

Article

# New Challenge for Classics: Neutral Zinc Complexes Stabilised by 2,2'-Bipyridine and 1,10-Phenanthroline and Their Application in the Ring-Opening Polymerisation of Lactide

Janna Börner <sup>1</sup>, Ulrich Flörke <sup>1</sup>, Artjom Döring <sup>1</sup>, Dirk Kuckling <sup>1</sup>, Matthew D. Jones <sup>2</sup> and Sonja Herres-Pawlis <sup>3,\*</sup>

<sup>1</sup> Department Chemie, Universität Paderborn, Warburger Straße 100, 33098 Paderborn, Germany; E-Mails: janna.boerner@uni-paderborn.de (J.B.); ulrich.floerke@uni-paderborn.de (U.F.); artjom.doering@uni-paderborn.de (A.D.); dirk.kuckling@uni-paderborn.de (D.K.)

<sup>2</sup> Department of Chemistry, University of Bath, Claverton Down, Bath BA27AY, UK; E-Mail: mj205@bath.ac.uk

<sup>3</sup> Department Chemie, Technische Universität Dortmund, Otto-Hahn-Straße 6, 44227 Dortmund, Germany

\* Author to whom correspondence should be addressed; E-Mail: sonja.herres-pawlis@tu-dortmund.de; Tel.: +49-231-755-3832; Fax: +49-231-755-5048.

Received: 30 October 2009 / Accepted: 3 December 2009 / Published: 8 December 2009

---

**Abstract:** The zinc acetato and triflato complexes of 2,2'-bipyridine and 1,10-phenanthroline were prepared and completely characterised. The whole series (including the already described dichlorido complexes and the ligands themselves) were screened for their catalytic activity in the solvent free ring-opening polymerisation of D,L-lactide. The acetato and triflato complexes were found to be active initiators and polylactides could be obtained in almost quantitative yields or with high molecular weights, up to 145,000 g/mol.

**Keywords:** biopolymers; zinc; ring-opening polymerisation; lactide; sustainable chemistry; N-donor ligands

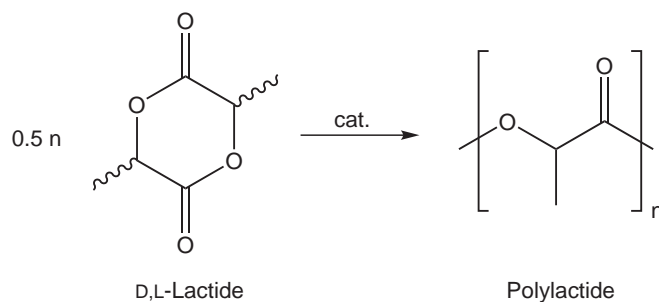
---

## 1. Introduction

Modern approaches towards green and sustainable chemistry focus on the substitution of petrochemical-based plastics with biorenewable and biodegradable materials.[1–6]. Polylactide (PLA)

is an aliphatic polyester which is produced by controlled metal-initiated ring-opening polymerisation (ROP) of lactide, the cyclic diester of lactic acid (Figure 1). Due to their favourable properties resulting in a wide range of applications (e.g., packaging materials, drug delivery systems, surgical implants), PLAs have been proven to be the most attractive and useful class of biodegradable polyesters among the numerous polyesters studied to date [7].

**Figure 1.** Ring-opening polymerisation of D,L-lactide.



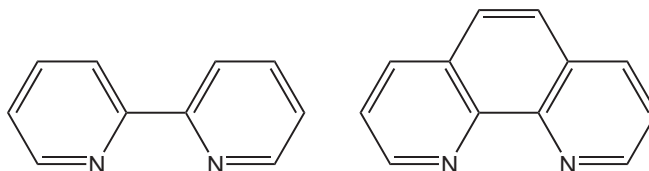
Based on the 12 principles of green chemistry introduced by P. T. Anastas and J. C. Warner [8–10] PLA can be described as sustainable polymer in context of green chemistry. It is produced from inexpensive annually renewable resources, and after its lifetime it can be recycled or it degrades through simple hydrolysis of the ester linkages into non-toxic, harmless natural products. Thus PLA is also a low-impact greenhouse gas polymer because the  $\text{CO}_2$  generated during the biodegradation is balanced by an equal amount taken from the atmosphere during the growth of plant feedstock [10]. By using environmentally desirable solvent free reaction conditions the waste disposal of the production process can be further improved. Thus, the change of PLA from a specialty material to a large-volume commodity plastic is required in reference to green chemistry [7, 11–17].

Consequently, the development of new single-site metal catalysts for the ROP of lactide has seen tremendous growth over the past decade. Several important ligand classes have been used to stabilise catalytic active complexes, including simple alkoxides and carboxylates,  $\beta$ -diiminates, tris(pyrazolyl)borates, phenolates, guanidates, Schiff bases, bis(phosphinimino)methanides and salen ligands.[5, 11, 12, 14, 18–21] However, their high polymerisation activity is often combined with high sensitivity which can be ascribed to the anionic character of these ligands. Thus, for industrial purposes, there is an exigent need for initiators that tolerate air, moisture and small impurities in the monomer [14].

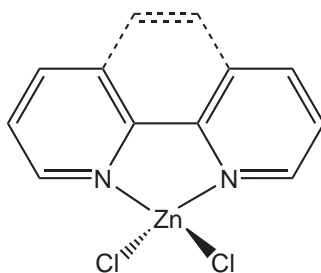
Up to now, only few systems using neutral ligands have been described. They apply strong donor systems like guanidines,[22, 23], phosphinimines,[24] and imidazolin-2-imines [25]. To find new neutral ligands for the development of ROP active single-site metal catalysts we focused our interest on 2,2'-bipyridine (bipy, **1**) and 1,10-phenanthroline (phen, **2**), some of the most widely used bidentate ligands in coordination chemistry (Figure 2). They are commercially available, easy to handle and can stabilise complexes with a wide range of transition metals due to their favourable donor properties. To date several zinc complexes containing **1** and **2** were synthesised, [26–29, 29–38] but to the best of our knowledge, none has been tested for their ability to initiate the ring-opening polymerisation of cyclic lactones. Herein we report on the synthesis and characterisation of four novel zinc acetate and triflate complexes stabilised by 2,2'-bipyridine and 1,10-phenanthroline. They together with already described

chloride complexes (Figure 3) [39, 40] and the ligands themselves were screened for their catalytic activity in the solvent free ROP of D,L-lactide.

