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Mixed ligands supported yttrium alkyl complexes: Synthesis, characterization and catalysis toward lactide polymerization

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Abstract

Treatment of yttrium tris(alkyl)s, $Y(CH_2SiMe_3)_3(THF)_2$, by equimolar $H(C_5Me_4)SiMe_3(HCp')$ and indene (Ind-H) afforded $(\eta^5\text{-}Cp')Y(CH_2SiMe_3)_2(THF)$ (**1**) and $(\eta^5\text{-}Ind)Y(CH_2SiMe_3)_2(THF)$ (**2**) via alkane elimination, respectively. Complex **1** reacted with methoxyamino phenols, $4,6\text{-}(CH_3)_2\text{-}2\text{-}[(MeOCH_2CH_2)_2\text{-}NCH_2]\text{-}C_6H_2\text{-}OH$ (HL^1) and $4,6\text{-}(CMe_3)_2\text{-}2\text{-}[(MeOCH_2CH_2)_2\text{-}NCH_2]\text{-}C_6H_2\text{-}OH$ (HL^2) gave mixed ligands supported alkyl complexes $[(\eta^5\text{-}Cp')(L)]Y(CH_2SiMe_3)$ (**3**: $L = L^1$; **4**: $L = L^2$). Whilst, complex **2** was treated with HL^2 to yield $[(\eta^5\text{-}Ind)(L^2)]Y(CH_2SiMe_3)$ (**5**). The molecular structures of **3** and **5** were confirmed by X-ray diffraction to be mono(alkyl)s of THF-free, adopting pyramidal and tetragonal-bipyramidal geometry, respectively. Complexes **3** and **5** were high active initiators for the ring-opening polymerization of L-lactide to give isotactic polylactide with high molecular weight and narrow to moderate polydispersity.
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Keywords: Yttrium; Alkyl complex; Lactide; Polymerization; Mixed ligands

1. Introduction

Rare earth metal alkyl complexes stabilized by cyclopentadienyl (Cp) ligands have been extensively developed in the past decades, which exhibited tremendous catalytic activities toward polymerizations of polar and non-polar monomers [1–5]. Meanwhile, multidentate non-Cp ligands have also attracted increasing attention, since these ligands could provide proper steric and electronic environment for compensating coordinative unsaturation of metal centers [6–11]. Comparatively, rare earth metal complexes bearing mixed Cp/non-Cp ligands have been less exploited, however, they have received considerable attention recently

due to the merits of the combined ligands [12,13]. For instance, mixed Cp*/bipyridine supported lutetium complexes reported by Cameron et al. reacted with carbon monoxide leading to interesting intramolecular C–H activation of the bipyridine ligand [12]. Lanthanide complexes stabilized by mixed Cp*/bis(phosphinimino)-methanide ligands could initiate controllable ring-opening polymerization of ε-caprolactone [14]. Thus, further exploration of rare earth metal complexes bearing one Cp moiety and a non-Cp ligand is of obvious interest.

Indene (Ind-H) has been demonstrated to be a more sterically demanding yet planar π ligand [15]. The differences of the steric and electronic properties between indenyl and cyclopentadienyl moieties would be reflected in the molecular structure and reactivity of the corresponding complexes. Therefore, we synthesized yttrium alkyl complexes bearing mixed Cp/*N,O*-multidentate or mixed Ind/*N*,

O-multidentate ligands. Herein, we report the preparation and characterization of these novel complexes. The influence of ligand framework on molecular structure of these complexes and their catalytic behavior toward the ring-opening polymerization (ROP) of L-lactide will also be discussed.
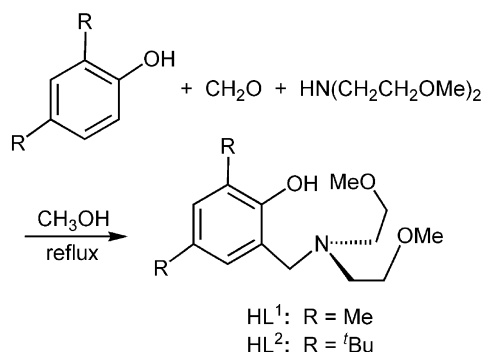
2. Results and discussion

2.1. Synthesis of ligands

Following the modified literature procedures [16], ligands HL[1] and HL[2] were synthesized by Mannich condensations of the corresponding substituted phenols, para-formaldehyde and bis(2-methyloxyethyl)amine in refluxing methanol (Scheme 1). ^{1}H NMR data were consistent with the formation of the targeted products.
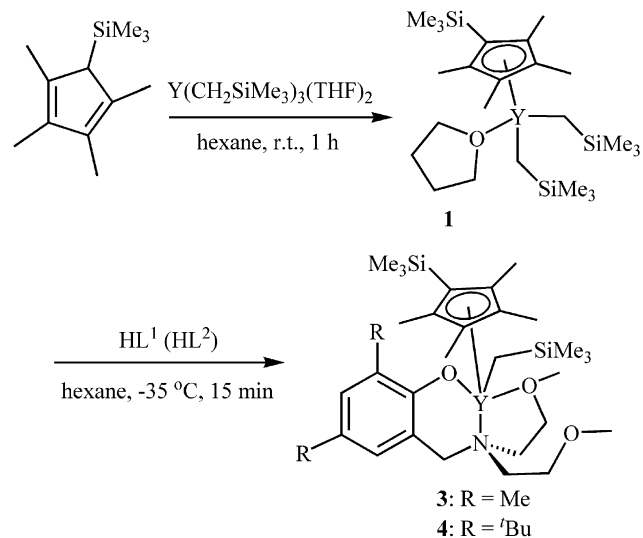
2.2. Synthesis and characterization of complexes 3 and 4

