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Synthesis, structure, and catalytic activity of organolanthanides with chiral biphenyl-based tridentate amidate ligands

Qiuwen Wang [a], Furen Zhang [a], Haibin Song [b], Guofu Zi [a,*]

[a] Department of Chemistry, Beijing Normal University, Beijing 100875, China
[b] State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

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ABSTRACT

Four new chiral organolanthanide amidate complexes have been readily prepared in good yields *via* silylamine elimination reaction between Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = Sm, Y, Yb) and chiral amidate ligands, (*R*)-2-(mesitoylamino)-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl (**1**H) and (*R*)-2-(mesitoylamino)-2′-dimethylamino-6,6′-dimethyl-1,1′-biphenyl (**2**H). The steric effect of the ligand coupled with the size effect of the lanthanide ion plays an important role in complex formation. For example, treatment of **1**H with half equiv of Sm[N(SiMe$_3$)$_2$]$_3$ gives the C_2-symmetric bis-ligated amidate complex (σOMe:κO:κN-**1**)$_2$SmN(SiMe$_3$)$_2$ (**3**) in 75% yield, while reaction of **1**H or **2**H with half equiv of Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = Y, Yb) affords the C_1-symmetric bis-ligated amidate complexes [(κO:κN-**1**)(σOMe:κO:κN-**1**)]LnN(SiMe$_3$)$_2$ (Ln = Y (**4**), Yb (**5**) and the C_1-symmetric mono-ligated amidate complex (σNMe$_2$:κO:κN-**2**)Y[N(SiMe$_3$)$_2$]$_2$ (**6**), respectively, in good yields. These organolanthanide amidate complexes have been characterized by various spectroscopic techniques, elemental analyses, and X-ray diffraction analyses. They are active catalysts for asymmetric hydroamination/cyclization of aminoalkenes and ring-opening polymerization of *rac*-lactide, affording cyclic amines in excellent conversions with good ee values and isotactic-rich polylactides, respectively.

1. Introduction

Chiral organolanthanide complexes based on non-Cp multidentate ligands have received growing attention in the past two decades [1–13]. One of the initial driving forces for this work is the longstanding interest in the development of catalysts for intramolecular asymmetric alkene hydroamination [6–13], since the hydroamination is a highly atom-economical process in which an amine N–H bond is added to an unsaturated carbon–carbon bond leading to the formation of nitrogen-containing heterocycles that are prevalent in naturally occurring and/or biologically and pharmacologically active compounds [14–24]. Up to date, many non-Cp chiral organolanthanide catalysts for asymmetric alkene hydroamination have been studied [25–50], however, only a small number of successful catalysts have been reported affording significant enantioselectivity (>90% ee) [36], and those highly enantioselective inductions are observed only for one or two substrates. Thus, the development of new lanthanide catalysts for asymmetric alkene hydroamination is a desirable and challenging goal.

Ligand modification plays a key role in developing new catalyst precursors for asymmetric synthesis. In recent years, we have developed a series of chiral non-Cp multidentate ligands, and their Ag(I), Cu(II), Rh(I), Ta(V), Ti(IV), Zn(II), Zr(IV) and lanthanide metal complexes are useful catalysts for a wide range of transformations [51–73]. Among these, group 4 metal complexes with chiral biaryl-based amidate ligands are useful chiral catalysts for the hydroamination/cyclization [66,69,70], which is also observed by Schafer and others [74–77]. For example, the bis-ligated zirconium complexes (**1**)$_2$Zr(NMe$_2$)$_2$ and (**2**)$_2$Zr(NMe$_2$)$_2$, derived from amidate ligands (*R*)-2-(mesitoylamino)-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl (**1**H) and (*R*)-2-(mesitoylamino)-2′-dimethylamino-6,6′-dimethyl-1,1′-biphenyl (**2**H), are effective chiral catalysts for hydroamination/cyclization of aminoalkenes, in which excellent conversions (up to 100%) and moderate enantioselectivities (up to 57% ee) have been obtained [66,70]. In our ongoing research, we are now focusing on the preparation of this type of bis-ligated catalysts coordinated by chiral C_1-symmetric tridentate ligands, and to further explore the coordination chemistry of the chiral amidate ligands **1**H and **2**H, we have recently extended our work to lanthanide chemistry. Herein, we report on some observations concerning the chemistry of amidate ligands **1**H and **2**H with

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

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lanthanide amides, and the applications of the resulting complexes as catalysts for the asymmetric hydroamination/cyclization of aminoalkenes and the polymerization of *rac*-lactide.