**Figure 2.** Bischelating ligands 2,2'-bipyridine (bipy, **1**, l) and 1,10-phenanthroline (phen, **2**, r).



**Figure 3.** Schematic depiction of [Zn(bipy)Cl<sub>2</sub>] (**1a**) and [Zn(phen)Cl<sub>2</sub>] (**2a**) [39, 40].

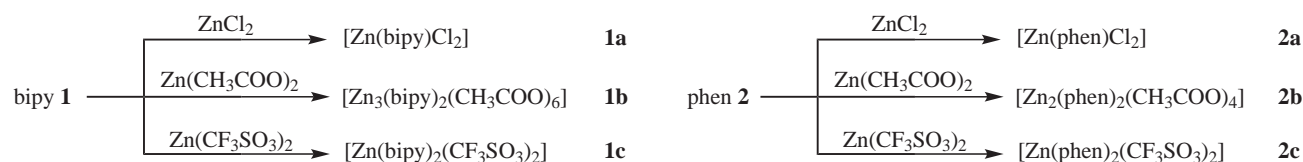


## 2. Results and Discussion

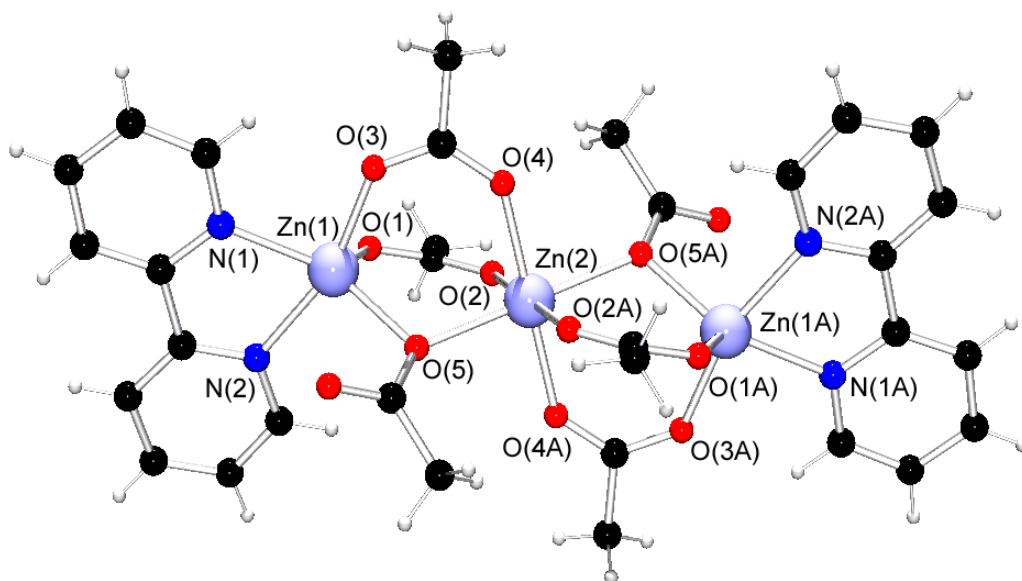
### 2.1. Complex Syntheses

The zinc complexes **1a** [39] and **2a** [40] were prepared according to literature procedures. [Zn<sub>3</sub>(bipy)<sub>2</sub>-(CH<sub>3</sub>COO)<sub>6</sub>] (**1b**), [Zn<sub>2</sub>(phen)<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub>] (**2b**), [Zn(bipy)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>] (**1c**) and [Zn(phen)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>] (**2c**) were obtained as colourless crystal solids in 88-98% yields by simple stirring of **1** and **2** with Zn(OAc)<sub>2</sub> and Zn(OTf)<sub>2</sub> in a dry aprotic solvent (THF/MeCN) (see Figure 4). Single crystals were prepared either by cooling a saturated solution slowly to room temperature or by slow diffusion of diethyl ether into the solution. The molecular structures of **1b-2c** (Figures 5–7) were determined by X-ray crystallography. The crystals obtained show a high stability towards moisture and air. They can be handled and stored in air, whereas the corresponding zinc salts (ZnCl<sub>2</sub>, Zn(OAc)<sub>2</sub> and Zn(OTf)<sub>2</sub>) are sensitive towards hydrolysis and are rather hygroscopic.

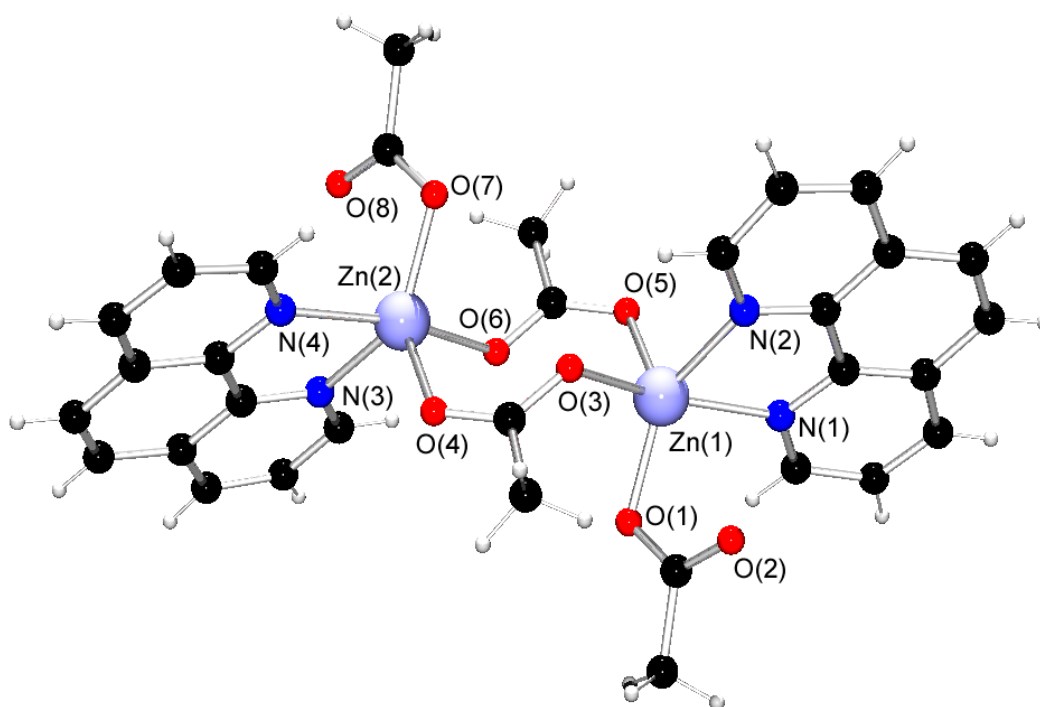
**Figure 4.** Schematic synthesis of **1a-2c**.



**Figure 5.** Molecular structure of  $[\text{Zn}_3(\text{bipy})_2(\text{CH}_3\text{COO})_6]$  (**1b**) as determined at 120 K.