Reaction of $HC_5Me_4SiMe_3$ (HCp′) with 1 equiv. of yttrium tris(alkyl)s, $Y(CH_2SiMe_3)_3(THF)_2$, took place immediately upon addition at room temperature. The reaction mixture was remained for 1 h under stirring to afford mono-cyclopentadienyl yttrium bis(alkyl) complex $(\eta^5$-Cp′$)Y(CH_2SiMe_3)_2(THF)$ (1) [17]. Further reaction between 1 and HL[1] at −35 °C for 15 min gave mixed ligands supported mono(alkyl) complex $(\eta^5$-Cp′$)(L^1)$-$Y(CH_2SiMe_3)$ (3) via alkane elimination (Scheme 2). The ^{1}H NMR spectrum of 3 displays that the methylene protons of YCH_2SiMe_3 are diastereotopic to give an AB spin around δ −0.45 (J_{H-H} = 8 Hz) and −0.99 ppm (J_{H-H} = 8 Hz). The AB lines split further into doublets due to coupling with yttrium atom (J_{Y-H} = 4 Hz). This suggests that 3 is asymmetric in solution state.

The solid-state structure of complex 3 was figured out by X-ray diffraction analysis as shown in Fig. 1. The complex is seven-coordinate mono(alkyl) without solvated THF molecule. The Cp′ moiety coordinates to yttrium atom in a η^5-mode, meanwhile the L[1] fragment bonds to yttrium atom in a tridentate O,N,O mode, generating distorted pyramidal geometry around the metal center. The chelating oxygen and nitrogen atoms combined with the alkyl carbon

Scheme 2. Synthetic pathway for complex 3 and 4.

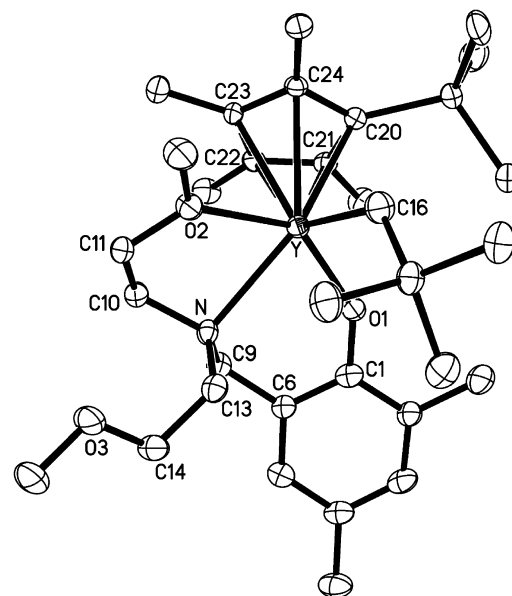Fig. 1. X-ray structure of 3 with 35% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity.
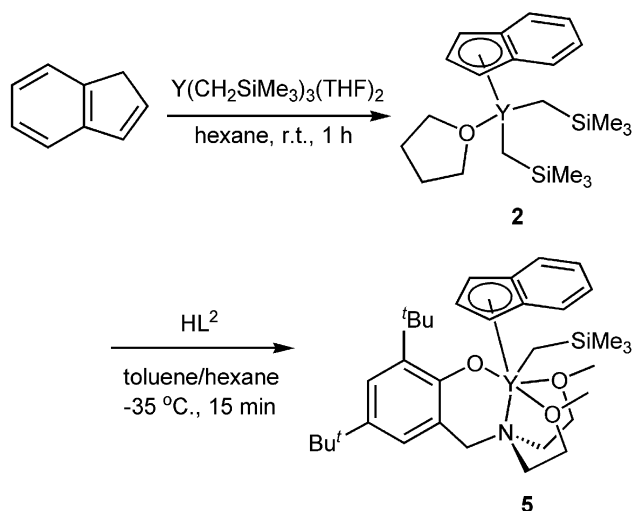
atom form the base, while the center of the Cp′ ring occupies the apex. It is noteworthy that one pendent OCH_3 group coordinates to yttrium ion while the other is hanging away with respect to the steric environment and electron saturation of central metal ion. This is consistent with the ^{1}H NMR spectrum analysis. The coordinating OCH_3 group gives a resonance at δ = 2.88 ppm, shifting up field compared to the free ligand (δ = 3.23 ppm). In contrast, the signal of the non-coordinating OCH_3 appears at δ = 3.10 ppm, much close to that of free ligand. The similar situation has been observed in a zinc alkyl complex $[4,6$-$^tBu_2$-2-$(Et_2NCH_2CH_2)_2NCH_2$-C_6H_2-$O]Zn(CH_2CH_3)$, where only one of the two diethylamino donor bonds to the metal ion [18].

