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Synthesis, structure, and catalytic activity of binuclear lanthanide complexes with chiral NOBIN-based NNO ligands

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ABSTRACT

Two new amido binuclear complexes $\{(\mathbf{1})YN(SiMe_3)_2\}_2 \cdot C_7H_8$ ($\mathbf{3} \cdot C_7H_8$) and $\{(\mathbf{2})SmN(SiMe_3)_2\}_2 \cdot C_6H_{14}$ ($\mathbf{4} \cdot C_6H_{14}$) have been readily prepared in good yields by amine elimination reaction between $Ln[N(SiMe_3)_2]_3$ (Ln = Sm, Y) and chiral NNO ligands, (*S*)-2-(pyridin-2-ylmethylamino)-2′-hydroxy-1,1′-binaphthyl ($\mathbf{1}H_2$) and (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl ($\mathbf{2}H_2$), respectively. They both 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 moderate 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 decades [1–11]. One of the initial driving forces for this work is the long-standing interest in the development of catalysts for intramolecular asymmetric alkene hydroamination [6–11], 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 heterocycles that are found in numerous biologically and pharmacologically active compounds. To date, many non-Cp chiral catalysts based on lanthanide metals for asymmetric alkene hydroamination have been widely studied [6–28], however, only a small number of highly enantioselective reactions (>90% ee) have been reported [12]. Thus, the development of new lanthanide catalysts for asymmetric alkene hydroamination is a desirable and challenging goal.

In recent years, 2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN) as its (*R*) or (*S*) enantiomers has been modified to give variants which bear appropriate structural and electronic features for intended specific reactions, and its derivatives have exhibited good to excellent enantioselectivities in a number of asymmetric transformations [29–31]. For example, the ruthenium complexes with the ligand 2-(pyridin-2-ylmethylamino)-2′-hydroxy-1,1′-binaphthyl ($\mathbf{1}H_2$) are useful catalysts for a range of asymmetric transformations [32–34], and in some cases, the enantioselectivity is high up to 96.7% ee [34]. However, to our knowledge, no example of chiral lanthanide catalyst based on 2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN) has been reported yet, in contrast to binaphthol, biphenol, binaphthylamine and biphenylamine [29–31,35,36,1,37–40]. More recently, we have reported a new series of organolanthanides based on chiral NOBIN [41–43]. These organolanthanides have shown good catalytic activity in the polymerization of methyl methacrylate (MMA), the ring-opening polymerization of *rac*-lactide, and the hydroamination/cyclization of the aminoalkenes [41–43]. We have therefore started exploring the NOBIN ligand in the lanthanide chemistry. Herein, we report on some observations concerning the chemistry of ligands (*S*)-2-(pyridin-2-ylmethylamino)-2′-hydroxy-1,1′-binaphthyl ($\mathbf{1}H_2$) and (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl ($\mathbf{2}H_2$), which are prepared from (*S*)-2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN), with lanthanide amides and the use of the resulting complexes as catalysts in the asymmetric hydroamination/cyclization of aminoalkenes and the polymerization of *rac*-lactide.

2. Experimental

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

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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. (*S*)-2-(pyridin-2-ylmethylamino)-2′-hydroxy-1,1′-binaphthyl (**1**H_2) [34], (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl (**2**H_2) [42], Ln[N(SiMe3)2]3 [44], 2,2-dimethylpent-4-enylamine [27], 2,2′-dimethylhex-5-enylamine [27], and 1-(aminomethyl)-1-allylcyclohexane [28] 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. 1H and 13C 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**)$_2$YN(SiMe$_3$)$_2$}$_2$ · C_7H_8 (**3** · C_7H_8)