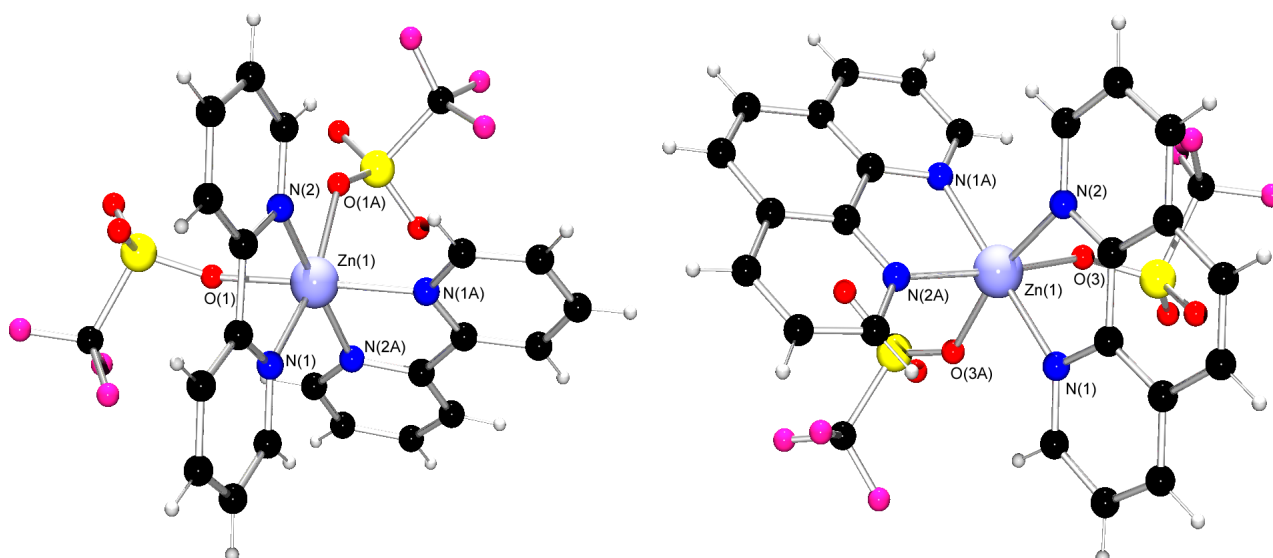
**Figure 6.** Molecular structure of  $[\text{Zn}_2(\text{phen})_2(\text{CH}_3\text{COO})_4]$  (**2b**) as determined at 120 K.



The chlorido complexes **1a** and **2a** exhibit simple tetrahedral coordination geometry, where the zinc atom is fourfold coordinated by the two N-donor atoms of the chelating ligand and two chlorides, respectively (Figure 3). The acetato complexes **1b** and **2b** possess a polynuclear structure. In **1b**, two Zn atoms are surrounded by the N-donor atoms of **1** and three oxygen atoms of three acetato bridging ligands connecting each Zn atom with a third Zn atom located between them. Consequently, the latter shows an octahedral coordination environment whereat each corner is occupied by an acetato oxygen

atom. Interestingly, in each case two acetato ligands bridge the Zn atoms via two oxygen functions but the third acetato ligand connects the metal atoms via only one oxygen atom of the acetate group. **2b** is a binuclear species that is also bridged by acetato ligands. Each Zn atom is coordinated by the N-donors of **2** in a chelating manner, and two oxygen atoms of two acetato ligands connecting them both and generating an eight-membered heterocycle. To complete the trigonal bipyramidal coordination sphere of each metal atom the fifth coordination site is occupied by a non-bridging acetato ligand. The zinc triflate complexes **1c** and **2c** exhibit an analogous structure motif. Each zinc atom is surrounded by the four N-donor atoms of two chelate ligands and two oxygen atoms of two triflate ligands generating an octahedral coordination environment.

**Figure 7.** Molecular structure of  $[\text{Zn}(\text{bipy})_2(\text{CF}_3\text{SO}_3)_2]$  (**1c**) and of  $[\text{Zn}(\text{phen})_2(\text{CF}_3\text{SO}_3)_2]$  (**2c**) as determined at 120 K.



Due to the rigid structure of **1** and **2**, the bite angles of the described complexes differ slightly, ranging from 75.8(1) to 79.3(1) $^\circ$  but showing slightly higher values for the triflate complexes. Regarding the Zn-N bond length, it is notable that in all complexes, except **1b**, one of the bonds is with a difference of 0.010 (**1c**), 0.024 (**2c**) and 0.104 Å (**2b**) slightly longer than the other. Their absolute values range from 2.102(1) to 2.210(2) Å. The values for the Zn-O bonds in **1b** and **2b** depend on the coordination mode of the acetato ligands. In **1b** the Zn-O bonds between the bridging acetato ligands and the zinc atoms that are also coordinated by the pyridine ligands are in average with 2.010 Å generally shorter than those belonging to the  $\text{ZnO}_6$  octahedron (av. 2.111 Å). In **2b** the non-bridging acetato ligand possesses the shortest Zn-O value with av. 1.983 Å. The value for the bridging ligand, whose oxygen atom is occupying the equatorial coordination site of the trigonal bipyramid, is with av. 2.004 Å longer than the latter Zn-O bond length, but not as long as the Zn-O bond belonging to the oxygen atom occupying the axial coordination site of the trigonal bipyramid (av. 2.087 Å). Due to their similar structure, the Zn-O bond lengths of **1c** (2.191(1) Å) and **2c** (2.189(1) Å) possess equal values. Selected bond length and angles are summarised in Table 1.

**Table 1.** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] of **1b**, **2b**, **1c**, and **2c**.

	<b>1b</b>	<b>2b</b>	<b>1c</b>	<b>2c</b>
Zn-N	2.143 (2), 2.148(2)	2.104(2), 2.208(2), 2.104(2), 2.210(2)	2.102(1), 2.112(1)	2.102(1), 2.126(1)
Zn-O	2.018(2), 2.019(2), 1.992(1), 2.071(2), 2.102(1), 2.161(1)	1.981(2), 2.004(2), 2.096(2), 1.984(2), 2.003(2), 2.078(2)	2.191(1)	2.189(1)
N-Zn-N	75.8(1)	76.7(1) 77.0(1)	78.1(1)	79.3(1)
O-Zn-O	98.0(1), 98.0(1), 99.3(1) 180.0, 93.0(1), 87.0(1), 90.1(1), 89.9(1), 87.9(1), 92.1(1), 180.0, 180.0	117.3(1), 95.9(1), 100.2(1), 116.4(1), 97.7(1), 96.3(1)	83.3(1)	83.6(1)
$\angle(\text{ZnN}_2, \text{ZnN}_2)$			82.0(1)	85.0(1)

## 2.2. Polymerisation Activity

The complexes **1a** to **1c** and **2a** to **2c**, as well as the ligands **1** and **2** were tested for their ability to initiate the ring-opening polymerisation of D,L-lactide. For preliminary polymerisation tests the monomer (used without further purification) and the initiator (I/M ratio 1:500) were heated for 24 h or 48 h at 150 °C. After the reaction time, the melt was dissolved in dichloromethane, and the PLA was precipitated in cold ethanol, isolated and dried under vacuum at 50 °C. In order to rate the catalytic activity of the complexes, the polymer yield was determined and the molecular weights as well as the polydispersity of the PLA were determined by gel permeation chromatography (see Table 2). The tacticity was analysed by homonuclear decoupled  $^1\text{H}$  NMR spectroscopy [41].

We found that the pure ligands as well as the chloride complexes show even after 48 h no catalytic activity whereas the zinc acetato and zinc triflato complexes possess the ability to produce PLA. Due to the fact that the acetate containing complexes provide polymers with significantly higher molecular weights and higher yields as their triflate containing analogues, it is obvious that the catalytic activity strongly depends on the character of the anionic component of the zinc complex. We reported this strong dependence in previous studies by using bis-chelated zinc guanidine complexes [22]. In addition, the complexes stabilised by **1** exhibit a higher activity as those stabilised with **2**. The extension of reaction time from 24 to 48 h leads in the case of **1c** and **2c** to an increase of yield and molecular weight, whereas in polymerisations initiated with **1b** and **2b** a decrease of molecular weight can be observed which may be caused by side reactions such as interchain or intrachain transesterification resulting in a chain-transfer reaction [42, 43]. It is also remarkable that the molecular weights of the polymers obtained by utilising **1c** and **2c** were significantly high in relation to the obtained yield. These PLA samples also show with  $P_r$  values of 0.59 and 0.61 a slight heterotactic enchainment whereas the values of samples obtained using **1b** and **2b** (0.50) imply that the complex structure shows no ability to affect the tacticity of the formed polymer.

