

# Preparation and structures of enantiomeric dinuclear zirconium and hafnium complexes containing two homochiral N atoms, and their catalytic property for polymerization of *rac*-lactide†

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The hydroxy- and phenoxy-bridged dinuclear zirconium and hafnium complexes **2** and **3** of an amine-pyridine-bis(phenolate) ligand ( $H_2L$ ) were prepared from the reaction of  $Na_2L$  and  $ZrCl_4$  in the presence of 0.5 equiv of water in THF, while the reaction of  $H_2L$  with NaH and then with  $ZrCl_4$  in the freshly distilled THF gave an eight-coordinate bis(homoleptic) mononuclear complex  $L_2Zr$  (**1**). Two homochiral N atoms were created in each complex upon coordination of the unsymmetric tertiary amine ligands to the metal centers. Enantiomeric dinuclear complexes **2** and **3** both undergo spontaneous resolution during crystallization. The molecular structure of each enantiomer of **2** and **3**, as well as the structure of **1**, was determined by X-ray analysis and the circular dichroism spectra of  $N(R)N(R)$ -**2** and  $N(S)N(S)$ -**2** were studied. The racemates of **2** and **3** catalyzed controlled polymerization of *rac*-lactide in terms of the linearity of molecular weight *versus* conversion, forming isotactic-rich polylactide in high yields with a narrow polydispersity.

## Introduction

The development of organometallic chemistry of group 4 metal complexes remains an interesting topic for decades, mainly due to the remarkable catalytic properties of organotitanium and -zirconium complexes in polymerization of alkenes<sup>1</sup> and their unique reactivity in some special reactions such as hydrozirconation<sup>2</sup> and cyclization of  $\alpha,\omega$ -dienes and -enynes.<sup>3</sup> In recent years, investigations on the preparation and reactivity of nonmetallocene group 4 metal complexes have attracted considerable attention, generally in the drive for fundamental new coordination chemistry of group 4 metals and their potential applications as Lewis acid catalysts. Because of the convenient preparation, variable structures, and rich chemistry of the  $N_xO_y$ -mixed chelating ligands, numerous complexes of group 4 metals containing amine-bis(phenolate),<sup>4</sup> diamine-bis(phenolate),<sup>5-7</sup> amine-tris(phenolate),<sup>8,9</sup> phenoxyketimine,<sup>10</sup> as well as salen ligands were reported.<sup>11-13</sup> Some of them were found to be highly efficient catalysts for polymerization of alkenes,<sup>5,10,14</sup> ring-opening polymerization of cyclic esters,<sup>4,6-8,11</sup> and asymmetric epoxidation of alkenes.<sup>13</sup> In an effort to extend the territory of  $N_xO_y$ -ligands

involving early transition metals and to pursue our interests in ring opening polymerization of lactide, we have set out to prepare group 4 metal complexes containing an unsymmetric  $N_2O_2$ -ligand ( $H_2L$ , Fig. 1) and to study their structures and catalytic property. Upon coordination of this unsymmetric  $N_2O_2$ -ligand to a metal center, the chirality of the tertiary amine in the ligand can be fixed to form a pair of enantiomeric complexes. It would be very interesting if we could utilize the chirality at the N atom of complexes in asymmetric organic synthesis or stereocontrolled polymerization.

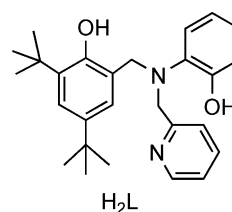


Fig. 1 The structure of unsymmetric  $N_2O_2$ -ligand  $H_2L$ .

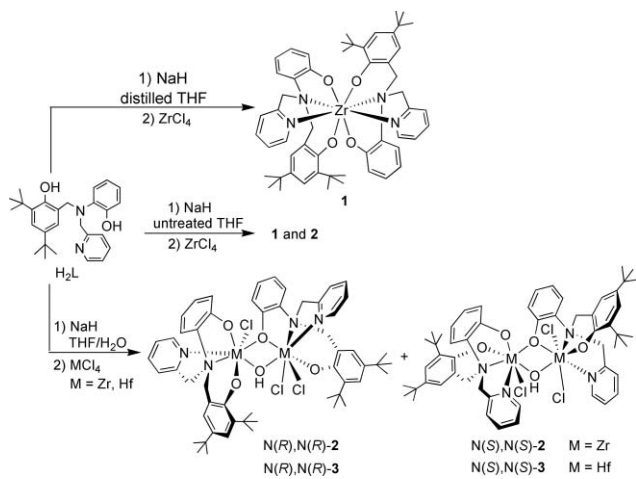
In this paper, we report the preparation and structures of enantiomeric dinuclear Zr and Hf complexes (**2** and **3** in Scheme 1) containing two homochiral N atoms, as well as a bis(homoleptic) mononuclear complex  $L_2Zr$  (**1**). Both of the dinuclear racemates undergo spontaneous resolution (conglomerate) during crystallization. Therefore, the molecular structure of each enantiomer,  $N(R)N(R)$ -**2**,  $N(S)N(S)$ -**2**,  $N(R)N(R)$ -**3**, and  $N(S)N(S)$ -**3**, were well characterized by single crystal X-ray analysis. To the best of our knowledge, they are the only structurally characterized dinuclear transition metal complexes with two homochiral N atoms. Preliminary results on the catalytic property of **2** and **3** for controlled and stereoselective ring-opening polymerization of *rac*-lactide were also described in the paper.