2. Experimental section

2.1. General methods

All experiments 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. (*R*)-2-(mesitoylamino)-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl (**1**H) [70], (*R*)-2-(mesitoylamino)-2′-dimethylamino-6,6′-dimethyl-1,1′-biphenyl (**2**H) [66], Ln[N(SiMe$_3$)$_2$]$_3$ [78], 2,2-dimethylpent-4-enylamine [31], 2,2-dimethylhex-5-enylamine [31], and 1-(aminomethyl)-1-allylcyclohexane [42] were prepared according to literature methods. 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 complex (σOMe:κO:κN-1)$_2$SmN(SiMe$_3$)$_2$ (**3**)

A toluene solution (10 mL) of **1**H (0.37 g, 1.0 mmol) was slowly added to a toluene solution (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 light yellow solution. The solution was filtered, and the filtrate was concentrated to about 2 mL. Complex **3** was isolated as colorless crystals after this solution stood at room temperature for three days. Yield: 0.40 g (75%). M.p.: 140–142 °C (dec.). ^{1}H NMR (C_6D_6): δ 9.41 (d, J = 6.8 Hz, 2H, aryl), 8.40 (d, J = 6.8 Hz, 2H, aryl), 6.75 (m, 8H, aryl), 5.80 (s, 4H, aryl), 5.11 (s, 6H, OCH_3), 1.97 (s, 6H, CH_3), 1.78 (s, 6H, CH_3), 1.42 (s, 6H, CH_3), 0.31 (s, 12H, CH_3), −0.69 (s, 18H, Si(CH_3)$_3$). ^{13}C NMR (C_6D_6): δ 183.4, 153.9, 141.7, 137.6, 137.2, 137.1, 136.8, 136.2, 132.0, 131.3, 129.6, 129.1, 126.0, 124.7, 122.1, 67.9, 31.7, 27.0, 22.8, 16.6, 3.2. IR (KBr, cm^{-1}): ν 2960 (m), 1612 (s), 1577 (s), 1502 (s), 1462 (m), 1372 (s), 1259 (s), 1091 (s), 1017 (s), 972 (s), 796 (s). Anal. Calcd for $C_{56}H_{70}N_3O_4Si_2Sm$: C, 63.71; H, 6.68; N, 3.98. Found: C, 63.88; H, 6.72; N, 4.02%.

2.3. Preparation of complex [(κO:κN-1)(σOMe:κO:κN-1)]YN(SiMe$_3$)$_2$ (**4**)

This compound was prepared as colorless crystals from the reaction of **1**H (0.37 g, 1.0 mmol) with Y[N(SiMe$_3$)$_2$]$_3$ (0.28 g, 0.5 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **3**. Yield: 0.41 g (83%). M.p.: 210–212 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.74 (d, J = 7.7 Hz, 2H, aryl), 7.29 (d, J = 7.7 Hz, 2H, aryl), 7.02 (m, 2H, aryl), 6.87 (m, 2H, aryl), 6.81 (m, 2H, aryl), 6.72 (m, 4H, aryl), 6.49 (m, 2H, aryl), 3.80 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 2.22 (s, 6H, CH_3), 2.04 (s, 12H, CH_3), 1.98 (s, 6H, CH_3), 1.91 (s, 6H, CH_3), 0.44 (s, 18H, Si(CH_3)$_3$). ^{13}C NMR (C_6D_6): δ 180.4, 156.9, 144.1, 138.6, 137.6, 137.4, 136.2, 133.8, 133.4, 132.5, 130.6, 128.8, 127.2, 124.8, 122.3, 122.1, 58.2, 55.8, 22.3, 20.8, 19.8, 19.6, 4.8. IR (KBr, cm^{-1}): ν 2961 (m), 1612 (s), 1577 (s), 1498 (s), 1414 (s), 1259 (s), 1086 (s), 1016 (s), 958 (s), 818 (s), 796 (s). Anal. Calcd for $C_{56}H_{70}N_3O_4Si_2Y$: C, 67.65; H, 7.10; N, 4.23. Found: C, 67.75; H, 7.15; N, 4.21%.

2.4. Preparation of complex [(κO:κN-1)(σOMe:κO:κN-1)]YbN(SiMe$_3$)$_2$ (**5**)

This compound was prepared as colorless crystals from the reaction of **1**H (0.37 g, 1.0 mmol) with Yb[N(SiMe$_3$)$_2$]$_3$ (0.33 g, 0.5 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **3**. Yield: 0.39 g (73%). M.p.: 237–239 °C (dec.). IR (KBr, cm^{-1}): ν 2962 (m), 1608 (s), 1575 (s), 1443 (s), 1259 (s), 1085 (s), 1017 (s), 950 (s), 796 (s). Anal. Calcd for $C_{56}H_{70}N_3O_4Si_2Yb$: C, 62.37; H, 6.54; N, 3.90. Found: C, 62.42; H, 6.52; N, 3.94%.