A toluene solution (10 mL) of **1**H_2 (0.19 g, 0.5 mmol) was slowly added to a toluene solution (10 mL) of Y[N(SiMe$_3$)$_2$]$_3$ (0.28 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. **3** · C_7H_8 was isolated as yellow crystals after this solution stood at room temperature for three days. Yield: 0.25 g (75%). M.p.: 203–205 °C (dec.). 1H NMR (C_6D_6): δ 8.12 (d, J = 9.0 Hz, 2H), 8.07 (d, J = 5.2 Hz, 2H), 7.95 (m, 4H), 7.70 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.27 (m, 5H), 7.10 (m, 4H), 7.04 (d, J = 8.6 Hz, 2H), 6.80 (m, 2H), 6.75 (m, 2H), 6.64 (m, 2H), 6.33 (m, 2H), 6.20 (m, 4H), 5.98 (d, J = 8.6 Hz, 2H), 4.07 (d, J = 19.3 Hz, 2H), 3.96 (d, J = 19.3 Hz, 2H), 2.22 (s, 3H), 0.80 (s, 18H), −0.49 (s, 18H). 13C NMR (C_6D_6): δ 163.5, 155.1, 153.2, 145.5, 137.5, 137.2, 136.4, 132.6, 131.2, 128.4, 128.3, 127.2, 126.0, 125.6, 124.9, 124.2, 124.1, 122.2, 120.5, 118.9, 116.2, 112.1, 55.8, 22.1, 6.1, 4.0. IR (KBr, cm^{-1}): ν 3055 (w), 2946 (m), 1606 (m), 1588 (m), 1487 (s), 1419 (s), 1329 (s), 1231 (s), 1149 (m), 1087 (s), 979 (s), 962 (s), 813 (s), 739 (s). Anal. Calc. for $C_{71}H_{80}N_6O_2Si_4Y_2$: C, 63.66; H, 6.02; N, 6.27. Found: C, 63.82; H, 6.36; N, 6.12%.

2.3. Preparation of {(**2**)$_2$SmN(SiMe$_3$)$_2$}$_2$ · C_6H_{14} (**4** · C_6H_{14})

This compound was prepared as yellow crystals from the reaction of **2**H_2 (0.19 g, 0.5 mmol) with Sm[N(SiMe$_3$)$_2$]$_3$ (0.32 g, 0.5 mmol) in toluene (20 mL) and recrystallization from an n-hexane solution by a similar procedure as in the synthesis of **3** · C_7H_8. Yield: 0.25 g (70%). M.p.: 182–184 °C (dec.). IR (KBr, cm^{-1}): ν 3053 (w), 2930 (m), 1621 (w), 1595 (m), 1567 (s), 1504 (m), 1435 (s), 1391 (s), 1317 (s), 1262 (s), 1179 (s), 1034 (s), 968 (s), 809 (s), 744 (s). Anal. Calc. for $C_{68}H_{98}N_6O_2Si_4Sm_2$: C, 56.54; H, 6.84; N, 5.82. Found: C, 56.32; H, 6.68; N, 5.83%.

2.4. General procedure for asymmetric hydroamination/cyclization

In a nitrogen-filled glove box, pre-catalyst (0.008 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, or at 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. This transfer was quantitated by washing the NMR tube with a small amount of $CDCl_3$. 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 [27].

2.5. General procedure for polymerization of rac-lactide

In a glovebox, 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.

2.6. 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 [45]. All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 program package [46]. All the hydrogen atoms were geometrically fixed using the riding model. The crystal data and experimental data for **3** and **4** 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

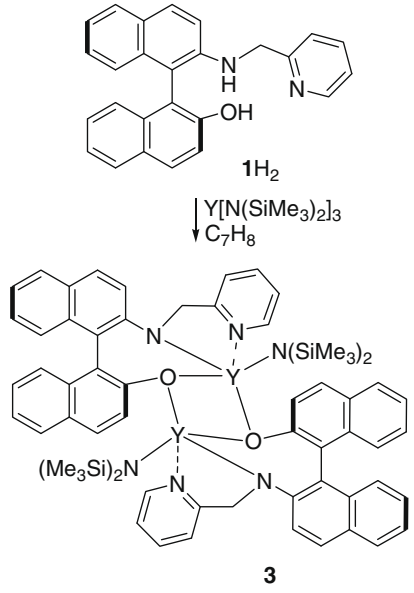
Treatment of (*S*)-2-(pyridin-2-ylmethylamino)-2′-hydroxy-1,1′-binaphthyl (**1**H_2) with 1 equiv. of Y[N(SiMe$_3$)$_2$]$_3$ in toluene gives the dimeric amide complex {(**1**)YN(SiMe$_3$)$_2$}$_2$ · C_7H_8 (**3** · C_7H_8) in 75% yield (Scheme 1). Our previous work has shown that interaction between (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-(pyrrol-2-ylmethylenea-

Table 1
Crystal data and experimental parameters for compounds **3** and **4**.