**Table 2.** Polymerisation of D,L-lactide in the presence of bipy, phen and their corresponding zinc complexes.

Initiator		Time <sup>d</sup> [h]	Yield [%]	M <sub>w</sub> [g/mol]	PD <sup>b</sup>	P <sub>r</sub> <sup>c</sup>
bipy	<b>1</b>	48	0	-	-	-
[Zn(bipy)Cl <sub>2</sub> ]	<b>1a</b>	48	0	-	-	-
[Zn <sub>3</sub> (bipy) <sub>2</sub> (CH <sub>3</sub> COO) <sub>6</sub> ]	<b>1b</b>	24	95	80,000	1.8	0.50
[Zn <sub>3</sub> (bipy) <sub>2</sub> (CH <sub>3</sub> COO) <sub>6</sub> ]	<b>1b</b>	48	93	68,000	1.7	-
[Zn(bipy) <sub>2</sub> (CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> ]	<b>1c</b>	24	12	75,000	1.6	-
[Zn(bipy) <sub>2</sub> (CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> ]	<b>1c</b>	48	57	145,000	1.9	0.59
phen	<b>2</b>	48	0	-	-	-
[Zn(phen)Cl <sub>2</sub> ]	<b>2a</b>	48	0	-	-	-
[Zn <sub>2</sub> (phen) <sub>2</sub> (CH <sub>3</sub> COO) <sub>4</sub> ]	<b>2b</b>	24	94	56,000	1.7	0.50
[Zn <sub>2</sub> (phen) <sub>2</sub> (CH <sub>3</sub> COO) <sub>4</sub> ]	<b>2b</b>	48	89	45,000	1.9	-
[Zn(phen) <sub>2</sub> (CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> ]	<b>2c</b>	24	0	-	-	-
[Zn(phen) <sub>2</sub> (CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> ]	<b>2c</b>	48	21	87,000	2.0	0.61

<sup>a</sup> Reaction conditions: Catalyst (0.2 mol%), 150°C; <sup>b</sup> PD = M<sub>w</sub>/M<sub>n</sub> where M<sub>n</sub> is the number-average molar mass;

<sup>c</sup> From analysis of the <sup>1</sup>H homonuclear decoupled NMR spectrum using the equation P<sub>r</sub><sup>2</sup> = 2 [sis];[41] <sup>d</sup> reaction times were not necessarily optimised.

In order to classify the polymerisation activity of **1a**, **2a**, **1b**, **2b**, **1c** and **2c** their results are compared to those of the free salts and guanidine-pyridine zinc complexes that were tested under the same conditions [22]. Since ZnCl<sub>2</sub> gives after 48 h PLAs with M<sub>w</sub> values of 45,000 g/mol in yields of 85%, whereas the chlorido complexes **1a** and **2a** show no ability to catalyse the ROP of lactide, the possibility that the complexes decompose in the melt and the single components are the real initiators can be excluded. The reversed effect can be observed in the case of Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> and **1c** and **2c**. Whereas **1c** and **2c** are quite active, the free zinc salt did not show any catalytic performance. Zn(CH<sub>3</sub>COO)<sub>2</sub> is well known to initiate lactide polymerisation, but under the same conditions, it shows less catalytic activity than **1b** and **2b** and a broader distribution (t = 24 h, Y = 69%, M<sub>w</sub> = 130,000 g/mol, PD = 2.1). In comparison to the most active guanidine-pyridine zinc triflate complex (t = 24 h, Y = 93%, M<sub>w</sub> = 155,000 g/mol, PD = 2.2) out of a recently tested series of guanidine-pyridine zinc complexes, **1c** and **2c** show less catalytic activity whereas **1b** and **2b** provide a comparable activity. In addition their M<sub>w</sub> values that lie close to the expected values (based on the monomer to initiator ratio) and the relatively narrow distribution of molecular weight indicate a more controlled reaction.

These preliminary investigations using complexes stabilised by the neutral bis-chelating ligands, 2,2'-bipyridine and 1,10-phenanthroline, show that they provide PLAs with high yields or with high molecular weights. This together with their commercial availability, their high stability which makes them easy to handle and their favourable donor properties clearly demonstrate that they are a promising neutral ligand class for the development of single-site metal catalysts for the ROP of lactide.

### 3. Conclusions

In this contribution we reported on the synthesis and complete characterisation of four novel zinc complexes stabilised by the neutral bis-chelating ligands, 2,2'-bipyridine and 1,10-phenanthroline, that were proven to be active initiators in the solvent-free ring-opening polymerisation of D,L-lactide. They provide PLAs in almost quantitative yields or with high molecular weights up to 145,000 g/mol. This combined with commercial availability, high robustness resulting in an easy handling and favourable donor properties demonstrate the high potential of this neutral ligand class for the development of excellent and application-oriented single-site metal catalysts for the ROP of lactide. Optimisation of the reaction conditions to control the polymerisation process and the elucidation of the mechanism which is active without the presence of alcohols and alkoxides, as well as the development of more active catalysts are conducted in further studies.

### 4. Experimental Section

#### 4.1. Material and Methods

##### General Remarks

All manipulations were performed under pure dinitrogen (99.996%) or argon (99.996%) dried with P<sub>4</sub>O<sub>10</sub> granulate using Schlenk techniques or a glovebox. Solvents were dried and purified according to literature procedures[44] and also kept under inert gas. Zinc chloride (99.99%, Acros), zinc acetate (99.99%, Acros), zinc trifluoromethanesulfonate (98%, Aldrich), D,L-lactide (3,6-Dimethyl-1,4-dioxane-2,5-dione, Purac), 2,2'-bipyridine (Aldrich) and 1,10-phenanthroline (Aldrich) were used as purchased. The zinc complexes **1a** [39] and **2a** [40] were prepared according to literature procedures.

