 Hz, 2H, aryl), 5.48 (d, J = 7.5 Hz, 2H, aryl), 4.93 (t, J = 7.4 Hz, 2H, aryl), 4.42 (d, J = 7.6 Hz, 2H, aryl), 2.16 (d, J = 7.3 Hz, 2H, aryl), 1.49 (s, 18H, C*H*$_3$), 1.24 (s, 9H, C*H*$_3$), 1.02 (br s, 39H, C*H*$_3$), 0.28 (s, 2H, aryl), −1.45 (s, 18H, C*H*$_3$). ^{13}C NMR (C_6D_6): δ 180.0, 174.1, 165.1, 139.7, 138.6, 134.7, 134.1, 133.6, 132.7, 129.3, 128.6, 126.9, 126.1, 125.7, 124.4, 124.2, 122.0, 120.1, 115.6, 34.8, 33.7, 31.9, 31.6, 19.4, 19.0, 2.6. IR (KBr, cm^{-1}): ν 2964 (s), 1616 (s), 1568 (m), 1532 (s), 1451 (s), 1382 (s), 1260 (s), 1089 (s), 1020 (s), 987 (s), 799 (s). Anal. Calc. for $C_{70}H_{102}N_4O_4Si_4Sm_2$: C, 56.94; H, 6.96; N, 3.79. Found: C, 56.96; H, 6.89; N, 3.78%. A few yellow crystals suitable for X-ray diffraction analysis were selected.

2.7. Preparation of {(*2*)Yb[N(SiMe$_3$)$_2$]}$_2$ (*10*)

This compound was prepared as yellow crystals from the reaction of **2**H_2 (0.22 g, 0.5 mmol) with Yb[N(SiMe$_3$)$_2$]$_3$ (0.33 g, 0.5 mmol) in