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Synthesis, structures and catalytic activity of homo- and heteroleptic ketoiminate zinc complexes in lactide polymerization

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Dedicated to Prof. Dr. K. Jurkschat on the occasion of his retirement.

Abstract: The heteroleptic complex LZnEt (L = MeNacac = MeNC(Me)CHC(Me)O **1**) containing the sterically less demanding N,O-chelating ketoiminate (MeNacac) ligand was synthesized by reaction of ZnEt₂ with an equimolar amount of MeNacacH, whereas the reaction with two equivalents MeNacacH gave the homoleptic complex L₂Zn **5**. **1** reacts with ArOH (Ar = 2,6-Me₂-Ph) with ethane elimination and formation of LZnOAr (**2**). Addition of the Lewis base dmap (dmap = 4-dimethylamino pyridine) to **1** and **2** yielded the corresponding Lewis acid-base adducts dmap-Zn(L)Et **3** and dmap-Zn(L)OAr **4**. **1** - **5** were characterized by heteronuclear NMR and IR spectroscopy, elemental analysis and single crystal X-ray diffraction (**1** - **3**, **5**). Their technical application as catalysts in ring-opening polymerization (ROP) of *rac*-lactide in a CD₂Cl₂ solution at ambient temperature was investigated. **2** and **3** show the highest activities, whereas those of **1** and **5** are substantially lower. **2** and **3** polymerize *rac*-lactide (90 % conversion) within 140 (**3**) and 180 minutes (**2**), respectively. In contrast, **4** could only be investigated in bulk polymerization reactions due to its very poor solubility in common organic solvents. These studies proved that **4** is active in bulk polymerization, converting 93 % lactide to PLA at 140 °C within 20 minutes.

Introduction

In times of fast growing humankind and resource scarcity, mineral oil-based plastics become more and more unattractive. Although common plastics are economically preferred,^[1] polymers based on natural feedstock such as poly(lactide) (PLA) have the enormous advantage of biodegradability. Therefore, PLA is very attractive to the packaging industry and makes it also suitable for medical applications such as wound dressings, stents and tissue

of PLA is Sn(Oct)₂. Sn(Oct)₂ possesses the FDA approval but its toxicity for cells has definitively been proven.^[3] Since the complete extraction of residual tin from the polymer is rather impossible, there is a strong demand for alternative metal-based catalysts.^[4] In recent years, several groups reported on metal complexes based on *s*-block,^[5] *p*-block,^[6] *d*-block,^[7] and *f*-block metals,^[8] respectively, which have been found active in ring-opening polymerization (ROP) of lactide.^[9] Among these, zinc complexes have received particular attention since they have shown outstanding catalytic performances in melt processes and in solution-based processes.^[10] So far, several heteroleptic zinc complexes LZnX containing monoanionic alkyl,^[11] alkoxy,^[12] halide,^[13] and amide substituents (X)^[14] were successfully tested in ROP of lactide. Moreover, complexes containing chelating organic substituents such as scorpionate,^[15] Schiff-base,^[16] salen and other ligands have been investigated in ROP of lactide.^[17] β -diketiminato zinc complexes are of particular interest, and they were investigated experimentally^[18] and by means of quantum chemical calculations.^[19] β -diketiminato zinc complexes are well-defined living initiators for the ROP of (S,S)-lactide, *rac*-lactide and *meso*-lactide. Their activity was found to strongly depend on their structure in solution, and in particular weakly bonded dimeric species exhibited high activities. Moreover, the N-substituents have a crucial influence on the stereoselectivity and the polymerization rate.^[20] Recently, Williams *et al.* reported homobimetallic zinc catalysts with record-high turnover frequency (TOF) values up to 60000 h⁻¹ at ambient temperature.^[10a] In addition to β -diketiminato complexes, ketoiminate zinc complexes have also been explored in lactide polymerization^[21] and the influence of both steric and electronic variations of the N-substituents on the catalytic activity was demonstrated.^[22] Moreover, the catalytic activity of zinc complexes supported by tridentate N,N',O-chelating diamino- and aminoiminophenolate ligands was shown to depend on the nature of the central N-donor function, since tertiary amines were less active compared to complexes containing a central secondary amine or imine group.^[23]

We are generally interested in the synthesis, structure and reactivity of homo- and heteroleptic zinc complexes containing N,N'-chelating ligands such as β -diketiminates^[24] and amidinates,^[25] O,O'-chelating carboxylates^[26] and N,O-chelating ketoiminates.^[27] The catalytic activity of bidentate β -diketiminato^[10d] and carboxylate zinc complexes^[10g] as well as of tridentate ketoiminate zinc complexes in ROP of *rac*-lactide was also studied by us and the crucial role of the side-arm donor group on the catalytic activity was revealed.^[11] Herein, we report on the synthesis of heteroleptic (**1** - **4**) and homoleptic (**5**) ketoiminate zinc complexes containing the smallest possible alkyl group (Me) bound to the N-atom of the ketoiminate ligand. In contrast to

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engineering.^[2] The industrially preferred catalyst in the synthesis

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known ketoiminate zinc catalysts, which are almost exclusively kinetically stabilized by bulky organic substituents, the zinc atoms in the new heteroleptic complexes **1** - **4** are not protected by any sterically demanding group. The use of sterically less demanding substituents is expected to favor the coordination of the monomer (lactide) to the Lewis-acidic metal center, which is the initial step in the polymerization of lactide.