#### 4.2. Physical Measurements

Spectra were recorded with the following spectrometers: NMR: Bruker Avance 500. The NMR signals were calibrated to the residual signals of the deuterated solvents ( $\delta_H$  (CDCl<sub>3</sub>) = 7.26 ppm,  $\delta_H$ (CD<sub>3</sub>CN) = 1.94 ppm). Samples for homonuclear decoupling were prepared by dissolving 10 mg of the polymer in 1 mL of CDCl<sub>3</sub> (Aldrich) and the samples were left for 2 hours to ensure full dissolution [45]. The <sup>1</sup>H homonuclear decoupled spectra were recorded on a Bruker Avance 400 MHz spectrometer and referenced to residual solvent peaks. The parameter P<sub>r</sub> (probability of heterotactic enchainment) was determined via analysis of the respective integrals of the tetrads, using P<sub>r</sub><sup>2</sup> = 2 [sis]. For the NMR analysis of the respective integrals of the tetrads [sis], see the work of Coates *et al.* [41] IR: Nicolet P510. - MS (EI, 70 eV): Finnigan MAT 95. -Elemental analyses: elemental vario MICRO cube, device CHNS-932 from Leco Instruments. **Crystal structure analyses:** Crystal data for the crystal structures **1b**, **2b**, **1c** and **2c** are presented in Table 3. Data were collected on a Bruker-AXS SMART [46] APEX CCD, using MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å) and a graphite monochromator. Data reduction and absorption correction were performed with SAINT and SADABS [46]. The structures were solved by direct and conventional Fourier methods, and all non-hydrogen atoms refined



anisotropically by full-matrix least-squares techniques based on  $F^2$  (SHELXTL [46]). Hydrogen atoms were derived from difference Fourier maps and placed at idealised positions, riding on their parent C atoms, with isotropic displacement parameters  $U_{iso}(H) = 1.2U_{eq}(C)$  and  $1.5U_{eq}(C_{methyl})$ . All methyl groups were allowed to rotate but not to tip. Full crystallographic data (excluding structure factors) for **1b**, **2b**, **1c** and **2c** have been deposited with the Cambridge Crystallographic Data Centre as supplementary no. CCDC-752689 (**1b**), CCDC-752690 (**2b**), CCDC-752691 (**1c**) and CCDC-752692 (**2c**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

**Table 3.** Crystallographic data for the compounds **1b**, **2b**, **1c** and **2c**.

	<b>1b</b>	<b>2b</b>	<b>1c</b>	<b>2c</b>
Empirical formula	C <sub>32</sub> H <sub>34</sub> N <sub>4</sub> O <sub>12</sub> Zn <sub>3</sub>	C <sub>32</sub> H <sub>28</sub> N <sub>4</sub> O <sub>8</sub> Zn <sub>2</sub>	C <sub>22</sub> H <sub>16</sub> F <sub>6</sub> N <sub>4</sub> O <sub>6</sub> S <sub>2</sub> Zn	C <sub>26</sub> H <sub>16</sub> F <sub>6</sub> N <sub>4</sub> O <sub>6</sub> S <sub>2</sub> Zn
Molecular mass	862.74	727.32	675.88	723.92
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P $\bar{1}$	P2 <sub>1</sub> /n	C2/c	C2/c
a / Å	8.0702(19)	11.296(5)	9.9580(14)	9.7694(14)
b / Å	9.651(2)	19.857(8)	14.126(2)	14.309(2)
c / Å	12.668(3)	13.535(6)	18.672(3)	19.609(3)
$\alpha / ^\circ$	105.050(4)			
$\beta / ^\circ$	98.355(4)	106.945(8)	101.468(3)	95.235(3)
$\gamma / ^\circ$	108.854(4)			
V / Å <sup>3</sup>	872.9(3)	2904(2)	2574.1(6)	2729.7(7)
Z	1	4	4	4
D <sub>calc</sub> / g cm <sup>-3</sup>	1.641	1.663	1.744	1.762
$\mu$ / mm <sup>-1</sup>	2.112	1.714	1.207	1.145
Temperature / K	120(2)	120(2)	120(2)	120(2)
$\Theta_{max}$ /	1.72 to 27.87	1.88 to 27.88	2.23 to 27.88	2.09 to 27.87
Reflections collected	7570	25283	11017	11816
Independent reflections	4113	6913	3076	3265
R1 [ $I \geq 2\sigma(I)$ ]	0.0276	0.042	0.026	0.026
wR2 (all data)	0.0834	0.1033	0.0714	0.0723
Largest diff. peak, hole / e Å <sup>-3</sup>	0.433 and -0.464	0.901 and -0.951	0.455 and -0.257	0.436 and -0.332

**Gel permeation chromatography:** The molecular weight and molecular weight distribution of obtained polylactide samples were determined by gel permeation chromatography (GPC) in THF as mobile phase at a flow rate of 1 mL/min. A combination of PSS SDV columns with porosities of 10<sup>5</sup> and 10<sup>3</sup> Å was used together with a HPLC pump (L6200, Merck Hitachi) and a refractive index detector (Smartline RI Detector 2300, Knauer). THF was used as mobile phase at a flow rate of 1 mLmin<sup>-1</sup>. Universal calibration was applied to evaluate the chromatographic results. Kuhn-Mark-Houwink (KMH) parameters for the polystyrene standards ( $K_{PS} = 0.011 \text{ mLg}^{-1}$ ,  $\alpha_{PS} = 0.725$ ) were taken from literature [47]. Previous GPC measurements utilizing online viscosimetry detection revealed the KMH parameters for polylactide ( $K_{PLA} = 0.053 \text{ mLg}^{-1}$ ,  $\alpha_{PLA} = 0.610$ ) [22].

#### 4.3. Preparation of Compounds

**[Zn<sub>3</sub>(bipy)<sub>2</sub>(CH<sub>3</sub>COO)<sub>6</sub>] (1b):** To a suspension of 0.5 mmol of zinc(II) acetate in dry THF, a solution of the ligand **1** (0.55 mmol) in THF was added under stirring. The resulting reaction mixture was stirred for 20 minutes. Due to the precipitation of the corresponding complex, the reaction mixture

was slowly heated under reflux. Dry MeCN was added to give a clear colourless solution. Colourless crystals suitable for X-ray diffraction could be obtained by slowly cooling to room temperature. **C<sub>32</sub>H<sub>34</sub>N<sub>4</sub>O<sub>12</sub>Zn<sub>3</sub>** (M = 862.80 g/mol): Colourless crystals; **Yield:** 0.280 g = 0.32 mmol = 97%; **m.p.** 168 °C. **<sup>1</sup>H-NMR** (500 MHz, CD<sub>3</sub>CN, 25 °C): δ [ppm] = 1.95 (s, 18H, CH<sub>3</sub>), 7.75 (m, 4H, CH), 8.24 (m, 4H, CH), 8.43 (m, 4H, CH), 8.85 (m, 4H, CH). **<sup>13</sup>C-NMR** (125 MHz, CD<sub>3</sub>CN, 25 °C): δ [ppm] = 21.6 (CH<sub>3</sub>), 122.0 (CH), 126.9 (CH), 141.3 (CH), 148.9 (C), 149.2 (CH), 179.4 (C). **IR** (KBr,  $\tilde{\nu}$ [cm<sup>-1</sup>]): 3103 m ( $\nu$ (C-H<sub>arom.</sub>)), 3089 m ( $\nu$ (C-H<sub>arom.</sub>)), 3066 m ( $\nu$ (C-H<sub>arom.</sub>)), 3033 m ( $\nu$ (C-H<sub>arom.</sub>)), 3008 m ( $\nu$ (C-H<sub>arom.</sub>)), 2927 w ( $\nu$ (C-H<sub>aliph.</sub>)), 2852 w ( $\nu$ (C-H<sub>aliph.</sub>)), 1599 vs ( $\nu$ (C-O)), 1577 s ( $\nu$ (C-O)), 1493 m, 1473 m, 1446 s, 1425 m, 1338 m, 1313 m, 1286 w, 1254 w, 1223 vw, 1161 w, 1109 w, 1061 m, 1028 m, 1018 m, 972 vw, 941 w, 904 vw, 773 m, 735 m, 692 m, 677 m, 658 m, 634 m, 649 m. **EI-MS** (m/z, (%)): 571 (70), 469 (4), 389 (18), 256 (6), 156 (100) [C<sub>10</sub>H<sub>8</sub>N<sub>2</sub><sup>+</sup>], 128 (18), 78 (14), 51 (12). **CHN analysis:** calculated: C 44.51, H 3.94, N 6.49; found: C 44.53, H 4.00, N 6.50.