Compound	**3** · C_7H_8	**4** · C_6H_{14}
Formula	$C_{71}H_{80}N_6O_2Si_4Y_2$	$C_{34}H_{49}N_3OSi_2Sm$
Formula weight	1339.59	722.29
Crystal system	Orthorhombic	Monoclinic
Space group	*P*212121	*P*21
a (Å)	15.519(2)	11.636(2)
b (Å)	18.728(2)	15.971(2)
c (Å)	46.425(3)	18.997(2)
β (°)	90	91.376(6)
V (Å^3)	13493.0(16)	3529.4(6)
Z	8	4
D_{calc} (g/cm^3)	1.319	1.359
μ(Mo/Kα)$_{calc}$ (mm^{-1})	1.831	1.760
Size (mm)	0.24 × 0.22 × 0.20	0.22 × 0.20 × 0.16
F(000)	5584	2612
2θ range (°)	2.76–52.00	6.04–50.00
No. of reflections, collected	94332	26704
No. of unique reflections [$R_{(int)}$]	26426 (0.0778)	12366 (0.0732)
No. of observed reflections	20795	11338
Abscorr (T_{max}, T_{min})	0.71, 0.67	0.72, 0.68
R	0.053	0.077
Rw	0.091	0.190
R_{all}	0.077	0.082
GOF	1.04	1.06

Table 2
Selected bond distances (Å) and bond angles (deg) for compounds **3** and **4**.

Compound **3** · C_7H_8			
Y(1)–O(1)	2.360(3)	Y(1)–O(2)	2.199(3)
Y(1)–N(1)	2.299(3)	Y(1)–N(2)	2.419(4)
Y(1)–N(5)	2.264(3)	Y(2)–O(1)	2.195(3)
Y(2)–O(2)	2.330(3)	Y(2)–N(3)	2.288(3)
Y(2)–N(4)	2.393(4)	Y(2)–N(6)	2.257(3)
Y(1)–Y(2)	3.5951(6)	Y(1)–O(1)–Y(2)	104.18(11)
Y(1)–O(2)–Y(2)	105.04(11)	Torsion (aryl–aryl)	67.9(2)
			78.7(2)
Compound **4** · C_6H_{14}			
Sm(1)–O(1)	2.420(10)	Sm(1)–O(2)	2.241(8)
Sm(1)–N(1)	2.528(12)	Sm(1)–N(2)	2.405(9)
Sm(1)–N(5)	2.297(11)	Sm(2)–O(1)	2.261(9)
Sm(2)–O(2)	2.435(9)	Sm(2)–N(3)	2.555(10)
Sm(2)–N(4)	2.370(11)	Sm(2)–N(6)	2.289(9)
Sm(1)–Sm(2)	3.7524(9)	Sm(1)–O(1)–Sm(2)	106.5(4)
Sm(1)–O(2)–Sm(2)	106.7(3)	Torsion (aryl–aryl)	77.4(4)
			79.8(4)

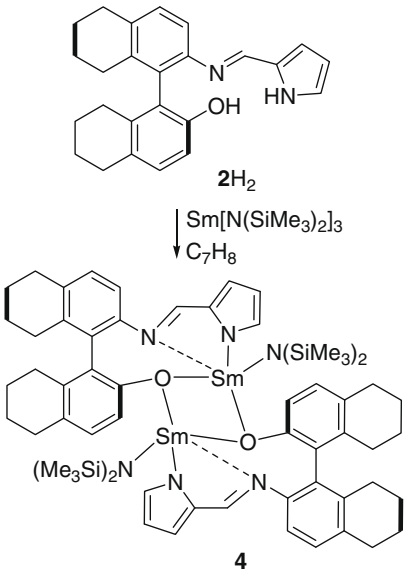


Scheme 1. Synthesis of complex **3**.

mino)-2′-hydroxy-1,1′-binaphthyl (**2**H_2) with 1 equiv. of Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = Y, Yb) gives the trinuclear complexes {(**2**)$_2$Ln}$_2$LnN(SiMe$_3$)$_2$ (Ln = Y, Yb) [42]. However, under similar reaction conditions, reaction of **2**H_2 with 1 equiv. of Sm[N(SiMe$_3$)$_2$]$_3$ does not lead to the expected trinuclear complex {(**2**)$_2$Sm}$_2$SmN(SiMe$_3$)$_2$, instead, a dimeric amide complex {(**2**)SmN(SiMe$_3$)$_2$}$_2$ · C_6H_{14} (**4** · C_6H_{14}) has been isolated in 70% yield (Scheme 2).