2.5. Preparation of complex (σNMe$_2$:κO:κN-2)Y[N(SiMe$_3$)$_2$]$_2$ (**6**)

This compound was prepared as colorless crystals from the reaction of **2**H (0.38 g, 1.0 mmol) with Y[N(SiMe$_3$)$_2$]$_3$ (0.28 g, 0.5 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a similar procedure as in the synthesis of **3**. Yield: 0.32 g (81%). M.p.: 132–134 °C (dec.). ^{1}H NMR (C_6D_6): δ 6.74 (s, 2H, aryl), 6.68 (m, 2H, aryl), 6.59 (s, 2H, aryl), 6.57 (s, 1H, aryl), 6.45 (s, 1H, aryl), 2.68 (s, 3H, CH_3), 2.61 (s, 6H, CH_3), 2.01 (s, 3H, CH_3), 1.89 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 0.41 (s, 18H, Si(CH_3)$_3$), 0.28 (s, 18H, Si(CH_3)$_3$). ^{13}C NMR (C_6D_6): δ 181.6, 146.9, 142.4, 139.9, 138.4, 137.2, 136.5, 134.2, 133.2, 133.0, 132.9, 132.4, 125.9, 121.5, 118.6, 47.1, 27.2, 25.8, 21.0, 20.8, 6.4, 5.6. IR (KBr, cm^{-1}): ν 2962 (m), 2859 (w), 1613 (m), 1570 (m), 1495 (s), 1427 (s), 1260 (s), 1238 (s), 1096 (s), 938 (s), 812 (s). Anal. Calcd for $C_{38}H_{65}N_4OSi_4Y$: C, 57.40; H, 8.24; N, 7.05. Found: C, 57.53; H, 8.09; N, 6.83%.

2.6. General procedure for asymmetric hydroamination/cyclization

In a nitrogen-filled glove box, precatalyst (0.016 mmol), C_6D_6 (0.7 mL), and aminoalkene (0.32 mmol) were introduced sequentially into a J. Young NMR tube equipped with a Teflon screw cap. The reaction mixture was subsequently kept at room temperature, at 60 °C or 120 °C to achieve hydroamination, and the reaction was monitored periodically by ^{1}H NMR spectroscopy. The cyclic amine was vacuum transferred from the J. Young NMR tube into a 25 mL Schlenk flask which contained 62 mg (0.32 mmol) of (*S*)-(+)-*O*-acetylmandelic acid. The resulting mixture was stirred at room temperature for 2 h and the volatiles were removed *in vacuo*. The resulting diastereomeric salt was then dissolved in $CDCl_3$ and the enantiomeric excesses were determined by ^{1}H NMR spectroscopy [31].

2.7. General procedure for polymerization of rac-lactide

Under nitrogen gas, a Schlenk flask was charged with a solution of the complex (typically 0.005 mmol) in toluene (0.2 mL) or THF (0.2 mL). To this solution was added rapidly a toluene or THF solution (5.0 mL) of *rac*-lactide (5.0 mmol), and the reaction mixture was vigorously stirred for 1 h at room temperature. The polymerization was quenched by the addition of acidified methanol. The resulting precipitated polylactide was collected, washed with methanol several times, and dried in vacuum at 50 °C overnight. The microstructure of polymers was determined by homodecoupled ^{1}H NMR experiments [79–81].

2.8. X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Rigaku Saturn CCD diffractometer at 113(2) K using graphite

monochromated Mo Kα radiation (λ = 0.71070 Å). An empirical absorption correction was applied using the SADABS program [82]. All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 program package [83]. All the hydrogen atoms were geometrically fixed using the riding model. The crystal data and experimental data for **3**–**6** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

3. Results and discussion

3.1. Synthesis and characterization of complexes

It has been shown that organolanthanide amidate complexes can be efficiently prepared *via* silylamine elimination reaction between Ln[N(SiMe$_3$)$_2$]$_3$ and protic amidate ligands [73,84,85]. Therefore it is rational to propose that the acidic proton in the chiral amidate ligands **1**H and **2**H would allow the similar silylamine elimination to occur between **1**H or **2**H and metal amides. In fact, treatment of (*R*)-2-(mesitoylamino)-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl (**1**H) with half equiv of Sm[N(SiMe$_3$)$_2$]$_3$ in toluene gives the C_2-symmetric bis-ligated amidate complex (σOMe:κO:κN-**1**)$_2$SmN(SiMe$_3$)$_2$ (**3**) in 75% yield (Scheme 1), while reaction of **1**H with half equiv of Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = Y, Yb) does not lead to the expected C_2-symmetric complexes (σOMe:κO:κN-**1**)$_2$LnN(SiMe$_3$)$_2$, instead, the C_1-symmetric bis-ligated amidate complexes [(κO:κN-**1**)(σOMe:κO:κN-**1**)]LnN(SiMe$_3$)$_2$ (Ln = Y (**4**), Yb (**5**)) have been isolated in good yields (Scheme 1), presumably due to the size effect of the lanthanide ions [86]. However, under similar reaction conditions, treatment of **2**H with half equiv of Y[N(SiMe$_3$)$_2$]$_3$ (Ln = Y, Yb) does not give the expected bis-ligated amidate complex (σNMe$_2$:κO:κN-**2**)$_2$YN(SiMe$_3$)$_2$ or [(κO:κN-**2**)(σNMe$_2$:κO:κN-**2**)]YN(SiMe$_3$)$_2$, instead, the C_1-symmetric mono-ligated amidate complex (σNMe$_2$:κO:κN-**2**)Y[N(SiMe$_3$)$_2$]$_2$ (**6**) has been isolated in 81% yield (Scheme 2), presumably due to the steric effect of the ligand.