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† Electronic supplementary information (ESI) available: Experimental details for the synthesis of  $H_2L$ , spectroscopic characterization and X-ray crystallographic data for  $H_2L$  and complexes **1**–**3**, and homonuclear decoupled <sup>1</sup>H NMR spectra for polymers obtained. CCDC reference numbers 299272, 732095, 732096, 732097, 732098 and 752514. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c001148g



Scheme 1

## Results and discussion

### Synthesis and spectroscopic characterization of 1–3

The amine-pyridine-bis(phenolate) ligand ( $H_2L$ ) was conveniently prepared by three conventional procedures:<sup>7,15</sup> (1) the condensation of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde and 2-aminophenol in MeOH; (2) the *in situ* reduction of the Schiff base obtained in step (1) using  $NaBH_4$ ; and (3) the  $S_N2$  reaction of 2-(chloromethyl)pyridine with the amine-bis(phenolate) intermediate in  $CH_2Cl_2$  (see Scheme S1 and Fig. S1 in the ESI†). The analytically pure product  $H_2L$  was obtained as an off-white solid in an overall yield of 45% after recrystallization and washing with acetone/hexane.

The reaction of  $Na_2L$  with  $ZrCl_4$  in the freshly distilled THF gave complex **1** (Scheme 1), which was identified by HR-MS,  $^1H$  NMR and elemental analysis. The HR-MS spectrum of **1** ( $m/z = 945.6729$ , Calcd 945.3872 for  $[M + Na]^+$ , Fig. S2†) in  $CH_2Cl_2$ /acetone shows that complex **1** is an eight-coordinate mononuclear Zr complex coordinated by two  $L^{2-}$  ligands, that is,  $L_2Zr$ . The  $^1H$  NMR spectrum of **1** displays eight AX doublets at  $\delta = 3.38$ – $5.67$  ppm for the four  $CH_2$  protons in  $L_2Zr$  (Fig. S3†), and four singlets for the protons of four *tert*-butyl groups at  $\delta = 1.31$ , 1.27, 1.14, and 0.63 ppm. In addition to the signals in the region of  $\delta = 6.31$ – $7.63$  ppm for the protons in aromatic rings, two doublets at  $\delta = 9.40$  and 9.81 ppm were observed for the *ortho*-proton in each pyridyl group. These two doublets shift downfield by 0.85 and 1.26 ppm, respectively, as compared to the signal at  $\delta = 8.55$  ppm for the corresponding pyridyl proton in the free ligand. These observations indicate that the pyridyl N atoms in two amine-pyridine-bis(phenolate) ligands are both coordinated to the Zr center in an unsymmetric configuration.

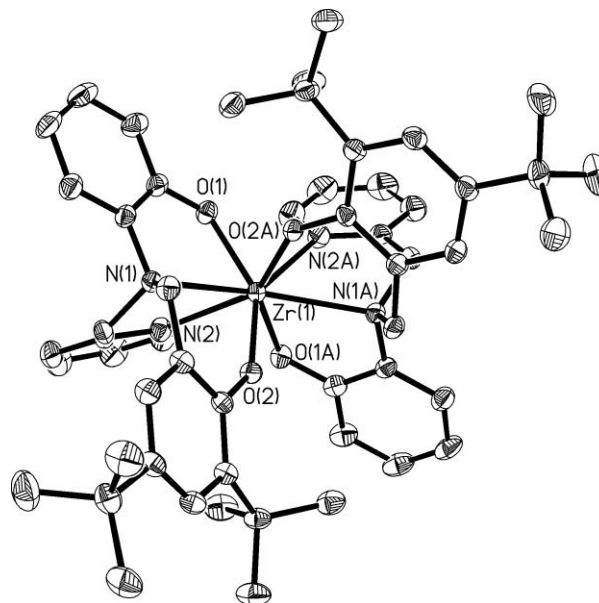
A hydroxy- and phenoxy-bridged dinuclear zirconium complex (**2**) was obtained together with  $L_2Zr$  (**1**) from the reaction of  $H_2L$ , NaH and  $ZrCl_4$  if the untreated THF was used (Scheme 1). It is proposed that the hydroxy bridge in the dinuclear complex **2** comes from the small amount of water existing in THF. Since the eight-coordinate complex  $L_2Zr$  without any good leaving group is of no interest to us, we try to favor the formation of dinuclear complex **2** by addition of 0.5 equiv of water to the reaction solution. The reaction of  $H_2L$  and NaH in the presence of 0.5 equiv of water in

THF, followed by addition of  $ZrCl_4$  in several portions afforded dinuclear complex **2** in 42% yield (Scheme 1). The dinuclear Hf complex **3** was prepared in 45% yield under the same conditions using  $HfCl_4$  as starting reagent.