Both the 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 spectrum of **3** supports the ratio of toluene, amino group N(SiMe$_3$)$_2$, and ligand **1** is 1:2:2, and its ^{13}C NMR spectrum is consistent with the conclusions.

The single-crystal X-ray diffraction analyses shows that there are two molecules {(**1**)YN(SiMe$_3$)$_2$}$_2$ and two solvate toluene molecules for **3**, and one molecule {(**2**)SmN(SiMe$_3$)$_2$}$_2$ and one solvate n-hexane molecule for **4** in the lattice. Coordination of two ligand



Scheme 2. Synthesis of complex **4**.

anions **1** or **2** and two amido N(SiMe$_3$)$_2$ groups around two lanthanide ions results in the formation of the dimeric complexes {(**1**)YN(SiMe$_3$)$_2$}$_2$ and {(**2**)SmN(SiMe$_3$)$_2$}$_2$ (Figs. 1 and 2). Each Ln^{3+} is σ-bound to two nitrogen atoms and two oxygen atoms from the ligand anions **1** or **2** and one nitrogen atom from the amido N(SiMe$_3$)$_2$ group in a distorted-trigonal–bipyramidal geometry with the average distance of Ln–N (2.320(4) Å) for Y and (2.407(12) Å) for Sm, respectively, and the average distance of Ln–O (2.271(3) Å) for Y and (2.339(10) Å) for Sm, respectively. The average Ln–O–Ln angles are 104.6(1)° for Y and 106.6(4)° for

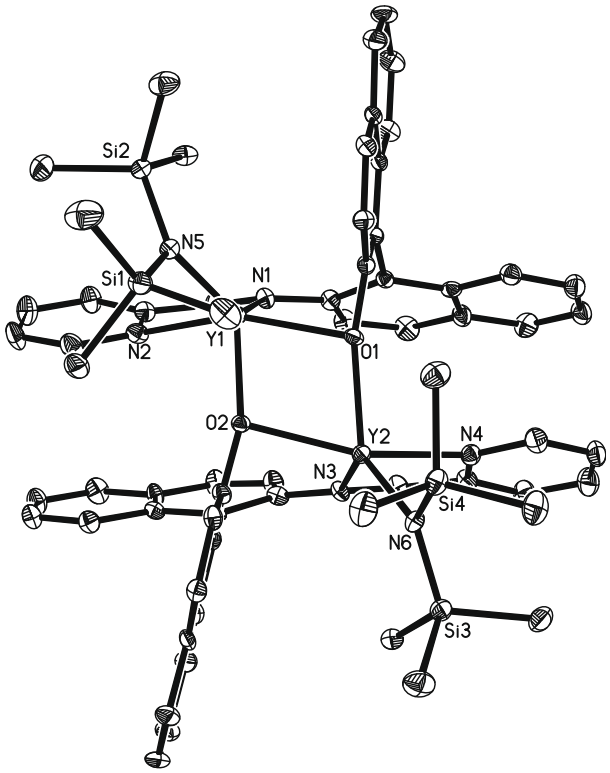


Fig. 1. Molecular structure of **3** (thermal ellipsoids drawn at the 35% probability level).

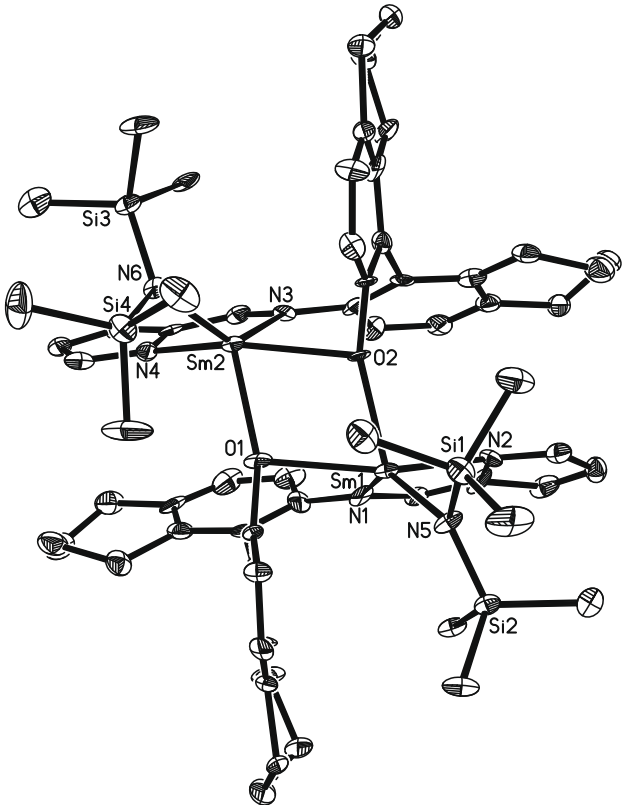


Fig. 2. Molecular structure of **4** (thermal ellipsoids drawn at the 35% probability level).