These complexes are stable in a dry nitrogen atmosphere, while they are very sensitive to moisture. They are soluble in organic solvents such as THF, DME, pyridine, toluene, and benzene, and only slightly soluble in *n*-hexane. They have been characterized by various spectroscopic techniques, elemental analyses, and single-crystal X-ray diffraction analyses. The ^{1}H NMR spectra of **3** and **4** supports the ratio of amino group N(SiMe$_3$)$_2$ and ligand **1** is 1:2, and the ^{1}H NMR spectrum of **3** shows it is symmetrical on the NMR time scales, consistent with its C_2-symmetric structure; while the ^{1}H NMR spectrum of **4** shows it is nonsymmetrical on the NMR time scales due to its C_1-symmetric structure. The ^{1}H NMR spectrum of **6** supports the ratio of amino group N(SiMe$_3$)$_2$ and ligand **2** is 2:1, and shows it is nonsymmetrical on the NMR time scales, consistent with its C_1-symmetric structure. Their ^{13}C NMR spectra are consistent with the conclusions.

The solid-state structure of **3** shows that the Sm^{3+} is σ-bound to two nitrogen atoms and four oxygen atoms from two ligands **1** and one nitrogen atom from the amido N(SiMe$_3$)$_2$ group in a doubly capped trigonal-bipyramidal geometry (Fig. 1) in which O(1) and O(3) occupy apical positions and N(1) and N(2) are capping two faces of trigonal-bipyramidal surface with the average distance of Sm–N (2.448(8) Å), and the average distance of Sm–O (2.515(6) Å), respectively. The distance of Sm–N(SiMe$_3$)$_2$ is 2.312(6) Å, which is close to that found in [(*S*)-2-Me$_2$N–C$_{20}$H$_{12}$-2′-(NCHC$_4$H$_3$N)]$_2$SmN(SiMe$_3$)$_2$ (2.258(2) Å) [56]. The twisting between the phenyl rings of torsion angles are 63.6(3) and 61.0(3)°, which are smaller than those found in (**1**)$_2$Ti(NMe$_2$)$_2$ (73.3(1) and 69.3(1)°) and (**1**)$_2$Zr(NMe$_2$)$_2$ (69.7(2) and 71.3(2)°) [70].

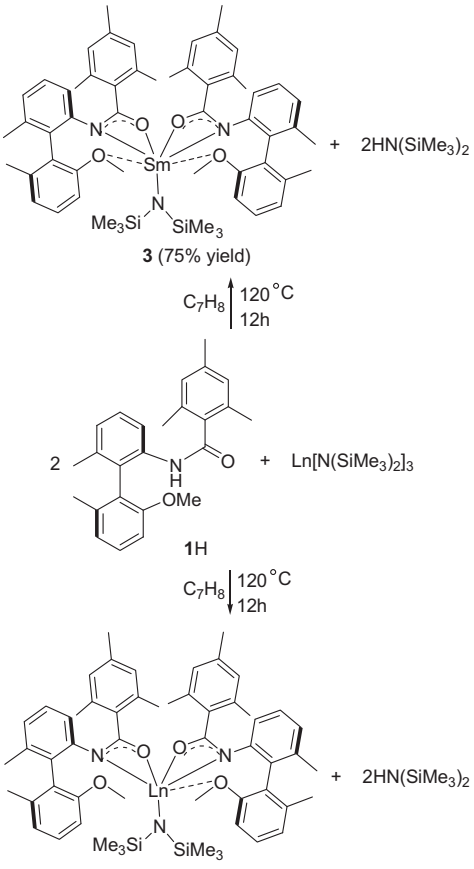
The single-crystal X-ray diffraction analyses confirm that **4** and **5** are isostructural. In each molecule [(κO:κN-**1**)(σOMe:κO:κN-**1**)]LnN(SiMe$_3$)$_2$, the Ln^{3+} is σ-bound to two nitrogen atoms and three

Table 2
Selected bond distances (Å) and bond angles (deg) for compounds **3-6**.

Compound	**3** (Sm)	**4** (Y)	**5** (Yb)	**6** (Y)
LnN (av.)	2.448(8)	2.388(2)	2.358(3)	2.380(2)
LnN(SiMe$_3$)$_2$	2.312(6)	2.240(2)	2.195(2)	2.244(2)
				2.259(2)
Ln–O (av.)	2.515(6)	2.343(2)	2.313(2)	
Ln–O(1)	2.668(6)	2.513(2)	2.482(2)	2.279(2)
Ln–O(3)	2.701(6)			
Ln–C	2.845(9)	2.749(3)	2.729(3)	2.725(3)
	2.867(8)	2.778(3)	2.752(3)	
Torsion (aryl–aryl)	63.6(3)	83.6(3)	83.5(3)	69.2(2)
	61.0(3)	63.6(3)	64.0(3)	

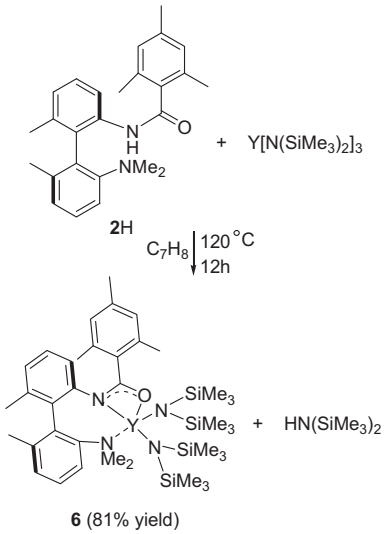
Table 1
Crystal data and experimental parameters for compounds **3**–**6**.