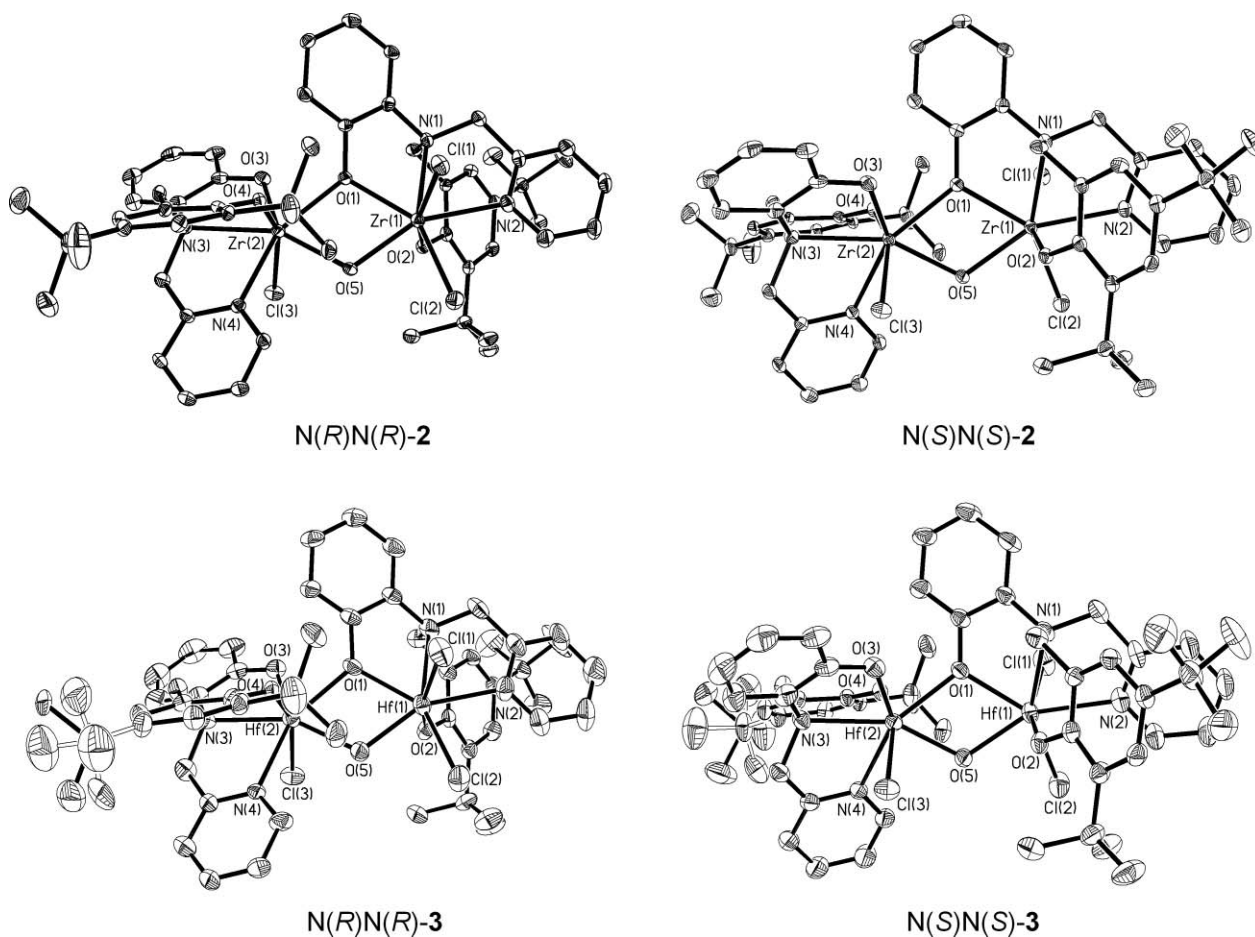
Complexes **2** and **3** were identified by HR-MS,  $^1H$  NMR, and elemental analysis. The HR-MS spectra of **2** ( $m/z = 1103.6931$ , Calcd 1103.2427 for  $[M-Cl]^+$ , Fig. S4†) and **3** ( $m/z = 1337.8264$ , Calcd 1337.2856 for  $[M+Na]^+$ , Fig. S6†) in  $CH_2Cl_2$ /acetone show that they are both dinuclear complexes in solution. Quite different  $^1H$  NMR spectra of the free ligand  $H_2L$  and the complexes were observed. The ligand  $H_2L$  displays two singlets at  $\delta = 4.35$  and 4.13 ppm for the four protons of two  $CH_2$  groups, while the  $^1H$  NMR spectrum of **2** displays eight AX doublets at  $\delta = 3.68$ – $5.36$  ppm with two low-field doublets overlapped for the eight inequivalent  $CH_2$  protons in the dinuclear complex (Fig. S5†). Furthermore, two doublets at  $\delta = 8.83$  and 9.62 ppm were observed for the *ortho*-protons of the two pyridyl groups in addition to the signals in the region of  $\delta = 6.42$ – $7.85$  ppm for other protons in aromatic rings. The two doublets arising from the *ortho*-protons of the two pyridyl groups shift downfield by 0.28 and 1.07 ppm, respectively, as compared to the signal at  $\delta = 8.55$  ppm for the corresponding pyridyl proton in the free ligand, which supports the coordination of the two pyridyl N atoms in **2**. Dinuclear complex **3** displays a very similar  $^1H$  NMR spectrum (Fig. S7†) as that of **2**. The  $^1H$  NMR data indicate that the two metal centers in each dinuclear complex are surrounded by different coordination environments.

### Molecular structures of 1–3

The molecular structure of **1** is shown in Fig. 2 with important bond lengths and angles listed in the figure caption. The two



**Fig. 2** Molecular structure of **1** showing 30% probability thermal ellipsoids. All hydrogen atoms and lattice solvent have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1–O2, 2.039(2); Zr1–O1, 2.101(2); Zr1–N2, 2.496(3); Zr1–N1, 2.517(2); O2–Zr1–O1, 143.93(8); O2–Zr1–N2, 89.00(9); O1–Zr1–N2, 72.44(9); O2–Zr1–N1, 72.87(8); O1–Zr1–N1, 71.34(8); N2–Zr1–N1, 65.80(8); O2A–Zr1–O1, 84.69(8); N2–Zr1–N1A, 141.30(8).



**Fig. 3** Molecular structures of  $N(R)N(R)$ -2,  $N(S)N(S)$ -2,  $N(R)N(R)$ -3, and  $N(S)N(S)$ -3 showing 30% probability thermal ellipsoids. All hydrogen atoms and lattice solvent have been omitted for clarity.