Sm complexes, respectively. The average distance of Ln–N($SiMe_3$)$_2$ is (2.261(3) Å) for Y and (2.293(11) Å) for Sm. The twisting between the aryl rings of torsion angles are 67.9(2)° and 78.7(2)° for Y, and 77.4(4)° and 79.8(4)° for Sm. The two Ln^{3+} centers within the dications are separated by 3.595(1) Å for Y and 3.752(1) Å for Sm, respectively. These structural data are close to those found in {[(*S*)-2-O-$C_{20}H_{12}$-2′-($NCHC_4H_3N$)]LnN($SiMe_3$)$_2$}$_2$ [41].

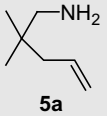
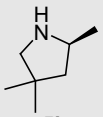
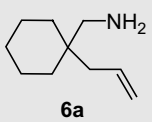
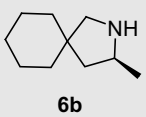
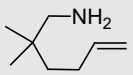
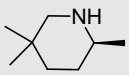
3.2. Catalytic activity

To examine the catalytic ability of the complexes **3** and **4**, the asymmetric hydroamination/cyclization of aminoalkenes and polymerization of *rac*-lactide have been evaluated 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 room temperature or elevated temperature in excellent conversions, and the samarium complex **4** is noticeably good at room temperature. Not surprisingly, given a more open coordination sphere the reaction is faster, but the ee value remains moderate (up to 55%; Table 3, entry 2). On moving to the smaller Y^{3+} ion (Table 3, entry 1), both the rate and the ee value fall slightly. Substrate **6a** is the most reactive of the aminoalkenes, giving the corresponding pyrrolidine within 16 h at room temperature. The data also show that the formation of six-membered rings can also be performed with our catalysts at 120 °C (Table 3, entries 5–6), and a moderate enantioselectivity (up to 34%), mediated by the catalyst **4**, has been obtained (Table 3, entry 6). The catalytic activities of the binuclear complexes amides **3** and **4** are more effective than trinuclear complexes {(**2**)$_2$Ln}$_2$LnN($SiMe_3$)$_2$ (Ln = Y, Yb) [42], but their enantioselectivities are poorer than those initiated by {(**2**)$_2$Ln}$_2$LnN($SiMe_3$)$_2$ (Ln = Y, Yb) [42] due to the steric effect. Although the enantiomeric excesses obtained remains moderate, it should be noted that there are only few lanthanide catalysts for these reactions that give a significant ee (>90%) at all [12].

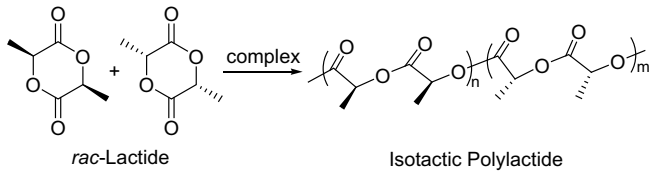
The complexes **3** and **4** are also active catalysts for the ring-opening polymerization (ROP) of racemic-lactide under mild conditions (Table 4). Yttrium complex **3** allows the complete conversion of 1000 equiv of lactide within 1 h at room temperature in toluene at [*rac*-LA]=1.0 mol L^{-1} (Table 4, entry 1). Polymerizations with this yttrium initiator/catalyst proceed much more slowly in THF (Table 4, entry 3), 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 metal-based systems [47]. This difference in activity between toluene and THF solvent is not observed with complex **4** (Table 4, entries 2 and 4); however, the samarium complex is less active than yttrium complex **3** in toluene medium (Table 4, entries 1 and 2). The resulting polylactides are all isotactic-rich under the condi-

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

Entry	Pre-catalyst (M)	Substrate	Product	Temperature (°C)	Time (h)	Conversion (%)[b]	ee (%)[c]
1	**3** (Y)	 **5a**	 **5b**	20	16	95	54
2	**4** (Sm)			20	16	98	55
3	**3** (Y)	 **6a**	 **6b**	20	16	100	48
4	**4** (Sm)			20	16	100	54
5	**3** (Y)	 **7a**	 **7b**	120	16	92	30
6	**4** (Sm)			120	16	95	34

[a] *Conditions*: C_6D_6 (0.70 mL), aminoalkene (0.32 mmol), catalyst (0.008 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 [27].