Compound	**3**	**4**	**5**	**6**
Formula	$C_{56}H_{70}N_3O_4Si_2Sm$	$C_{56}H_{70}N_3O_4Si_2Y$	$C_{56}H_{70}N_3O_4Si_2Yb$	$C_{38}H_{65}N_4OSi_4Y$
Formula weight	1055.68	994.24	1078.37	795.21
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P12_11$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	9.388(1)	9.404(2)	9.421(2)	9.101(2)
b (Å)	23.244(3)	23.396(4)	23.402(5)	18.548(4)
c (Å)	12.073(2)	23.539(4)	23.412(4)	26.265(5)
β (deg)	96.87(1)	90	90	90
V (Å^3)	2615.5(5)	5178.9(16)	5161.5(17)	4433.9(16)
Z	2	4	4	4
D_{calc} (g/cm^3)	1.340	1.275	1.388	1.191
μ(Mo/Kα)$_{calc}$ (mm^{-1})	1.216	1.220	1.906	1.455
Size (mm)	0.20 × 0.20 × 0.20	0.32 × 0.30 × 0.28	0.24 × 0.22 × 0.18	0.42 × 0.18 × 0.16
F(000)	1098	2104	2228	1696
2θ range (deg)	3.40 to 55.88	2.46 to 55.76	3.48 to 55.78	2.68 to 55.72
No. of reflns, collected	18,674	49,892	44,920	30,356
No. of unique reflns	10,561 (R_{int} = 0.0368)	12,344 (R_{int} = 0.0690)	12,286 (R_{int} = 0.0427)	10,384 (R_{int} = 0.0443)
No. of obsd reflns	9788	10,287	11,568	8314
Abscorr (T_{max}, T_{min})	0.79, 0.79	0.73, 0.70	0.73, 0.66	0.80, 0.58
R	0.074	0.052	0.030	0.037
R_w	0.193	0.087	0.060	0.073
R_{all}	0.077	0.065	0.032	0.048
gof	1.05	0.99	0.99	0.85



Scheme 1. Synthesis of complexes **3**–**5**.

oxygen atoms (one oxygen atom from MeO group) from two ligands **1** and one nitrogen atom from amino group $N(SiMe_3)_2$ in a distorted-pentagonal-pyramidal geometry (Figs. 2 and 3) in which N(3) occupies apical position, the other MeO group is far away from the metal center. The solution NMR characterization data is also consistent with this C_1-symmetric binding mode, as the ^1H NMR spectrum of **4** shows two signals at 3.80 and 3.56 ppm for



Scheme 2. Synthesis of complex **6**.

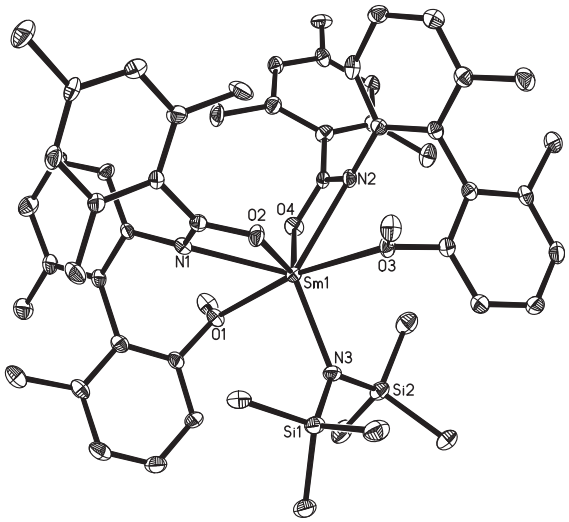


Fig. 1. Molecular structure of **3** (thermal ellipsoids drawn at the 35% probability level).

MeO group, attributable to a binding (σOMe) and a free MeO group, respectively. The average distance of Ln–N is 2.388(2) Å for Y, and 2.358(3) Å for Yb, respectively, and the average distance of Ln–O is 2.343(2) Å for Y, and 2.313(3) Å for Yb, respectively. The distances of $Ln–N(SiMe_3)_2$ 2.240(2) Å for Y, and 2.195(2) Å) for Yb, are comparable to the corresponding values of 2.208(3) Å for Y, and 2.169(3) Å for Yb found in $[(S)\text{-}2\text{-}Me_2N–C_{20}H_{12}\text{-}2'\text{-}(NCHC_4H_3N)]_2LnN(SiMe_3)_2$ [56]. The twisting between the phenyl rings of torsion angles are 73.4(1) and 74.0(1)° for Y, and 74.4(2) and 74.7(2)° for Yb, which are comparable to those found in **3** (63.6(3) and 61.0(3)°), $(\mathbf{1})_2Ti(NMe_2)_2$ (73.3(1) and 69.3(1)°) and $(\mathbf{1})_2Zr(NMe_2)_2$ (69.7(2) and 71.3(2)°) [70].