N atoms of the unsymmetric amines in the chelating  $N_2O_2$  ligands of **1** are homochiral in a molecule. Each unit cell of **1** contains an  $N(R)N(R)$  and an  $N(S)N(S)$  isomer to form a racemic crystal. Therefore the crystal of **1** belongs to an achiral space group  $P2_1/c$ . The crystal structure of **1** shows the central Zr atom is coordinated by the four oxygen and four nitrogen atoms of two tetradentate  $N_2O_2$  ligands. The crystallographic result is consistent with the  $^1H$  NMR spectrum of **1**. The Zr–N (2.496–2.517 Å) and the Zr–O distances (2.039–2.101 Å) are in good agreement with those previously observed in the mononuclear zirconium complexes bearing  $N_2O_2$ -tetradentate ligands.<sup>6,7,16</sup>

The single crystal X-ray analysis shows that complexes **2** and **3** are unusual asymmetric dinuclear complexes containing a hydroxy and a phenoxy bridge. The N atom of the tertiary amine in  $L^{2-}$  becomes a chiral center due to the restriction on the conformation inversion of the unsymmetric tertiary amine upon coordination. Therefore, each dinuclear complex possesses two chiral N atoms. Interestingly, crystals of both **2** and **3** belong to the chiral space group  $P2_1,2_1,2_1$  and each asymmetric unit has only one molecule, which suggests that the enantiomeric dinuclear Zr and Hf complexes undergo spontaneous resolution during the crystallization process to form so-called conglomerates.<sup>17</sup> Such conglomeration of group 4 metal complexes have been scarcely reported in the literature.<sup>18</sup> Two types of crystals were

identified for each complex, that is,  $N(R)N(R)$  and  $N(S)N(S)$  enantiomers. The molecular structures of  $N(R)N(R)$ -2,  $N(S)N(S)$ -2,  $N(R)N(R)$ -3, and  $N(S)N(S)$ -3 are shown in Fig. 3 with the numbering scheme used for metal and heteroatoms. The important bond lengths and angles are listed in Table 1. Even though the formation of a heterochiral complex is theoretically possible, only complexes with homochiral N atoms were detected and no evidence for the  $N(R)N(S)$  dinuclear complex was found from X-ray analysis (Twenty grains of crystals of the zirconium complex (**2**) were measured). The interesting feature here is that there is an intramolecular templating effect upon coordination, leading to homochiral dimeric complexes rather than heterochiral or a mixture of diastereomers. This kind of intramolecular chiral induction upon coordination has been found in preparation of other transition metal complexes containing two chiral elements.<sup>19</sup>

Each Zr center of **2** is 7-coordinate in a distorted pentagonal bipyramidal geometry. The two zirconium atoms are inequivalently coordinated. One (Zr1) of zirconium atoms is coordinated by two Cl, two N and three O atoms, and the other zirconium (Zr2) by a Cl, two N and four O atoms (Fig. S9†). The diamond-shaped core of the dinuclear complex is formed by two zirconium atoms, a hydroxy and a phenoxy bridge. The distances between two Zr atoms are 3.6236(4) Å for  $N(S)N(S)$ -2 and 3.6238(6) Å for  $N(R)N(R)$ -2, which are longer than those

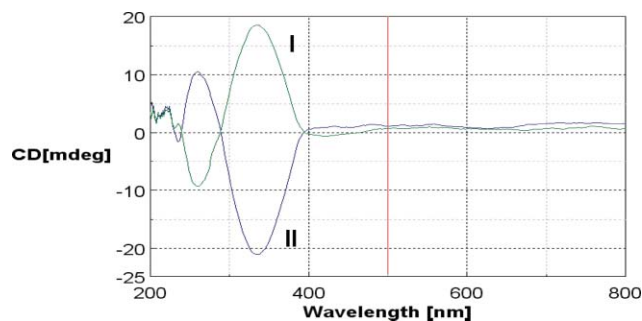
**Table 1** Selected bond lengths (Å) and angles (deg) for N(R)N(R)-2, N(S)N(S)-2, N(R)N(R)-3, and N(S)N(S)-3

	N(R)N(R)-2 (M = Zr)	N(S)N(S)-2 (M = Zr)	N(R)N(R)-3 (M = Hf)	N(S)N(S)-3 (M = Hf)
M2...M1	3.6238(6)	3.6236(4)	3.5960(6)	3.5998(3)
M1-O2	1.996(3)	1.997(2)	1.999(6)	1.999(4)
M1-O5	2.159(3)	2.1569(19)	2.117(6)	2.131(3)
M1-O1	2.172(3)	2.170(2)	2.158(6)	2.162(4)
M1-N2	2.422(3)	2.418(2)	2.385(6)	2.400(5)
M1-N1	2.444(3)	2.446(2)	2.434(7)	2.424(4)
M1-Cl1	2.4527(11)	2.4540(8)	2.437(3)	2.4437(17)
M1-Cl2	2.5156(11)	2.5155(8)	2.487(2)	2.4878(16)
M2-O4	2.004(3)	2.001(2)	1.968(6)	1.990(4)
M2-O3	2.023(2)	2.0232(19)	2.018(6)	2.027(3)
M2-O5	2.133(2)	2.1325(19)	2.119(5)	2.114(3)
M2-O1	2.218(3)	2.2142(18)	2.211(5)	2.206(3)
M2-N4	2.375(3)	2.377(2)	2.375(6)	2.361(4)
M2-N3	2.441(3)	2.448(2)	2.382(7)	2.412(4)
M2-Cl3	2.5086(11)	2.5104(9)	2.482(2)	2.4878(15)
O2-M1-O1	103.11(10)	102.94(8)	101.4(2)	101.42(14)
N2-M1-N1	69.49(11)	69.51(8)	69.4(3)	69.72(17)
Cl1-M1-Cl2	88.61(4)	88.56(3)	88.41(11)	88.39(7)
O4-M2-O3	107.34(11)	107.44(9)	106.0(2)	106.12(17)
N4-M2-N3	69.63(11)	69.59(8)	69.9(2)	69.47(14)
O3-M2-Cl3	86.81(8)	86.63(7)	87.21(19)	87.05(13)
M2-O5-M1	115.20(11)	115.29(9)	116.2(3)	115.98(16)
M1-O1-M2	111.27(10)	111.47(8)	110.8(2)	110.98(15)
O4-M2-Cl3	155.18(8)	155.05(6)	157.26(16)	157.14(9)
O2-M1-Cl1	158.12(8)	158.13(6)	159.75(18)	159.41(10)
O2-M1-Cl2	98.12(8)	98.19(6)	98.77(17)	98.58(11)
O5-M1-O1	66.35(9)	66.23(7)	66.2(2)	66.02(12)
O5-M2-O1	65.97(9)	65.87(7)	65.3(2)	65.52(13)