**[Zn(bipy)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>] (1c):** A suspension of zinc triflate (1 mol) and ligand **1** in dry THF was stirred for 20 min and then heated under reflux. Dry MeCN was added to give a clear colourless solution which was slowly cooled to room temperature affording colourless crystals suitable for X-ray diffraction. **C<sub>22</sub>H<sub>16</sub>F<sub>6</sub>N<sub>4</sub>O<sub>6</sub>S<sub>2</sub>Zn** (M = 676.99 g/mol): Colourless crystals; **Yield:** 0.300 g = 0.44 mmol = 88%; **m.p.** 291 °C. **<sup>1</sup>H-NMR** (500 MHz, CD<sub>3</sub>CN, 25 °C): δ [ppm] = 7.74 (m, 4H, CH), 8.32 (m, 4H, CH), 8.46 (m, 4H, CH), 8.57 (m, 4H, CH). **<sup>13</sup>C-NMR** (125 MHz, CD<sub>3</sub>CN, 25 °C): δ [ppm] = 122.1 (C), 122.9 (CH), 127.3 (CH), 141.8 (CH), 148.1 (CH), 148.9 (C). **IR** (KBr,  $\tilde{\nu}$ [cm<sup>-1</sup>]): 3114 w ( $\nu$ (C-H<sub>arom.</sub>)), 3097 w ( $\nu$ (C-H<sub>arom.</sub>)), 3086 w ( $\nu$ (C-H<sub>arom.</sub>)), 3074 w ( $\nu$ (C-H<sub>arom.</sub>)), 1610 m, 1601 m, 1579 m, 1568 w, 1493 m, 1477 m, 1446 m, 1306 vs, 1246 s, 1234 vs, 1219 s, 1176 m, 1161 s, 1120 w, 1107 w, 1063 w, 1026 vs, 980 vw, 904 vw, 895 vw, 818 vw, 771 s, 739 m, 654 m, 636 s, 580 w, 573 w, 517 m. **EI-MS** (m/z, (%)): 376 (2) [M<sup>+</sup> -2 CF<sub>3</sub>SO<sub>3</sub>], 373 (29), 371 (44), 369 (69), 348 (14), 346 (13), 243 (19), 241 (30), 239 (53), 157 (15), 156 (100) [C<sub>10</sub>H<sub>8</sub>N<sub>2</sub><sup>+</sup>], 155 (66), 130 (12), 129 (29), 128 (37), 78 (36) [C<sub>5</sub>H<sub>4</sub>N<sup>+</sup>], 52 (15), 51 (31), 50 (15). **CHN analysis:** calculated: C 39.0, H 2.4, N 8.3; found: C 39.0, H 2.6, N 8.2.

**[Zn<sub>2</sub>(phen)<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub>] (2b):** To a suspension of 0.5 mmol of zinc(II) acetate in dry THF, a solution of the ligand **2** (0.55 mmol) in THF was added under stirring. The resulting reaction mixture was stirred for 20 minutes. Due to the precipitation of the corresponding complex, the reaction mixture was slowly heated under reflux. Dry MeCN was added to give a clear colourless solution. Colourless crystals suitable for X-ray diffraction could be obtained by slowly cooling to room temperature. **C<sub>32</sub>H<sub>28</sub>N<sub>4</sub>O<sub>8</sub>Zn<sub>2</sub>** (M = 727.37 g/mol): Colourless crystals; **Yield:** 0.360 g = 0.49 mmol = 98%; **m.p.** 248 °C. **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>, 25 °C): δ [ppm] = 2.05 (s, 12H, CH<sub>3</sub>), 7.90 (dd, 4H, CH, <sup>3</sup>J = 4.7 Hz, <sup>3</sup>J = 8.2 Hz), 7.97 (s, 4H, CH), 8.52 (dd, 4H, CH, <sup>3</sup>J = 8.2 Hz, <sup>4</sup>J = 1.5 Hz), 9.31 (dd, 4H, CH, <sup>3</sup>J = 4.7 Hz, <sup>4</sup>J = 1.5 Hz). **<sup>13</sup>C-NMR** (125 MHz, CDCl<sub>3</sub>, 25 °C): δ [ppm] = 21.7 (CH<sub>3</sub>), 125.4 (CH), 126.8 (CH), 128.7 (C), 139.0 (CH), 141.1 (C), 150.4 (CH), 181.3 (C). **IR** (KBr,  $\tilde{\nu}$ [cm<sup>-1</sup>]): 3064 w ( $\nu$ (C-H<sub>arom.</sub>)), 3014 w ( $\nu$ (C-H<sub>arom.</sub>)), 2927 w ( $\nu$ (C-H<sub>aliph.</sub>)), 1599 s ( $\nu$ (C-O)), 1585 s ( $\nu$ (C-O)), 1516 m, 1495 w, 1425 m, 1387 m, 1333 m, 1257 vw, 1217 vw, 1140 m, 1101 w, 1049 vw, 1016 w, 937 vw, 924 vw, 868 w, 854 m, 783 vw, 729 m, 679 w, 667 w, 640 w, 623 vw. **EI-MS** (m/z, (%)): 577 (37), 575 (70),

573 (84), 571 (88), 569 (54), 393 (27), 391 (52), 389 (72), 387 (62), 385 (33), 197 (16), 194 (71), 183 (39), 180 (100) [ $C_{12}H_8N_2^+$ ], 179 (51), 154 (27). **CHN analysis:** calculated: C 52.79, H 3.85, N 7.70; found: C 52.62, H 3.83, N 7.72.