Scheme 1. Synthetic pathway for HL[1] and HL[2].

Table 1
Selected bond distances (Å) and angles (°) for **3**

Y–O(1)	2.114(2)	Y–C(21)	2.691(3)
Y–C(16)	2.406(3)	Y–C(23)	2.728(3)
Y–O(2)	2.418(2)	Y–C(22)	2.731(3)
Y–N	2.566(2)	Y–C(20)	2.691(3)
Y–C(24)	2.676(3)	Y–Cp′$_{\text{ring centroid}}$	2.410(3)
O(1)–Y–C(16)	99.70(11)	O(2)–Y–N	66.09(7)
O(1)–Y–O(2)	140.57(8)	O(1)–Y–C(24)	128.79(9)
C(16)–Y–O(2)	89.11(10)	C(16)–Y–C(24)	92.68(11)
O(1)–Y–N	76.31(8)	O(2)–Y–C(24)	88.57(9)
C(16)–Y–N	119.48(10)	N–Y–C(24)	137.02(9)

The Y–O(2) bond length (2.418(2) Å) is comparable to those observed for Y–O$_{\text{ether}}$ in a range of 2.45–2.50 Å [19] (Table 1), but longer than the distance between yttrium atom and the phenoxy oxygen atom (Y–O(1): 2.114(2) Å). The bond lengths formed by yttrium and carbon atoms of the Cp′ ring, Y-η^5-C$_{\text{Cp}'}$, ranging from 2.676(3) to 2.731(3) Å, are comparable to those of Dy-η^5-C$_{\text{Cp}}$ (2.638(2)–2.704(3) Å) in complex (C$_5$Me$_4$SiMe$_3$)Dy(CH$_2$SiMe$_3$)$_2$-(THF) [20]. The distance between yttrium atom and the centroid of Cp′ ring, Y–Cp′$_{\text{cent}}$ (2.410 Å), is comparable to that (2.386(7) Å) in complex [CH(PPh$_2$NSiMe$_3$)$_2$Y(η^5-C$_5$Me$_5$)Cl] if the difference of the ionic radii is considered [14]. The Y–N bond length (2.566(2) Å) and N–Y–O(2) bond angle (66.09(7)°) are close to the corresponding those (Y–N: 2.507(3) Å; N–Y–O(2): 67.25(8)°) found in complex [4,6-^{t}Bu$_2$-(MeOCH$_2$CH$_2$)$_2$N-C$_6$H$_2$O-]Y(CH$_2$SiMe$_3$)$_2$ [21]. The six-membered N,O-chelate ring YO(1)C$_3$N with a bite angle of 76.31(8)° has envelope conformation. The Y and N atoms sit about 0.5998 Å and 1.1095 Å, respectively, out of the twisted OC$_3$ plane.

Following the similar procedure, complex (η^5-Cp′)(L^2)-Y(CH$_2$SiMe$_3$) (**4**) was obtained by treatment of **1** with equimolar HL^2 at −35 °C (Scheme 2). The ^{1}H NMR spectrum of **4** displays similar pattern to that of **3**. One pendant OCH$_3$ group shows resonance at $\delta = 2.93$ ppm, indicating

coordination to the central metal. Whilst the other pendant OCH$_3$ group exhibits a signal at $\delta = 3.21$ ppm comparable to the free ligand. The AB spin around δ −0.76 and −0.29 ppm is assignable to the methylene protons of YCH$_2$SiMe$_3$. Thus, the ^{1}H NMR spectrum is informative enough to confirm complex **4** of a mono(alkyl) stabilized by mixed ligands albeit without X-ray diffraction.