The solid-state structure of **6** shows that the Y^{3+} is σ-bound to two nitrogen atoms and one oxygen atom from ligand **1** and two nitrogen atoms from two amido $N(SiMe_3)_2$ groups in a distorted-trigonal-bipyramidal geometry (Fig. 4) with the average distance of Y–N 2.380(2) Å, and the distance of Y–O 2.279(2) Å, respectively. The distances of $Y–N(SiMe_3)_2$ are 2.244(2) and 2.259(2) Å, which are close to those found in {2-(Me2N)-2′-[2,4,6-Me3C6H2)C(O)N]-

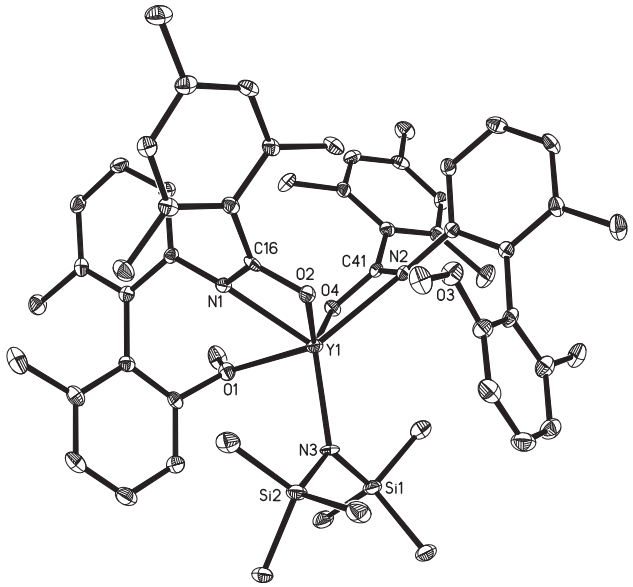


Fig. 2. Molecular structure of **4** (thermal ellipsoids drawn at the 35% probability level).

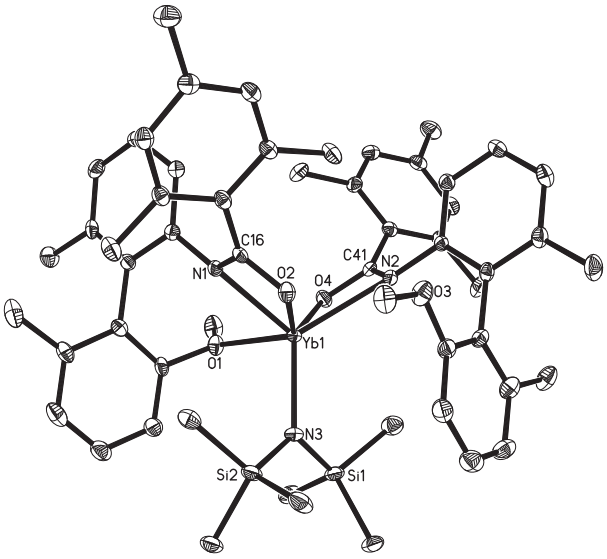


Fig. 3. Molecular structure of **5** (thermal ellipsoids drawn at the 35% probability level).

1,1′-$C_{20}H_{12}$}Y[$N(SiMe_3)_2$]$_2$ (2.265(5) and 2.244(5) Å) [73]. The twisting between the phenyl rings of torsion angle is 69.2(2)°, which is comparable to those found in (**2**)$_2$Ti(NMe_2)$_2$ (70.0(2) and 69.7(2)°) and (**2**)$_2$Zr(NMe_2)$_2$ (71.1(6) and 68.6(6)°) [66].

3.2. Catalytic activity

To evaluate the catalytic ability of the complexes **3**–**6**, the asymmetric hydroamination/cyclization of aminoalkenes and polymerization of *rac*-lactide have been tested under the conditions given in Tables 3 and 4, respectively.

The results (Table 3) clearly show that all substrates are converted to the cyclic product at 60 °C or elevated temperature in good conversions. The samarium complex **3** is a noticeably good catalyst at 60 °C, giving excellent conversion and good enantioselectivity (up to 66%; Table 3, entry 1). On decreasing the temperature from 60 °C to 20 °C, the ee value increases slightly but the rate falls significantly (Table 3, entry 2). When the complexes **4** (Y^{3+}) and **5** (Yb^{3+}) are used, the rate does not change much but the ee value decreases largely (Table 3, entries 3 and 4). When the mono-ligated complex **6** is used, the rate increases slightly but the ee value decreases significantly (Table 3, entry 5), presumably due to the steric effects. The organolanthanide amidate complexes **3**–**6** are also effective catalysts for the substrate **8a**, giving spiro-pyrrolidine products in excellent conversions with moderate enantioselectivity (Table 3, entries 6–9). The data also show that the formation of six-membered rings can also be performed with our catalysts at 120 °C (Table 3, entries 10–13), and a moderate enantioselectivity (up to 38%), mediated by the catalyst **3**, has been obtained (Table 3, entry 10). Like those C_1-symmetric bis-ligated complexes [(*S*)-2-MeO-$C_{20}H_{20}$-2′-($NCHC_4H_3N$)]$_2$LnN($SiMe_3$)$_2$ (Ln = Y, Yb) [64], complexes **4** and **5** are more chiral effective catalysts for the hydroamination/cyclization reaction than the C_1-symmetric mono-ligated complex **6**, but less than those initiated by C_2-symmetric bis-ligated complexes **3** and [(*S*)-2-Me_2N-$C_{20}H_{12}$-2′-