**[Zn(phen)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>] (2c):** To a suspension of 0.5 mmol of zinc(II) triflate in dry MeCN, a solution of the ligand **2** (0.55 mmol) in MeCN was added under stirring. The resulting reaction mixture was stirred for 20 minutes to give a clear solution, from which colourless crystals were obtained by diffusion of diethyl ether. **C<sub>26</sub>H<sub>16</sub>F<sub>6</sub>N<sub>4</sub>O<sub>6</sub>S<sub>2</sub>Zn** (M = 725.11 g/mol): Colourless crystals; **Yield:** 0.390 g = 0.54 mmol = 98%; **m.p.** > 300 °C. **<sup>1</sup>H-NMR** (500 MHz, CD<sub>3</sub>CN, 25 °C): δ [ppm] = 8.01 (dd, 4H, CH, <sup>3</sup>J = 4.7 Hz, <sup>3</sup>J = 8.2 Hz), 8.27 (s, 4H, CH), 8.79 (dd, 4H, CH, <sup>3</sup>J = 4.7 Hz, <sup>4</sup>J = 1.3 Hz), 8.85 (dd, 4H, CH, <sup>3</sup>J = 8.3 Hz, <sup>4</sup>J = 1.3 Hz). **<sup>13</sup>C-NMR** (125 MHz, CD<sub>3</sub>CN, 25 °C): δ [ppm] = 122.1 (C), 125.8 (CH), 127.5 (CH), 129.7 (C), 140.4 (C), 140.5 (CH), 148.8 (CH). **IR** (KBr,  $\tilde{\nu}$ [cm<sup>-1</sup>]): 3084 w ( $\nu$ (C-H<sub>arom.</sub>)), 3068 w ( $\nu$ (C-H<sub>arom.</sub>)), 1628 w, 1608 w, 1585 w, 1522 m, 1496 w, 1431 m, 1346 w, 1300 s, 1284 m, 1259 m, 1246 m, 1343 m, 1221 m, 1213 m, 1178 m, 1165 m, 1107 w, 1024 m, 999 w, 968 vw, 870 w, 850 m, 787 w, 758 vw, 729 m, 636 m, 580 w, 573 w, 516 m. **EI-MS** (m/z, (%)): 577 (6)M<sup>+</sup>-CF<sub>3</sub>SO<sub>3</sub>, 496 (6), 467 (10), 439 (19), 410 (12), 386 (16), 368 (10), 344 (22), 331 (26), 312 (16), 293 (26), 264 (13), 257 (17), 248 (18), 239 (21), 215 (25), 183 (33) [N<sub>2</sub>C<sub>12</sub>H<sub>8</sub><sup>+</sup> + 2H], 125 (22), 111 (36), 107 (36), 97 (57), 96 (43), 85 (42), 83 (58), 81 (44), 71 (59), 69 (68), 57 (100), 55 (77). **CHN analysis:** calculated: C 43.0, H 2.2, N 7.7; found: C 42.6, H 2.3, N 7.7.

#### 4.4. General Procedure for the Melt Polymerisation of D,L-lactide

D,L-Lactide (3,6-dimethyl-1,4-dioxane-2,5-dione, 3.603 g, 25 mmol) and the initiator (I/M ratio 1/500, calculated relative to the zinc centres) were weighed into a 50 mL flask, which was flushed with argon and closed with a glass stopper. The reaction vessel was then heated at 150 °C. After the reaction time the polymer melt was allowed to cool to room temperature and then was dissolved in 25 mL of dichloromethane. The PLA was precipitated in 350 mL of ice-cooled ethanol and dried in vacuo at 50 °C.

#### Acknowledgements

Financial support by the Fonds der Chemischen Industrie and by the Universität Paderborn (fellowships for S.H.-P.) is gratefully acknowledged. J.B. thanks the Stiftung der Deutschen Wirtschaft sdw for granting a doctoral fellowship. Furthermore, S.H.-P. thanks G. Henkel and K. Jurkschat for their valuable support.

#### References

1. *Biopolymers—Polyesters II Properties and Chemical Synthesis*; Doi, Y., Steinbüchel, A., Eds.; Wiley-VCH: Weinheim, Germany, 2002.
2. *Biopolymers—Polyesters III Application and Commercial Products*; Doi, Y., Steinbüchel, A., Eds.; Wiley-VCH: Weinheim, Germany, 2002.
3. Jacobsen, S.; Degee, P.; Fritz, H.; Dubois, P.; Jerome, R. Polylactide (PLA)—A new way of

- production. *Polym. Eng. Sci.* **1999**, *39*, 1311–1319.
4. Vert, M. Aliphatic polyesters: Great degradable polymers that cannot do everything. *Biomacromolecules* **2005**, *6*, 538–546.
  5. Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. Controlled ring-opening polymerization of lactide and glycolide. *Chem. Rev.* **2004**, *104*, 6147–6176.
  6. Wolf, O.; Crank, M.; Patel, M.; Marscheider-Weidemann, F.; Schleich, J.; Hsing, B.; Angerer, G. *Techno-economic Feasibility of Large-scale Production of Bio-based Polymers in Europe*; Technical Report No. EUR 22103 EN, European Commission: Brussels, Belgium, 2005.
  7. Kricheldorf, H. Syntheses and application of polylactides. *Chemosphere* **2001**, *43*, 49–54.
  8. Anastas, P.T.; Warner, J.C. *Green Chemistry: Theory and Practice*; Oxford University Press: New York, NY, USA, 1998.
  9. Anastas, P.; Zimmerman, J. Peer reviewed: Design through the 12 principles of green engineering. *Environ. Sci. Technol.* **2003**, *37*, 94–101.
  10. *Natural Fibres, Biopolymers, and Biocomposites*; Mohanty, A., Misra, M., Drzal, L., Eds.; CRC Press: New York, NY, USA, 2005.
  11. Gupta, A.; Kumar, V. New emerging trends in synthetic biodegradable polymers–Polylactide: A critique. *Europ. Polym. J.* **2007**, *43*, 4053–4074.
  12. Mehta, R.; Kumar, V.; Bhunia, H.; Upadhyay, S. Synthesis of poly(lactic acid): A review. *J. Macromol. Sci.-Pol. R.* **2005**, *C45*, 325–349.
  13. Garlotta, D. A literature review of poly(lactic acid). *J. Polym. Environ.* **2001**, *9*, 63–84.
  14. Platel, R.; Hodgson, L.; Williams, C. Biocompatible initiators for lactide polymerization *Polym. Rev.* **2008**, *48*, 11–63.
  15. Chmura, A.J.; Cousins, D.M.; Davidson, M.G.; Jones, M.D.; Lunn, M.D.; Mahon, M.F. Robust chiral zirconium alkoxide initiators for the room-temperature stereoselective ring-opening polymerisation of rac-lactide. *Dalton Trans.* **2008**, doi: 10.1039/b716304e.
  16. Vink, E.; Rabago, K.; Glassner, D.; Springs, B.; O'Connor, R.; Kolstad, J.; Gruber, P. The sustainability of NatureWorks<sup>TM</sup> polylactide polymers and Ingeo<sup>TM</sup> polylactide fibers: An update of the future. *Macromol. Biosci.* **2004**, *4*, 551–564.
  17. Sakai, K.; Taniguchi, M.; Miura, S.; Ohara, H.; Masumoto, T.; Shirai, Y. Making plastics from garbage: A novel process for Poly-L-Lactate production from municipal food waste. *J. Indust. Ecol.* **2004**, *7*, 63–74.
  18. O'Keefe, B.; Hillmyer, M.; Tolman, W. Polymerization of lactide and related cyclic esters by discrete metal complexes. *J. Chem. Soc. Dalton Trans.* **2001**, doi: 10.1039/b104197.
  19. Wheaton, C.; Hayes, P.; Ireland, B. Complexes of Mg, Ca and Zn as homogeneous catalysts for lactide polymerization. *Dalton Trans.* **2009**, *25*, 4832–4846.
  20. Wu, J.; Yu, T.; Chen, C.; Lin, C. Recent developments in main group metal complexes catalyzed/initiated polymerization of lactides and related cyclic esters. *Coordin. Chem. Rev.* **2006**, *250*, 602–626.
  21. Kamber, N.E.; Jeong, W.; Waymouth, R.M.; Pratt, R.C.; Lohmeijer, B.G.G.; Hedrick, J.L. Organocatalytic ring-opening polymerization. *Chem. Rev.* **2007**, *107*, 5813–5840.
  22. Börner, J.; Flörke, U.; Huber, K.; Döring, A.; Kuckling, D.; Herres-Pawlis, S. Lactide