2.3. Synthesis and characterization of complex 5

Treatment of indene (Ind-H) with 1 equiv. of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ at room temperature for 1 h gave an indenyl yttrium bis(alkyl) complex (η^5-Ind)Y(CH$_2$SiMe$_3$)$_2$(THF) (**2**) via alkane elimination. Reaction of **2** with equimolar HL^2 at −35 °C for 15 min afforded (η^5-Ind)(L^2)Y(CH$_2$SiMe$_3$) (**5**) as yellow powders (Scheme 3). Single crystals of **5** grew as yellow prisms from a mixture of toluene and hexane (1:3 v/v) at −35 °C within several days. The molecular structure of complex **5** was confirmed by X-ray diffraction to be unsolvated mono(alkyl) of eight-coordinate (Fig. 2). The indene moiety coordinates to yttrium ion in η^5-mode, whilst the phenoxide ligand chelates to yttrium ion in O,N,O,O tetradentate mode, generating distorted tetragonal-bipyramidal geometry core. The phenoxy oxygen O(1), methoxy oxygen O(3), the alkyl carbon C(22) and N atoms occupy the equatorial positions, while the center of the five-member ring of the indenyl fragment and the methoxy oxygen atom O(2) are axial. The bond lengths of Y–N (2.549(4) Å), Y–C(22) (2.433(5) Å), Y–O(1) (2.123(3) Å) are comparable to the corresponding data found in complex **3** (Y–N (2.566(2) Å), Y–C(16) (2.406(3) Å), Y–O(1) (2.114(2) Å)) and those in the dialkyl yttrium complex [(CH$_3$OCH$_2$CH$_2$)$_2$NCH$_2$-3,5-(CMe$_3$)$_2$-2-C$_6$H$_2$O]Y(CH$_2$SiMe$_2$Ph)$_2$ (Y–N (2.5345(14) Å, Y–C(22) 2.4453(19) Å, Y–O(3) 2.1140(11) Å) [6a]. The featuring

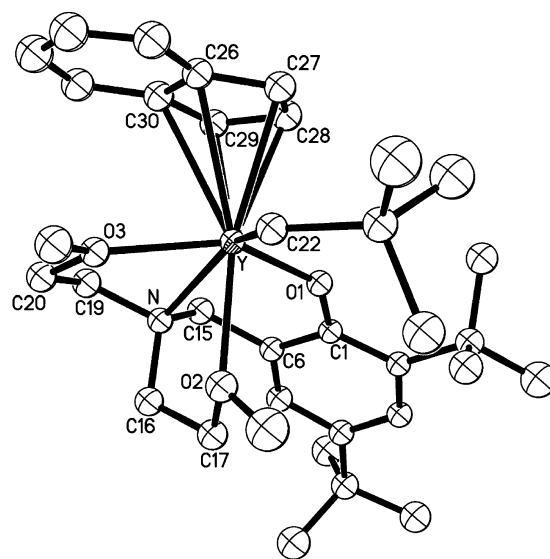Scheme 3. Synthetic pathway for complex **5**.

Fig. 2. X-ray structure of **5** with 35% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity.

bond angles of complex **5**, N–Y–O(1) (77.70(12)°) and N–Y–C(22) (144.32(16)°) are comparable to N–Y–O(1) (76.31(8)°) and N–Y–C(16) (119.48(10)°) in **3** and the corresponding those in the above mentioned dialkyl yttrium complex (N–Y–O(3), 78.55(4)°); N–Y–C(22), 99.28(6)°) [6a]. It is noteworthy that both pendent methoxy groups coordinate to yttrium ion and arrange in *cis*-positions. This is in contrast to the case of complex **3**, where only one methoxy group coordinates to yttrium ion. The difference is mostly attributed to the crowded environment caused by the indenyl moiety in **5**. The Y–O_{ether} bond lengths (Y–O(2), 2.533(4) Å and Y–O(3), 2.387(3) Å) are longer than Y–$O_{phenoxy}$ (Y–O(1), 2.123(3) Å). The bond angle formed by yttrium ion and methoxy oxygen atoms (O(2)–Y–O(3)) is 78.59(11)°, much smaller than the corresponding O(11)–Co–O(15) bond angle (121.31(4)°) in a cobalt analogue [4,6-$^tBu_2$-2-(MeOCH$_2$CH$_2$)$_2$NCH$_2$-C$_6$H$_2$O]Co(Cl$_2$) [18] (see Table 2).

2.4. Polymerization of ʟ-lactide initiated by complexes 3 and 5

Yttrium alkyl complexes **3** and **5** were active initiators for the ring-opening polymerization (ROP) of ʟ-lactide (ʟ-LA) under mild conditions. The polymerization initiated by complex **5** performed smoothly at room temperature in THF, and complete conversion was achieved within 2.5 h (Fig. 3). When the reaction time was prolonged over 5 h, no obvious decrease in conversion was observed, indicating the absence of degradation side-reaction. The influence of monomer-to-initiator ratio was investigated. For both catalytic systems, the molecular weight of the resultant polylactide (PLA) increased with the increase of monomer-to-initiator ratio, which was close to the theoretical value (Table 3). However, slightly deviation was observed when the ratio was raised over 800, which could be attributed to difficulty of monomer diffusion caused by viscosity of the system. We could also see from Table 3 that complex **5** was more efficient initiator than **3**, which initiated ROP of LA in more controllable manner to afford PLA with much narrow molecular weight distribution. This might be due to the more steric environment around the metal center in **5** caused by the coordination of two methoxy groups, whereas, only one methoxy group coordinates to
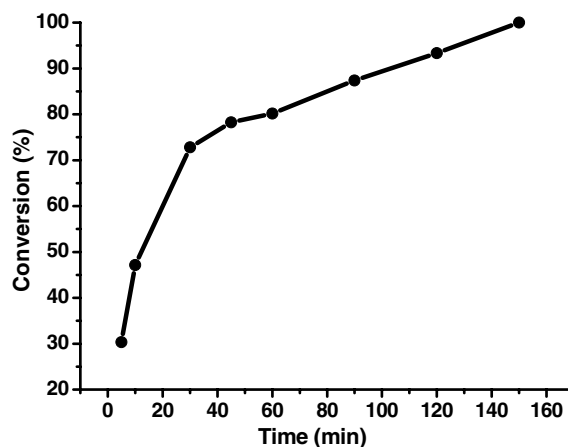