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



Entry	Complex	Solvent	Conversion (%)	M_n[b] (kg/mol)	M_w/M_n[b]	P_m[c] (%)
1	**3**	Toluene	100	72.9	1.21	68
2	**4**	Toluene	90	66.2	1.28	58
3	**3**	THF	88	59.3	1.26	59
4	**4**	THF	87	54.2	1.23	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 decoupling ^{1}H NMR spectrum in $CDCl_3$ at 25 °C.

tions examined. Molecular weights and polydispersities of the polymers produced ranged from 54.2 to 72.9 kg mol^{-1} and 1.21 to 1.28, respectively. The catalytic activities of **3** and **4** resemble that of [2-(2,6-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_4$H$_3$N]$_2$Y(CH$_2$SiMe$_3$)(THF)$_2$ [48], while the microstructure of the resulting polylactides are similar to those initiated by [(*S*)-2-MeO-C$_{20}$H$_{12}$-2′-(NCHC$_4$H$_3$N)]$_2$LnN(SiMe$_3$)$_2$}$_2$ [43].

4. Conclusions

In conclusion, two new binuclear lanthanide amides have been readily prepared from the reactions between Ln[N(SiMe$_3$)$_2$]$_3$ and chiral NNO ligands, (*S*)-2-(pyridin-2-ylmethylamino)-2′-hydroxy-1,1′-binaphthyl (**1**H$_2$) and (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl (**2**H$_2$). They have significant catalytic activity in the asymmetric hydroamination/cyclization of aminoalkenes, as well as the ring-opening polymerization of *rac*-lactide, although the overall performances of these catalytic processes are plagued by the poor degree of control of the polymerization and the moderate enantioselectivity of the formed amines, respectively.

When changes are made from pyrrol-2-ylmethyleneamino group to pyridin-2-ylmethylamino group, and from binaphthyl to H$_8$-binaphthyl, the ligands (*S*)-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl [41,42], (*S*)-2-(pyridin-2-ylmethylamino)-2′-hydroxy-1,1′-binaphthyl (**1**H$_2$), and (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl (**2**H$_2$) exhibit different reactivity patterns. For example, reaction of (*S*)-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl or **1**H$_2$ with Y[N(SiMe3)2]3 gives the binuclear complex {[(*S*)-2-O-C$_{20}$H$_{12}$-2′-(NCHC$_4$H$_3$N)]YN(SiMe$_3$)$_2$}$_2$ [41] or {(**1**)YN(SiMe$_3$)$_2$}$_2$ (**3**), respectively, while reaction of **2**H$_2$ with Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = Sm, Y) affords a binuclear complex {(**2**)SmN(SiMe$_3$)$_2$}$_2$ (**4**) or a trinuclear complex {(**2**)$_2$Y}$_2$YN(SiMe$_3$)$_2$ [42], presumably due to the steric effect of the ligand coupled with the size effect of the lanthanide ions [49]. The binuclear complexes **3** and **4** are more effective catalysts for the enantioselective hydroamination/cyclization reaction than the pyrrolate binuclear complexes {[(*S*)-2-O-C$_{20}$H$_{12}$-2′-(NCHC$_4$H$_3$N)]LnN(SiMe$_3$)$_2$}$_2$ (Ln = Y, Yb) [42], but less than those initiated by trinuclear complexes {(**2**)$_2$Ln}$_2$LnN(SiMe$_3$)$_2$ (Ln = Y, Yb) [42] presumably due to the steric effect of the complex coupled with the size effect of the lanthanide ions [49]. We are currently concentrating on this transformation, further efforts will focus on the optimization of the catalyst architecture to improve the enantiomeric excess for hydroamination/cyclization, and on the exploration of these catalysts towards other types of reactions.

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Appendix A. Supplementary material

CCDC 692309 and 692310 contain the supplementary crystallographic data for **3** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.11.061.

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