reported for other dinuclear Zr complexes.<sup>20</sup> Except for the longer Zr-O bonds in the bridges (Zr-O1, 2.170(2)–2.218(3) Å; Zr-O5, 2.1325(19)–2.159(3) Å), the other Zr-O (1.996(3)–2.0232(19) Å), Zr-N (2.375(3)–2.448(2) Å), and Zr-Cl bond lengths (2.4527(11)–2.5156(11) Å) are in good agreement with those observed in the zirconium complexes bearing a non-salen N<sub>2</sub>O<sub>2</sub>-tetradentate ligand.<sup>6,7,16</sup> The two chlorine atoms attached to the Zr(1) locate in a *cis* position with the bond angle Cl(1)–Zr(1)–Cl(2) of 88.61(4)° in N(R)N(R)-2 and 88.56(3)° in N(S)N(S)-2. The crystal structures of N(S)N(S)-3 and N(R)N(R)-3 enantiomers of the dinuclear Hf complex are essentially identical to N(S)N(S)-2 and N(R)N(R)-2, respectively.

### Circular dichroism (CD) spectroscopies of N(R)N(R)-2 and N(S)N(S)-2

To further confirm the spontaneous resolution of the enantiomers and the chirality of the dinuclear complexes, CD spectra of N(R)N(R)-2 and N(S)N(S)-2 were recorded, respectively. The absolute configuration of each single crystal of the complex was determined by X-ray diffraction studies before recording CD spectra. The mirror-image CD spectra reflecting opposite Cotton effects were observed for the individual grains of single crystals of N(R)N(R)-2 and N(S)N(S)-2 in the solid state (Fig. 4). The CD spectra of the CH<sub>2</sub>Cl<sub>2</sub> solutions of N(R)N(R)-2 and N(S)N(S)-2 did not show any noticeable change, indicating that the chiral dinuclear structures were essentially maintained in solution. The mother solution of the reaction and the powder of **2** collected directly from the crude product did not display any CD signals, which shows that the racemate of the product was formed in the reaction.

**Fig. 4** Circular dichroism spectra, curve I—the CD spectrum of N(R)N(R)-2 and curve II—the CD spectrum of N(S)N(S)-2 recorded in the solid state.

### Activity and stereoselectivity for *rac*-lactide polymerization

In recent years, some group 4 metal complexes of N<sub>x</sub>O<sub>y</sub> (X = Y = 2; X = 1, Y = 2, 3) ligands have been reported to be efficient catalysts for stereocontrolled ring-opening polymerization (ROP) of *rac*-lactide (*rac*-LA).<sup>6–8,11</sup> Transfer of the chirality at a N atom, spontaneously created upon coordination of a multidentate ligand, to polymers is interesting because stereoselectivity of polymerization can be approached without using any chiral auxiliary in the preparation of catalysts. We explored the catalytic activities of racemic dinuclear complexes **2** and **3** in the polymerization of *rac*-LA and studied the stereoselectivity of the reaction.

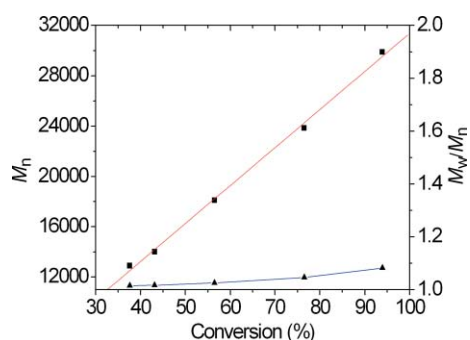
Representative results with complexes **2** and **3** as initiators for the ROP of *rac*-LA are collected in Table 2. Conversions of the monomer to PLA reached 91–94% in 10 h with **2** or **3** as initiator at a *rac*-LA/initiator molar ratio of 200. The narrow polydispersities ( $M_w/M_n = 1.02$ –1.08) and the linear correlation between the observed  $M_n$  and the conversion of monomer imply a living polymerization system (Fig. 5). The  $M_n$  values have been corrected by a Mark–Houwink factor of 0.58, due to the use of polystyrene standards.<sup>21</sup>