Fig. 3. Plot of ʟ-lactide conversion against time using complex **5**.

the metal center in **3**. The ^{1}H NMR spectrum of polylactide displayed a symmetric quartet resonance assigned to the methine proton at $\delta = 5.15$ ppm, indicating the configuration of monomer was remained in PLA and the negligible racemization.

3. Conclusion

In summary, we have demonstrated the syntheses and structures of several yttrium mono(alkyl) complexes stabilized by mixed cyclopentadienyl (or indenyl) and *N,O*-multidentate methoxyamino phenoxide moieties. All complexes are monomers of THF-free. The molecular structures and the catalytic performance are strongly dependent on the ligand framework. Complex **5** chelated by bulky *OONO*-multidentate ligand initiates more controllable ROP of ʟ-LA than the less steric counterpart **3** coordinated by *OON*-tridentate moiety, affording PLA with molecular weight closer to the theoretic value and more narrow molecular weight distribution.

4. Experimental

4.1. General methods

All the syntheses and manipulations of air- and moisture-sensitive materials were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MBRAUN glovebox. All solvents were purified from MBRAUN SPS system. Organometallic samples for NMR spectroscopic measurements were prepared in a glovebox by using NMR tubes sealed with paraffin film.^{1}H, ^{13}C NMR spectra were recorded on a Bruker AV400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) spectrometer. NMR assignments were confirmed by the ^{1}H–^{1}H (COSY) and ^{1}H–^{13}C (HMQC) experiments when necessary. IR spectra were recorded on a VERTEX 70 FT-IR spectrometer. Gel permeation chromatography (GPC) analyses of polymer samples were carried at 30 °C using THF as eluent on a Waters-410

Table 2
Selected bond distances (Å) and angles (°) for **5**

Y–O(1)	2.123(3)	Y–C(26)	2.926(5)
Y–O(2)	2.533(4)	Y–C(27)	2.757(6)
Y–O(3)	2.387(3)	Y–C(28)	2.711(5)
Y–C(22)	2.433(5)	Y–C(29)	2.796(5)
Y–N	2.549(4)	Y–C(30)	2.973(5)
O(1)–Y–O(2)	82.21(11)	O(3)–Y–C(22)	92.69(14)
O(1)–Y–O(3)	144.30(12)	O(3)–Y–N	67.05(12)
O(1)–Y–C(22)	114.09(15)	C(22)–Y–O(2)	81.90(15)
O(1)–Y–N	77.70(12)	C(22)–Y–N	144.32(16)
O(3)–Y–O(2)	78.59(11)	O(2)–Y–N	65.93(12)

Table 3
Effect of monomer-to-initiator ratio on polymerization of L-LA[a]

Entry	Cat.	$[LA]_0/[Y]_0$	Conv.[b] (%)	$M_{calc.}^{c} \times 10^{-4}$	$M_n^{d} \times 10^{-4}$	M_w/M_n^{d}
1	3	300	89.0	3.84	3.71	1.87
2	3	500	87.3	6.28	6.77	2.02
3	3	800	85.5	9.85	10.31	1.69
4	5	300	100.0	4.32	4.80	1.54
5	5	500	99.2	7.20	8.13	1.48
6	5	800	98.6	11.52	10.57	1.47
7	5	1000	98.90	14.40	13.69	1.57

[a] Conditions: THF, $[LA]_0 = 1.0$ mol/L, 20 °C, 2.5 h.
[b] Weight of polymer obtained/weight of monomer used.
[c] $M_{calc.} = ([LA]_0/[Y]_0) \times 144. 13 \times X$ (X = conversion).
[d] Measured by GPC calibrated with standard polystyrene samples.

instrument and calibrated using polystyrene standards. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). L-LA (Aldrich) was recrystallized from $CH_3COOCH_2CH_3$.

4.2. X-ray crystallographic studies

Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox. Data collections were performed at −86.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The crystallographic data and the refinement of complexes 3 and 5 are summarized in Table 4.