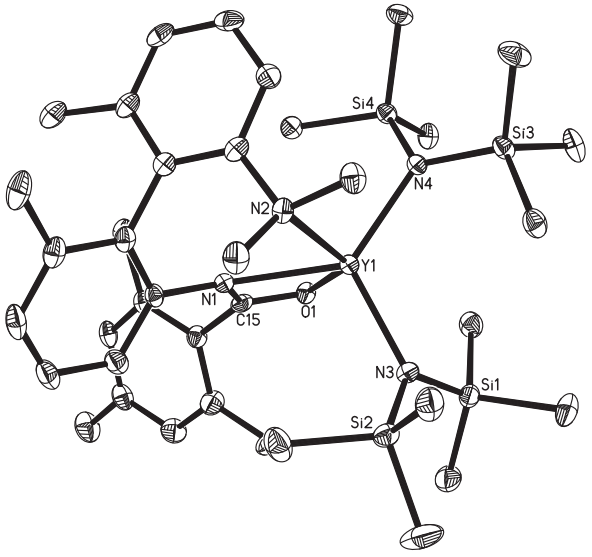
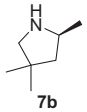
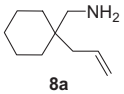
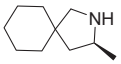
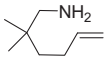
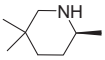


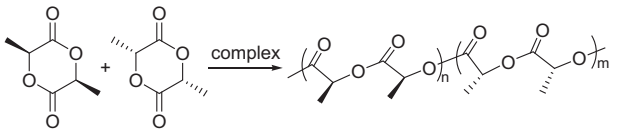
Fig. 4. Molecular structure of **6** (thermal ellipsoids drawn at the 35% probability level).

Table 3
Enantioselective hydroamination/cyclization of aminoalkenes.[a]

Entry	Precat. (M)	Substrate	Product	Temp. (°C)	Time (h)	Conv. (%)[b]	Ee (%)[c]
1	**3** (Sm)			60	16	95	66
2	**3** (Sm)			20	48	27	74
3	**4** (Y)			60	16	97	54
4	**5** (Yb)			60	16	90	50
5	**6** (Y)	**7a**	**7b**	60	16	100	13
6	**3** (Sm)			60	16	98	60
7	**4** (Y)			60	16	95	48
8	**5** (Yb)			60	16	92	45
9	**6** (Y)	**8a**	**8b**	60	16	100	12
10	**3** (Sm)			120	24	92	38
11	**4** (Y)			120	24	95	34
12	**5** (Yb)			120	24	90	28
13	**6** (Y)	**9a**	**9b**	120	24	100	24

[a] Conditions: C_6D_6 (0.70 mL), aminoalkene (0.32 mmol), catalyst (0.016 mmol).
[b] Determined by ^{1}H NMR based on *p*-xylene as the internal standard.
[c] Determined by ^{1}H NMR of its diastereomeric (*S*)-(+)-*O*-acetylmandelic acid salt [31].

Table 4
Polymerization of *rac*-lactide catalyzed by chiral organolanthanide amides **3**–**6**.[a]



Entry	Precat. (M)	Solvent	Conv. (%)	M_n[b] (kg/mol)	M_w/M_n[b]	P_m[c] (%)
1	**3** (Sm)	Toluene	93	72.9	1.24	72
2	**4** (Y)	Toluene	94	66.2	1.28	68
3	**5** (Yb)	Toluene	84	59.3	1.26	67
4	**6** (Y)	Toluene	100	74.2	1.31	58
5	**3** (Sm)	THF	94	71.8	1.36	70
6	**4** (Y)	THF	78	54.1	1.48	62
7	**5** (Yb)	THF	85	58.7	1.32	64
8	**6** (Y)	THF	93	73.8	1.35	54

[a] Conditions: 20 °C, precat./LA (mol/mol) = 1/1000; polymerization time, 1 h; solvent, 5 mL; [LA] = 1.0 mol/L.
[b] Measured by GPC (using polystyrene standards in THF).
[c] P_m is the probability of *meso* linkages between monomer units and is determined from the methine region of the homonuclear decoupled ^{1}H NMR spectrum in $CDCl_3$ at 25 °C [79–81].