More evidence for the stereoselective polymerization of *rac*-LA is given by the homonuclear decoupled <sup>1</sup>H NMR spectra of the methine region of the PLA samples derived from **2** and **3** (Fig. S10†), which suggests that the formation of chains in PLA is predominantly isotactic.<sup>22</sup> The  $P_m$  values are in the range of 0.65–0.72, which are higher than the  $P_m$  values (0.5–0.6) reported for the ROP of *rac*-LA initiated by mononuclear Zr and Hf complexes containing an analogous symmetric amine-pyridine-bis(phenolate)

**Table 2** Polymerization of *rac*-LA initiated by **2** and **3**<sup>a</sup>

Entry	Initiator	Mon.:		Conv. <sup>b</sup>	$M_n^c$	$M_w/M_n^c$	$P_m^d$	Activity <sup>e</sup>
		init.	Time/h					
1	<b>2</b>	100:1	3	94	15700	1.03	0.65	4.15
2	<b>2</b>	200:1	7	86	26800	1.05	0.72	3.29
3	<b>2</b>	200:1	10	94	30100	1.08	0.71	2.47
4	<b>3</b>	200:1	6	75	22800	1.02	0.68	3.27
5	<b>3</b>	200:1	10	91	28000	1.07	0.66	2.38

<sup>a</sup> Conditions: initiator 0.05 mmol, 130 °C, toluene 10 mL. <sup>b</sup> Determined by <sup>1</sup>H NMR. <sup>c</sup> Determined by GPC in THF, calibrated with polystyrene standards. The  $M_n$  values have been corrected by a Mark–Houwink factor of 0.58, due to the use of polystyrene standards.<sup>21</sup> <sup>d</sup>  $P_m$  is the probability of isotactic enchainment calculated by analysis of the homonuclear decoupled <sup>1</sup>H NMR spectra.<sup>22</sup> <sup>e</sup>  $g_{\text{pol}} \text{ mmol}_{\text{cat}}^{-1} \text{ h}^{-1}$ .



**Fig. 5** Plot of observed PLA  $M_n$  (■, left-hand axis) and molecular weight distribution (▲, right-hand axis) as functions of monomer conversion using racemic complex **2** as initiator with  $[rac\text{-LA}]_0/[2]_0 = 200$  in toluene at 130 °C.

ligand.<sup>7</sup> Most of the group 4 metal catalysts lead to the formation of atactic or heterotactic-rich poly(lactide) (PLA).<sup>8,11</sup> Even polymerization of *rac*-LA initiated with a titanium complex of a chiral  $\text{NO}_2$  ligand affords atactic PLA.<sup>23</sup> To the best of our knowledge, among group 4 metal catalysts only a salen zirconium complex was found to be an efficient initiator for stereoselective ROP of *rac*-LA to stereoblock PLA with isoselectivity up to 0.75.<sup>7</sup> Polymerization performed with enantiopure L-LA results in entirely isotactic PLA (Fig. S11†) and the epimerization in this catalytic system can be ruled out.<sup>24</sup> Although the stereocontrol mechanism of ROP of *rac*-LA initiated by **2** and **3** is not clearly understood to date, it is assumed that the asymmetric coordination environment around the metal centers of **2** and **3**, resulting from the chirality of the N(1) and N(3) atoms of the ligands, may play a role in governing stereoselective ROP of *rac*-LA. It is still not clear up to now whether the OH or Cl is the initiating ligand and whether the binuclear complexes or the dissociated mononuclear species act as active catalysts. Studies on the detailed mechanism and kinetics of *rac*-LA polymerization initiated by such metal complexes bearing chiral N atoms are in progress.

## Conclusion

Enantiomeric dinuclear zirconium and hafnium complexes (N(R)N(R)-**2**/N(S)N(S)-**2**, N(R)N(R)-**3**/N(S)N(S)-**3**) with a hydroxy and a phenoxy bridge were prepared and structurally characterized. Two homochiral N atoms were created in each molecule of complexes by an intramolecular templating effect upon coordination of the unsymmetric amine ligands. The most interesting point is that both chiral zirconium and hafnium dinuclear complexes are capable of self-resolving to give conglomerates during crystallization. The racemates of complexes **2** and **3** are catalytically active for the controlled and stereoselective polymerization of *rac*-LA. Preliminary results show that these initiators containing chiral N atoms have a moderate asymmetric induction to afford the isotactic-rich PLA in good yields with a narrow polydispersity. The chiral N atoms in the complexes **2** and **3** may play a role in governing stereoselective ROP of *rac*-LA. Modification of the unsymmetric amine ligand by introduction of substituents to the pyridyl group and/or hydroxyphenyl ring may improve the isoselectivity of PLA. Preparation of enantiomeric complexes of other metals with multidentate chiral N ligands and

their catalytic properties for stereoselective polymerization of *rac*-LA are currently under investigation.

## Experimental

### General procedures

All reactions and manipulations related to organometallic compounds were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Solvents were distilled prior to use by conventional methods. Organometallic reagents  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  were purchased from Aldrich. Other commercially available chemical reagents were used without further purification.  $^1\text{H}$  NMR spectra were recorded on Varian 400 and 600 NMR spectrometers. Mass spectra were recorded on an ESI-Q-TOF MS (Micro) instrument. Elemental analyses were performed with an Elementar Vario EL III elemental analyzer. Circular dichroism spectra were recorded on a J-810 instrument.