4.3. Synthesis of ligands

4.3.1. 4,6-(CH₃)₂-2-[(MeOCH₂CH₂)₂-NCH₂]-C₆H₂-OH (HL¹)

Paraformaldehyde (1.59 g, 52.8 mmol) and bis(2-methyloxyethyl)amine (6.0 mL, 40.63 mmol) were refluxed for 2 h. A solution of 2,4-di-methylphenol (4.93 mL, 40.78 mmol) in methanol (50 mL) was then added and the mixture and remained refluxing for another 24 h. Removal of the volatiles under reduced pressure afforded yellow oil, which was purified at 100 °C under vacuum for 2 h to afford HL¹ (10.31 g, 94% yield). ¹H NMR (300 MHz, CDCl₃): δ 2.20 (s, 6H, ArCH₃), 2.79 (m, 4H, NCH₂CH₂O), 3.33 (s, 6H, OCH₃), 3.51 (m, 4H, NCH₂CH₂O), 3.78 (s, 2H, ArCH₂N), 6.61 (s, 1H, ArH), 6.84 (s, 1H, ArH), 10.20 (br s, 1H, Ar–OH).

Table 4
Summary of crystallographic data of complexes 3 and 5

	3	5
Formula	$C_{31}H_{56}NO_3Si_2Y$	$C_{41}H_{59}NO_3SiY$
Molecular weight	635.86	730.89
Crystal system	Monoclinic	Orthorhombic
Space group	$P2(1)/n$	$Pbca$
a (Å)	12.7001(17)	8.9458(4)
b (Å)	17.371(2)	25.8181(13)
c (Å)	16.060(2)	34.9027(17)
α (°)	90.00	90.00
β (°)	96.143(2)	90.00
γ (°)	90.00	90.00
V (Å³)	3522.7(8)	8061.3(7)
Z	4	8
Measurement temperature (°C)	−86.5	−86.5
$D_{calc.}$ (g cm⁻³)	1.199	1.204
Radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)
$2\theta_{max}$ (°)	52.06	52.10
μ (mm⁻¹)	1.752	1.512
$F(000)$	1360	3112
Number of observed reflections	6900	7936
Number of parameters refined	357	201
Goodness-of-fit	1.041	0.906
R_1	0.0453	0.0682
wR_2	0.0975	0.1870

4.3.2. 4,6-(CMe₃)₂-2-[(MeOCH₂CH₂)₂-NCH₂]-C₆H₂-OH (HL²)

Following the similar procedure, reaction of paraformaldehyde (1.32 g, 44.0 mmol) with bis(2-methyloxyethyl)amine (5.0 mL, 33.86 mmol) and 2,4-di-tert-butylphenol (7.01 g, 33.98 mmol) led to the isolation of HL² as golden-brown oil (11.3 g, 95% yield). ¹H NMR (300 MHz, CDCl₃):δ 1.19 (s, 9H, C(CH₃)₃), 1.34 (s, 9H, C(CH₃)₃), 2.72 (t, 4H, $J = 5$ Hz, NCH₂CH₂O), 3.31 (s, 6H, OCH₃), 3.43 (t, 4H, $J = 5$ Hz, NCH₂CH₂O), 3.75 (s, 2H, ArCH₂N), 6.74 (s, 1H, ArH), 7.11 (s, 1H, ArH), 10.45 (s, 1H, ArOH).

4.4. Syntheses of complexes

4.4.1. [(η⁵-Cp′)L¹]Y(CH₂SiMe₃) (3)

To a hexane solution (2.0 mL) of Y(CH₂SiMe₃)₃(THF)₂ (0.2 g, 0.4 mmol) was dropwise added equivalent HCp′

(0.0786 g, 0.4 mmol in 2.0 mL of hexane) at room temperature. The mixture was then stirred for 1 h. To the above mixture was added hexane solution (2.0 mL) of HL^1 (0.108 g, 0.4 mmol) at $-35\,°C$. The reaction mixture was maintained for 15 min, than concentrated to 3 mL and kept at $-35\,°C$ for 12 h to give white solids. The solids were washed carefully with a small amount of cold hexane (1 mL) and dried in vacuum to afford complex **3** in 83% yields (0.211 g). Colorless single crystals for X-ray analysis grew from a solution of hexane at $-35\,°C$ within 24 h. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ −0.99 (ABX, dd, 1H, $J_{H–H} = 8$ Hz, $J_{Y–H} = 4$ Hz, YCH_2SiMe_3), −0.45 (ABX, dd, 1H, $J_{H–H} = 8$ Hz, $J_{Y–H} = 4$ Hz, YCH_2SiMe_3), 0.40 (s, 9H, YCH_2SiMe_3), 0.59 (s, 9H, $C_5Me_4SiMe_3$), 2.07 (s, 3H, $ArCH_3$), 2.11 (s, 3H, $ArCH_3$), 2.34 (s, 3H, $C_5Me_4SiMe_3$), 2.41 (s, 3H, $C_5Me_4SiMe_3$), 2.45 (s, 3H, $C_5Me_4SiMe_3$), 2.68 (s, 3H, $C_5Me_4SiMe_3$), 2.56–2.61 (m, 4H, NCH_2CH_2OMe, $NCH_2CH_2O(Me)Y$, $NCH_2CH_2O(Me)Y$), 2.74 (m, 1H, $NCH_2CH_2O(Me)Y$), 2.88 (s, 3H, $NCH_2CH_2O(Me)Y$), 2.91 (s, 1H, NCH_2CH_2OMe), 3.10 (s, 3H, NCH_2CH_2OMe), 3.30 (br, 2H, CH_2N, NCH_2CH_2OMe), 3.58 (m, 1H, NCH_2CH_2OMe), 3.84 (s, 1H, CH_2N), 6.72 (s, 1H, ArH), 7.15 (s, 1H, ArH), ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 3.51 (s, 3C, $C_5Me_4SiMe_3$), 5.01 (s, 3C, CH_2SiMe_3), 12.44 (d, 2C, $J = 14.8$ Hz, $ArCH_3$), 14.98, 15.26, 18.18, 21.28 (s, 4C, C_5Me_4), 25.70 (d, 1C, $J = 48.5$ Hz, YCH_2SiMe_3), 32.40 (s, 1C, $Me_4(C_4–C–)SiMe_3$), 43.34 (s, 1C, $NCH_2CH_2O(Me)Y$), 52.25 (s, 1C, $NCH_2CH_2O(Me)Y$), 58.96 (br, 1C, $O(Me)Y$), 58.96 (br, 1C, CH_2N), 62.35 (s, 1C, OMe), 67.34 (s, 1C, NCH_2CH_2OMe), 70.01 (s, 1C, NCH_2CH_2OMe), 120.11, 122.31, 122.93, 123.73 (s, 4C, $Me_4(C_4-C-)SiMe_3$), 126.44, 127.38, 128.26–128.74, 133.27 (6C, aryls); IR (KBr pellets): 623, 683, 752, 836, 850, 915, 953, 983, 1026, 1093, 1162, 1200, 1248, 1278, 1325, 1377, 1411, 1480, 1553, 1610, 2730, 2859, 2915, 3666; Anal. Calc. for $C_{31}H_{56}NO_3Si_2Y$: C, 58.56; H, 8.88; N, 2.20. Found: C, 58.57; H, 8.90; N, 2.17%.