- polymerisation with air-stable and highly active zinc complexes with guanidine-pyridine hybrid ligands. *Chem.-Eur. J.* **2009**, *15*, 2362–2376.
23. Börner, J.; Herres-Pawlis, S.; Flörke, U.; Huber, K. [Bis(guanidine)]zinc complexes and their application in lactide polymerisation. *Eur. J. Inorg. Chem.* **2007**, *36*, 5645–5651.
  24. Wheaton, C.A.; Ireland, B.J.; Hayes, P.G. Activated zinc complexes supported by a neutral, phosphinimine-containing ligand: Synthesis and efficacy for the polymerization of lactide. *Organometallics* **2009**, *28*, 1282–1285.
  25. Börner, J.; Flörke, U.; Glöge, T.; Bannenberg, T.; Tamm, M.; Jones, M.D.; Döring, A.; Kuckling, D.; Herres-Pawlis, S. New insights into the lactide polymerisation with neutral n donor stabilised zinc complexes: Comparison of Imidazolin-2-Imine vs. Guanidine complexes. *J. Mol. Cat.* **2009**, (accepted).
  26. Wissing, E.; Kaupp, M.; Boersma, J.; Spek, A.L.; van Koten, G. Alkylation reactions of dialkylzinc compounds with 1,4-diaza-1,3-butadienes: Cationic and radical anionic organozinc intermediates. Molecular structure of the cationic organozinc species [MeZn(tert-BuN:CHCH:N-tert-Bu)]O<sub>3</sub>SCF<sub>3</sub> and Me<sub>2</sub>Zn(bpy) (bpy = 2,2'-Bipyridine). *Organometallics* **1994**, *13*, 2349–2356.
  27. Rodrigues, B. Acetatobis (2, 2'-bipyridyl) zinc (II) hexafluorophosphate monohydrate. *Acta Crystallogr. E* **2004**, *60*, m1169–m1171.
  28. Cao, F.; Shen, Y.; Kan, Z. Bis(benzoato-κ<sup>2</sup>O,O')(2,2'-bipyridyl-κ<sup>2</sup>N,N')zinc(II). *Acta Crystallogr. E* **2006**, *62*, m2955–m2956.
  29. Chen, X.; Wang, R.; Yu, X. Tris(2,2'-bipyridine)zinc(II) perchlorate. *Acta Crystallogr. C* **1995**, *51*, 1545–1547.
  30. Chen, X.; Xu, Z.; Yu, X.; Mak, T. Preparation and Crystal-Structures of Bis(O-phenanthroline)-(acetato)zinc(II) perchlorate and Bis(2,2'-bipyridine)(pyridinioacetato)zinc(II) diperchlorate. *Polyhedron* **1994**, *13*, 2079–2083.
  31. Covelo, B.; Carballo, R.; Vazquez-Lopez, E.; Garcia-Martinez, E.; Castineiras, A.; Balboa, S.; Niclos, J. Supramolecular architectures of neutral and cationic complexes of transition metals with lactate and 1,10-phenanthroline. *Cryst. Eng. Comm.* **2006**, *8*, 167–177.
  32. Erras-Hanauer, H.; Mao, Z.; Liehr, G.; Clark, T.; van Eldik, R. Structures of carbonato and bicarbonato complexes of bis(1,10-phenanthroline)zinc(II): Experiment and theory. *Eur. J. Inorg. Chem.* **2003**, *2003*, 1562–1569.
  33. Zhu, Y.; Zhong, K.; Lu, W. Bis(1,10-phenanthroline-κ<sup>2</sup>N,N')(sulfato-κ<sup>2</sup>O,O')-zinc(II) 1,2-ethenediol solvate. *Acta Crystallogr. E* **2006**, *62*, m2725–m2726.
  34. Rodrigues, B. Acetatobis (1, 10-phenanthroline) zinc (II) tetrafluoroborate. *Acta Crystallogr. E* **2004**, *60*, m1166–m1168.
  35. Fu, X.; Li, M.; Wang, C.; Wang, X. Diaquamalonato(1,10-phenanthro-line)zinc(II). *Acta Crystallogr. C* **2006**, *62*, m13–m15.
  36. Fu, X.; Wang, X.; Li, M.; Wang, C. Dibenzoato(1,10-phenanthroline)zinc(II). *Acta Crystallogr. E* **2006**, *62*, m773–m775.

37. Fitzgerald, W.; Hathaway, B.; Simmons, C.J. The crystal structure and electronic properties of the complexes acetatobis(1,10-phenanthroline)copper(II) perchlorate dihydrate, acetatobis(1,10-phenanthroline)copper(II) nitrate dihydrate, and acetatobis(1,10-phenanthroline)zinc(II) tetrafluoroborate dihydrate. *J. Chem. Soc., Dalton Trans.* **1985**, *1*, 141–149.
38. Yu, C.H.; Zhang, R.C. Chlorobis(1,10-phenanthroline- $[\kappa]^2N,N'$ )zinc(II) nitrate monohydrate. *Acta Crystallogr. E* **2006**, *62*, m1758–m1759.
39. Khan, M.; Tuck, D. The structure of (2,2'-bipyridine)dichlorozinc(II),  $Zn(C_{10}H_8N_2)Cl_2$ . *Acta Crystallogr. C* **1984**, *40*, 60–62.
40. Reimann, C.; Block, S.; Perloff, A. Crystal and molecular structure of dichloro(1,10-phenanthroline)zinc. *Inorg. Chem.* **1966**, *5*, 1185–1189.
41. Chamberlain, B.M.; Cheng, M.; Moore, D.R.; Ovitt, T.M.; Lobkovsky, E.B.; Coates, G.W. Polymerization of Lactide with zinc and magnesium  $\beta$ -diiminate complexes: Stereocontrol and mechanism. *J. Am. Chem. Soc.* **2001**, *123*, 3229–3238.
42. Schwach, G.; Coudane, J.; Engel, R.; Vert, M. Stannous octoate-initiated versus zinc-initiated polymerization of racemic lactide—effects on configurational structures. *Polym. Bull.* **1994**, *32*, 617–623.
43. Chisholm, M.; Gallucci, J.; Yin, H. Cyclic esters and cyclodepsipeptides derived from lactide and 2, 5-morpholinediones. *Proc. Natl. Acad. Sci.* **2006**, *103*, 15315–15320.
44. Leonard, J.; Lygo, B.; Procter, G. *Praxis der Organischen Chemie*; VCH Weinheim, Germany, 1996.
45. Zell, M.; Padden, B.; Paterick, A.; Thakur, K.; Kean, R.; Hillmyer, M.; Munson, E. Unambiguous determination of the  $^{13}C$  and  $^1H$  NMR stereosequence assignments of polylactide using high-resolution solution NMR spectroscopy. *Macromolecules* **2002**, *35*, 7700–7707.
46. Bruker, SMART (Version 5.62), SAINT (Version 6.02), SHELXTL (Version 6.10) and SADABS (Version 2.03); Bruker AXS: Madison, WI, USA, 2002.
47. Mark, J.E., Ed. *Polymer Data Handbook*; Oxford University Press: Oxford, UK, 1999.