### Preparation of the ligand $\text{H}_2\text{L}$

Unsymmetric ligand  $\text{H}_2\text{L}$  was prepared according to a modified procedure of the literature (Scheme S1, see ESI† for details).<sup>7,15</sup> Ligand  $\text{H}_2\text{L}$  was obtained as an off-white crystalline solid (0.94 g, 45%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 293 K):  $\delta = 8.55$  (d, 1H, Py,  $J = 4.8$  Hz), 7.39–6.61 (9H, Ph and Py), 4.35 (s, 2H, N- $\text{CH}_2$ -Ph), 4.13 (s, 2H, N- $\text{CH}_2$ -Py), 1.28 and 1.17 (2 s, each for 9H,  $\text{CH}_3$  of *tert*-Bu) (Fig. S1†). Anal. Calcd for  $\text{C}_{27}\text{H}_{34}\text{N}_2\text{O}_2$ : C, 77.48; H, 8.19; N, 6.69. Found: C, 77.39; H, 8.11; N, 6.62. The crystal structure of  $\text{H}_2\text{L}$  was determined by single crystal X-ray analysis (Fig. S8†).

### Preparation of complex **1**

Sodium hydride (0.1 g, 4.0 mmol) was added to a solution of  $\text{H}_2\text{L}$  (0.56 g, 1.34 mmol) in THF (30 mL), which was freshly distilled from sodium/diphenyl ketone. The suspension was stirred for 4 h. After cooling the mixture to 0 °C,  $\text{ZrCl}_4$  (0.31 g, 1.34 mmol) was added in portions to the solution. The suspension was stirred for 16 h at room temperature. The mixture was filtered and the filtrate was concentrated to dryness. The crude product was recrystallized with THF/hexane to give  $\text{L}_2\text{Zr}$  (**1**) as a white crystalline solid. Yield: 41%. The crystal of complex **1** suitable for X-ray analysis was obtained from  $\text{CH}_2\text{Cl}_2$ /hexane.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.40, 9.81 (2d, 2H, 2Py,  $J = 5.6$  Hz), 7.63–6.31 (18H, Ph and Py), 5.67, 5.26 (2d, 2H, N- $\text{CH}_2$ -Py,  $J = 14.4$  Hz), 4.92, 4.88 (2d, 2H, N- $\text{CH}_2$ -Ph,  $J = 11.6$  Hz), 4.48, 4.33 (2d, 2H, N- $\text{CH}_2$ -Py,  $J = 14.4$  Hz), 3.82, 3.38 (2d, 2H, N- $\text{CH}_2$ -Ph,  $J = 11.6$  Hz), 1.31, 1.27, 1.14, 0.63 (4 s, each for 9H, *t*Bu) (Fig. S3†). HR-MS:  $m/z = 945.6729$  (Calcd 945.3872)  $[\text{M}+\text{Na}]^+$  (Fig. S2†). Anal. Calcd for  $\text{C}_{55}\text{H}_{64}\text{N}_4\text{O}_4\text{Zr}$ : C, 70.17; H, 6.98; N, 6.06. Found: C, 70.01; H, 6.89; N, 5.98.

### Preparation of complex **2**

Sodium hydride (0.1 g, 4.0 mmol) was added to a solution of  $\text{H}_2\text{L}$  (0.56 g, 1.34 mmol) in THF (30 mL) containing about 0.5 equiv of water (10  $\mu\text{L}$ , 0.6 mmol). The suspension was stirred for 2 h. The further reaction and work-up are the same as that for preparation of **1**. The white solid obtained was recrystallized with acetone/hexane and the product was dried *in vacuo*. Yield:

**Table 3** Crystallographic data for N(R)N(R)-2, N(S)N(S)-2, N(R)N(R)-3, and N(S)N(S)-3

	N(R)N(R)-2·3C <sub>3</sub> H <sub>6</sub> O	N(S)N(S)-2·3C <sub>3</sub> H <sub>6</sub> O	N(R)N(R)-3·C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>	N(S)N(S)-3·C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>
Formula	C <sub>63</sub> H <sub>83</sub> Cl <sub>3</sub> N <sub>4</sub> O <sub>8</sub> Zr <sub>2</sub>	C <sub>63</sub> H <sub>83</sub> Cl <sub>3</sub> N <sub>4</sub> O <sub>8</sub> Zr <sub>2</sub>	C <sub>58</sub> H <sub>75</sub> Cl <sub>3</sub> N <sub>4</sub> O <sub>7</sub> Hf <sub>2</sub>	C <sub>58</sub> H <sub>75</sub> Cl <sub>3</sub> N <sub>4</sub> O <sub>7</sub> Hf <sub>2</sub>
Formula weight	1313.12	1313.12	1403.55	1403.55
Crystal size/mm	0.15 × 0.10 × 0.18	0.09 × 0.11 × 0.26	0.18 × 0.31 × 0.33	0.15 × 0.28 × 0.35
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> /Å	14.6214(13)	14.6194(6)	14.6202(9)	14.5989(6)
<i>b</i> /Å	15.8246(14)	15.8232(6)	15.7804(11)	15.7790(7)
<i>c</i> /Å	27.544(3)	27.5609(11)	27.372(2)	27.3541(17)
<i>V</i> /Å <sup>3</sup>	6373.0(10)	6375.5(4)	6315.1(7)	6301.2(5)
<i>Z</i>	4	4	4	4
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.369	1.368	1.476	1.480
$\mu$ /mm <sup>-1</sup>	0.508	0.507	3.462	3.469
<i>F</i> <sub>000</sub>	2736	2736	2808	2808
$\theta$ Range/deg	1.48–26.04	1.48–26.04	1.90–27.53	1.90–30.21
Reflections collected	35696	36319	41552	32869
Independent reflections	12536	12553	14412	16730
<i>R</i> <sub>int</sub>	0.0623	0.0461	0.0831	0.0374
<i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0423, 0.0799	0.0347, 0.0713	0.0546, 0.0971	0.0398, 0.0684
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0575, 0.0844	0.0399, 0.0732	0.0952, 0.1126	0.0716, 0.0785
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.921	0.948	0.975	0.970
Residual electron density/e Å <sup>-3</sup>	0.613, -0.478	0.628, -0.372	1.251, -1.093	1.250, -0.684
Flack	-0.07(3)	-0.08(2)	-0.003(10)	-0.009(7)

$$^a R_1 = \sum \|F_o\| - |F_c| / \sum \|F_o\|, \quad ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