4.4.2. $[(\eta^5$-Cp')$L^2]Y(CH_2SiMe_3)$ (4)

Following a procedure similar to that described for the preparation of **3**, treatment of a hexane solution (2.0 mL) of $Y(CH_2SiMe_3)_3(THF)_2$ (0.2 g, 0.4 mmol) with 1 equiv. of Cp′ (0.0786 g, 0.4 mmol in 2.0 mL of hexane) followed by addition of HL^2 (0.141 g, 0.4 mmol in 2.0 mL of hexane) at $-35\,°C$ afforded complex **4** (0.19 g, 80%). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ −0.76 (ABX, 1H, $J_{H–H} = 12$ Hz, YCH_2SiMe_3), −0.29 (ABX, 1H, $J_{H–H} = 12$ Hz, YCH_2SiMe_3), 0.31 (s, 9H, YCH_2SiMe_3), 0.56 (s, 9H, $SiMe_3$), 1.52 (s, 9H, $ArCMe_3$), 1.90 (s, 9H, $ArCMe_3$), 2.10 (s, 3H, $C_5Me_4SiMe_3$), 2.14 (s, 3H, $C_5Me_4SiMe_3$), 2.36 (s, 3H, $C_5Me_4SiMe_3$), 2.41 (s, 3H, $C_5Me_4SiMe_3$), 2.61–2.69 (m, 5H, $NCH_2CH_2O(Me)Y$, $NCH_2CH_2O(Me)Y$, NCH_2CH_2OMe), 2.93 (m, 3H, $NCH_2CH_2O(Me)Y$), 2.93 (m, 1H, $NCH_2CH_2O(Me)Y$), 3.21 (br s, 3H, NCH_2CH_2OMe), 3.43 (s, 1H, $NCH_2CH_2O(Me)Y$), 3.59 (s, 1H, NCH_2CH_2OMe), 4.01 (d, 2H, $J = 12$ Hz, CH_2N), 7.00 (s, 1H, ArH), 7.69 (s, 1H, ArH), ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 3.75 (s, 3C, $SiMe_3$), 5.62 (s, 3C, CH_2SiMe_3), 12.515, 12.973, 15.458, 15.728 (s, 4C, $CpMe_4$), 25.96 (d, 1C, $J = 46.4$ Hz, YCH_2SiMe_3), 31.04 (s, 3C, $ArCMe_3$), 32.63 (s, 3C, $ArCMe_3$), 32.40 (s, 1C, $Me_4(C_4–C–)SiMe_3$), 34.64, 36.10 (s, 2C, CMe_3); 43.20 (s, 1C, CH_2CH_2OMe), 51.83 (s, 1C, $CH_2CH_2O(Me)Y$), 58.94 (s, 1C, $CH_2CH_2O(Me)Y$), 59.57 (s, 1C, CH_2N), 62.61 (s, 1C, CH_2CH_2OMe), 67.42 (s, 1C, $CH_2CH_2O(Me)Y$), 70.06 (s, 1C, CH_2CH_2OMe), 121.62, 122.95 (s, 4C, $Me_4(C_4-C-)SiMe_3$), 125.23, 125.62 (s, 2C, aryls) 128.25–128.74 (s, 4C, aryls); IR (KBr pellets): 622, 646, 683, 724, 745, 809, 839, 877, 910, 952, 985, 1024, 1090, 1166, 1202, 1247, 1308, 1361, 1389, 1415, 1443, 1478, 1548, 1604, 2954, 3425; Anal. Calc. for $C_{37}H_{68}NO_3Si_2Y$: C, 61.72; H, 7.84; N, 1.95. Found: C, 61.75; H, 7.85; N, 1.92%.