$(NCHC_4H_3N)]_2LnN(SiMe_3)_2$ (Ln = Sm, Y, Yb) [56], due to the coordination effect of the oxygen atom (from MeO group) [64].

The complexes **3**–**6** are also active catalysts for the ring-opening polymerization (ROP) of *racemic*-lactide under mild conditions (Table 4). Yttrium complex **4** allows the 94% complete conversion of 1000 equiv of lactide within 1 h at room temperature in toluene at [*rac*-LA] = 1.0 mol L^{-1} (Table 4, entry 2). Polymerizations with this yttrium initiator/catalyst proceed much more slowly in THF (Table 4, entry 6), presumably due to the competitive coordination between the monomer and this donor solvent, as often observed in this type of ROP reactions promoted by oxophilic meta-based systems [44,87]. This difference in activity between toluene and THF solvent is not observed with complexes **3** and **5** (Table 4, entries 1, 3, 5 and 7); however, the ytterbium complex **5** is less active than yttrium complex **4** in toluene medium (Table 4, entries 2 and 3). The reasons for the different solvent dependence between the yttrium complex and ytterbium or samarium complex, are not clear at this time, however, the nature of the rare earth metal ions and lanthanide metal ions seems to be a major reason for this difference. When the mono-ligated complex **6** is used, again, the difference in activity between toluene and THF solvent is observed, while the rate increases slightly (Table 4, entries 4 and 8). The resulting polylactides are all isotactic rich under the conditions examined. Molecular weights and polydispersities of the polymers produced ranged from 54.1 to 74.2 kg mol^{-1} and 1.24 to 1.48, respectively. The catalytic activities of **3**–**6** resemble that of $[2\text{-}(2,6\text{-}^{i}Pr_2C_6H_3N{=}CH)C_4H_3N]_2Y(CH_2SiMe_3)(THF)_2$ [88], while the microstructure of the resulting polylactides are similar to those initiated by $[(S)\text{-}2\text{-}MeO\text{-}C_{20}H_{12}\text{-}2'\text{-}(NCHC_4H_3N)]_2LnN(SiMe_3)_2\}_2$ [64]. The enantioselectivity of the complexes in the *rac*-lactide polymerization process is not clear at this time, however, the coordination environment around the metal center seems to be a major factor for this selectivity. Further computational investigation of the ligand architecture for this transformation is still ongoing.

4. Conclusions

In conclusion, four new chiral organolanthanide amidate complexes have been readily prepared from the reactions between $Ln[N(SiMe_3)_2]_3$ and chiral ligands, (*R*)-2-(mesitoylamino)-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl (**1**H) and (*R*)-2-(mesitoylamino)-2′-dimethylamino-6,6′-dimethyl-1,1′-biphenyl (**2**H). They are active catalysts for the asymmetric hydroamination/cyclization of aminoalkenes, as well as the ring-opening polymerization of *rac*-lactide.

When a change is made from methoxyl group to dimethylamino group, the ligands (*R*)-2-(mesitoylamino)-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl (**1**H) and (*R*)-2-(mesitoylamino)-2′-dimethylamino-6,6′-dimethyl-1,1′-biphenyl (**2**H) exhibit different reactivity patterns. For example, treatment of **1**H with half equiv of $Sm[N(SiMe_3)_2]_3$ gives the C_2-symmetric bis-ligated amidate complex (σOMe:κO:κN-**1**)$_2$SmN(SiMe$_3$)$_2$ (**3**), while reaction of **1**H or **2**H with half equiv of $Ln[N(SiMe_3)_2]_3$ (Ln = Y, Yb) affords the C_1-symmetric bis-ligated amidate complexes $[(\kappa O{:}\kappa N\text{-}\mathbf{1})(\sigma OMe{:}\kappa O{:}\kappa N\text{-}\mathbf{1})]LnN(SiMe_3)_2$ (Ln = Y (**4**), Yb (**5**)) and the C_1-symmetric mono-ligated amidate complex (σNMe_2:κO:κN-**2**)Y[N(SiMe$_3$)$_2$]$_2$ (**6**), respectively, presumably due to the steric effect of the ligand coupled with the size effect of the lanthanide ions [86]. The C_1-symmetric bis-ligated complexes **4** and **5** are more chiral effective catalysts for the enantioselective hydroamination/cyclization reaction than the C_1-symmetric mono-ligated complex **6**, but less than those initiated by C_2-symmetric bis-ligated complexes **3** and $[(S)\text{-}2\text{-}Me_2N{-}C_{20}H_{12}\text{-}2'\text{-}(NCHC_4H_3N)]_2LnN(SiMe_3)_2$ (Ln = Sm, Y, Yb) [56]. We are currently concentrating on these transformations, further efforts will focus on mechanistic investigations, optimization of the catalyst architecture to improve the enantioselectivity or stereoselectivity for hydroamination/cyclization or *rac*-lactide polymerization, and on the exploration of these catalysts towards other types of reactions.

Acknowledgements

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Supplementary material

CCDC 791534, 791535, 791536, and 791537 contain the supplementary crystallographic data for **3**, **4**, **5** and **6**, respectively. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

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