320 mg (42%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.83 (d, 1H, Py, *J* = 6.0 Hz), 9.62 (d, 1H, Py, *J* = 5.6 Hz), 7.85–6.42 (18H, Ph and Py), 5.39, 5.28 (2d, 2H, N-CH<sub>2</sub>-Py, *J* = 15.0 Hz), 4.87 (d, 1H, N-CH<sub>2</sub>-Ph, *J* = 12.4 Hz), 4.76 (d, 1H, N-CH<sub>2</sub>-Ph, *J* = 12.8 Hz), 4.63 (d, 1H, N-CH<sub>2</sub>-Py, *J* = 14.4 Hz), 4.54 (d, 1H, N-CH<sub>2</sub>-Py, *J* = 14.8 Hz), 3.68 (d, 2H, N-CH<sub>2</sub>-Ph, *J* = 12.0 Hz), 1.32, 1.28, 1.15, 1.14 ppm (4 s, each for 9H, 4*t*Bu) (Fig. S5†). HR-MS: *m/z* = 1103.6931 (Calcd 1103.2427) [M-Cl]<sup>+</sup> (Fig. S4†). Anal. Calcd for C<sub>54</sub>H<sub>65</sub>Cl<sub>3</sub>N<sub>4</sub>O<sub>5</sub>Zr<sub>2</sub>: C, 56.95; H, 5.75; N, 4.92. Found: C, 56.74; H, 5.68; N, 4.84.

### Preparation of complex 3

Complex 3 was prepared by essentially an identical procedure as that for 2 by using HfCl<sub>4</sub> as the starting reagent. Yield: 395 mg (45%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.86 (d, 1H, 2Py, *J* = 5.2 Hz), 9.68 (d, 1H, 2Py, *J* = 4.8 Hz), 7.86–6.40 (18H, Ph and Py), 5.23, 5.33 (2d, 2H, N-CH<sub>2</sub>-Py, *J* = 14.8 Hz), 4.89 (d, 1H, N-CH<sub>2</sub>-Py, *J* = 12.8 Hz), 4.75 (d, 1H, N-CH<sub>2</sub>-Ph, *J* = 5.2 Hz), 4.71 (d, 1H, N-CH<sub>2</sub>-Ph, *J* = 5.6 Hz), 4.63 (d, 1H, N-CH<sub>2</sub>-Py, *J* = 12.8 Hz), 3.70, 3.67 (2d, 2H, N-CH<sub>2</sub>-Ph, *J* = 7.2 Hz), 1.34, 1.31, 1.17, 1.16 (4 s, each for 9H, 4*t*Bu) (Fig. S7†). HR-MS: *m/z* = 1337.8264 (Calcd 1337.2856) [M+Na]<sup>+</sup> (Fig. S6†). Anal. Calcd for C<sub>54</sub>H<sub>65</sub>Cl<sub>3</sub>N<sub>4</sub>O<sub>5</sub>Hf<sub>2</sub>·CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>: C, 49.63; H, 5.39; N, 3.99. Found: C, 49.79; H, 5.36; N, 3.87.

### X-Ray crystallography for 1–3 and H<sub>2</sub>L

X-Ray diffraction measurements were performed on a Bruker Smart Apex II CCD diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 298 K using the  $\omega$ -2 $\theta$  scan mode. Data processing was accomplished with the SAINT processing program.<sup>25</sup> Intensity data were corrected for absorption by the SADABS program.<sup>26</sup> The structures were solved by direct methods and refined on *F*<sup>2</sup> against full-matrix least-squares meth-

ods using the SHELX-97 program package.<sup>27</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed by geometrical calculation and refined in a riding model. Crystallographic data for N(R)N(R)-2, N(S)N(S)-2, N(R)N(R)-3 and N(S)N(S)-3 are listed in Table 3 and those for 1 and H<sub>2</sub>L are listed in Table S1.†

### Typical procedure for polymerization of *rac*-LA

All polymerization operations were performed under a nitrogen atmosphere using standard Schlenk techniques. Toluene was distilled under nitrogen from sodium/diphenyl ketone and ethyl acetate was distilled from calcium hydride prior to use. *rac*-Lactide (LA from Aldrich) was recrystallized three times from ethyl acetate. Molecular weight and molecular weight distribution were determined by gel permeation chromatography (PL-GPC 220). The GPC column was eluted with THF at 40 °C at a rate of 1 mL min<sup>-1</sup> and the data were calibrated with polystyrene standards. The *M*<sub>n</sub> values have been corrected by a Mark-Houwink factor of 0.58.<sup>21</sup>

The toluene solution (10 mL) of the racemic initiator 2 (0.057 g, 0.05 mmol) and *rac*-LA (1.44 g, 10 mmol) was stirred at 130 °C for 10 h. The reaction was stopped by cooling the tube quickly with an ice-water bath. A sample was taken from the resulting solution for determination of the conversion of *rac*-LA by <sup>1</sup>H NMR spectroscopy. The volatiles were removed *in vacuo* and the residue was dissolved in a minimum amount of CH<sub>2</sub>Cl<sub>2</sub>. The polymer was precipitated with addition of cold methanol. The resulting solid was washed with methanol (3 × 20 mL) and dried under high vacuum.

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