4.4.3. $[(\eta^5$-Ind)$L^2]Y(CH_2SiMe_3)$ (5)

To a hexane solution (2.0 mL) of $Y(CH_2SiMe_3)_3(THF)_2$ (0.2 g, 0.4 mmol) was added dropwise equivalent indene (0.047 g, 0.4 mmol in 2.0 mL of hexane) under stirring. The mixture was then reacted for 1 h at room temperature. To the resultant mixture was added dropwise a solution of HL^2 (0.141 g, 0.4 mmol in 2.0 mL of toluene) at $-35\,°C$. After stirred for 15 min, the reaction mixture was concentrated to 1 mL, and 2 mL hexane was added. The mixture was kept at $-35\,°C$ for 12 h to give yellow solids. The solids were washed carefully by a small amount of hexane (1 mL) and dried in vacuum to afford complex **5** in 78% yields (0.22 g). Yellow single crystals for X-ray analysis grew from a mixture of toluene and hexane at $-35\,°C$ (1:3 v/v) within 24 h. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ −1.23 (s, 2H, YCH_2SiMe_3), 0.42 (s, 9H, YCH_2SiMe_3), 1.42 (s, 9H, $ArCMe_3$), 1.81 (s, 9H, $ArCMe_3$), 2.18 (s, 2H, $NCH_2CH_2O(Me)Y$), 2.40 (s, 2H, $NCH_2CH_2O(Me)Y$), 2.59 (s, 3H, $NCH_2CH_2O(Me)Y$), 2.76 (m, 2H, $NCH_2CH_2O(Me)Y$), 2.84 (s, 3H, $NCH_2CH_2O(Me)Y$), 3.0 (s, 2H, $NCH_2CH_2O(Me)Y$), 3.58 (s, 2H, CH_2N), 6.92, 7.59 (s, 2H, ArH), 6.30, 7.00, 7.02, 7.14(m, 4H, C_9H_4); ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 5.78 (s, 3C, CH_2SiMe_3), 26.26 (s, 1C, YCH_2SiMe_3), 32.40 (s, 3C, $ArCMe_3$), 32.72 (s, 3C, $ArCMe_3$), 34.73 (s, 2C, CMe_3); 44.78 (s, 1C, $CH_2CH_2O(Me)Y$), 54.08 (s, 1C, $CH_2CH_2O(Me)Y$), 59.26 (s, 1C, $CH_2CH_2O(Me)Y$), 61.07 (s, 1C, CH_2N), 63.91 (s, 1C, $CH_2CH_2O(Me)Y$), 68.34 (s, 1C, $CH_2CH_2O(Me)Y$), 70.19 (s, 1C, $CH_2CH_2O(Me)Y$), 58.87, 120.81, 122.62, 123.23, 124.42, 132.91, 133.06, 144.34, 146.10 (9C, C_9H_4), 126.73, 127.42, 128.25–130.74 (6C, aryls); IR (KBr pellets): 645, 670, 699, 717, 745, 766, 793, 809, 848, 863, 910, 1010, 1022, 1034, 1055, 1083, 1136, 1168, 1203, 1218, 1237, 1279, 1302, 1322, 1330, 1361, 1383, 1415, 1445, 1476, 1561, 1603, 2863, 2897, 2950, 3039, 3684; Anal. Calc. for $C_{41}H_{59}NO_3SiY$: C, 67.38; H, 8.14; N, 1.92. Found: C, 67.41; H, 8.16; N, 1.91%.

4.5. Polymerization of L-lactide

A typical procedure for polymerization of L-lactide was performed in a 25 mL round-bottom flask in a glove-box. To a stirred solution of L-lactide (0.5 g, 3.472 mmol) in 3.0 mL THF was added a THF solution (1.0 mL) of complex **5** (5.04 mg, 6.94 µmol, $[LA]_0/[Y]_0 = 500$) (Table 3, entry 5). The polymerization was proceeded for 2.5 h at room temperature and then terminated by 1.0 mL of a mixture of $HCl/CH_3OH/CHCl_3$ (1:100:600 v/v) to give white solids. Filtered, washed with ethanol, and then dried at 40 °C for 24 h *in vacuo* gave PLA (0.496 g, 99.2%). The molecular weight and the molecular weight distribution of the resulting polymer were determined by GPC. The microstructure was characterized by ^1H NMR spectrum.

Acknowledgements

Appendix A. Supplementary material

CCDC 637045 and 637131 contain the supplementary crystallographic data for **3** and **5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.06.054.

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