Results and Discussion

Synthesis and characterization. The reaction of ketoimine LH [$L = \text{MeNacac} = \text{MeNC}(\text{Me})\text{CHC}(\text{Me})\text{O}$] with an equimolar amount of diethyl zinc in THF at $-60\text{ }^{\circ}\text{C}$ occurred with elimination of ethane and formation of the heteroleptic zinc complex LZnEt **1** in good yields, whereas the analogous reaction with 0.5 equivalents of ZnEt_2 yielded the homoleptic complex L_2Zn **5**. Reaction of **1** with 2,6-dimethylphenol (HOAr , $\text{Ar} = 2,6\text{-Me}_2\text{-C}_6\text{H}_3$) gave the heteroleptic complex LZnOAr **2**. The Lewis-acidic character of **1** and **2** was revealed by reactions with equimolar amounts of 4-dimethylamino pyridine (dmap), yielding almost quantitatively the corresponding dmap-stabilized complexes $(\text{dmap})\text{Zn}(\text{L})\text{Et}$ **3** and $(\text{dmap})\text{Zn}(\text{L})\text{OAr}$ **4** (Scheme 1). In contrast, **5** failed to react with dmap due to the presence of two N,O-chelating ligands.

Scheme 1: Synthesis of **1-5**.

1 - **5** were characterized by elemental analysis, IR spectroscopy and heteronuclear (^1H , ^{13}C) NMR spectroscopy. ^1H NMR spectra each showed the expected four singlets due to the backbone C-H and three Me groups of the ketoiminate ligand in the expected 1:3:3:3 relative intensity as well as the Et (**1**), OR (**2**) and dmap groups (**3**, **4**) bonded to the zinc atom. Single crystals of **1**, **2**, **3** and **5** were obtained from solutions in THF upon storage at $-30\text{ }^{\circ}\text{C}$ for 12 h. Table 1 summarizes selected bond lengths and angles of **1** - **3** and **5**. **1** crystallizes in the monoclinic space group $C2/c$ (Fig. 1) with the molecule placed on special position $4d$ (centre of inversion). The Zn(1) atom is coordinated by the N,O-chelating MeNacac ligand and the Et group. An additional bond to the O2' atom of the symmetry

equivalent MeNacac results in the formation of a Zn_2O_2 ring and a step-like conformation of the molecule with an angle of $68.45(4)^{\circ}$ between the best planes of the adjacent rings. The C_3NO backbone of the MeNacac ligand is flat (r.m.s. deviation from best plane $0.0199\text{ \AA}$) and the zinc atom is slightly off-set ($0.5089(11)\text{ \AA}$) away from the symmetry equivalent ligand, resulting in a strongly distorted tetrahedral environment of the zinc atom. The bonds to the heteroatoms are roughly perpendicular ($83.40(3)$ to $102.49(3)^{\circ}$, Table 1), while the $\text{C}_{\text{Et}}\text{-Zn-N/O}$ bond angles are significantly larger than the tetrahedral angle ($113.29(4)$ to $129.83(4)^{\circ}$). The Zn-N and Zn-O bonds within the asymmetric unit of **1** are (within s.u.) equal to the mean values derived from the CSD for Zn ketiminato complexes.^[28] The Zn-O bond lengths within the Zn_2O_2 ring ($2.1243(8)\text{ \AA}$) agree with those reported for tricyclic Zn ketiminato complexes,^[29] while a Zn complex containing a ketiminato ligand with an additional hemilabile side-arm donor shows shorter Zn-O bond lengths ($2.0781(12)$ and $2.0904(12)\text{ \AA}$).^[11]

Figure 1. Solid state structure of **1**, thermal ellipsoids are shown at 50% probability levels. Symmetry generated part displayed in pale colors.

Figure 2. Solid state structure of **2**, thermal ellipsoids are shown at 50% probability levels. Symmetry generated part displayed in pale colors. Disordered solvent and hydrogen atoms omitted for clarity.

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Compound **2** crystallizes in the monoclinic space group *C2/c* with the molecule placed on a two-fold rotational axis and disordered THF (total occupancy 75%), resulting in a C_2 symmetric dimer with phenolate ligands bridging the two Zn atoms (Fig. 2).

Table 1. Central bond lengths (Å) and bond angles (°) of **1** - **3** and **5**.

	1	2	3	5
Zn1–O1	2.0153(8)	1.920(2)	1.9817(6)	1.9574(10) ^[a]
Zn1–N1	2.0100(9)	1.952(3)	2.0230(8)	1.9713(11) ^[b]
Zn1–O2	–	1.975(2)	–	–
Zn1–O2'	–	1.984(2)	–	–
Zn1–C _{Et}	1.9780(11)	–	1.9952(9)	–
Zn1–O1'	2.1243(8)	–	–	1.9574(10) ^[a]
Zn1–N _{DMAP}	–	–	2.1121(7)	–
Zn1–N1'	–	–	–	1.9713(11) ^[b]
O1–Zn1–N1	92.25(3)	100.45(10)	94.05(3)	96.47(4)
O1–Zn1–O2	–	120.51(9)	–	–
N1–Zn1–O2	–	121.61(10)	–	–
O1–Zn1–N _{DMAP}	–	–	95.52(3)	–
O1–Zn1–C _{Et}	129.83(4)	–	129.57(4)	–
N1–Zn1–C _{Et}	125.84(4)	–	118.05(4)	–
O1'–Zn1–N1	102.49(3)	–	–	112.06(4)
O1'–Zn1–C _{Et}	113.29(4)	–	–	–
O1'–Zn1–O1	83.40(3)	–	–	111.67(6)
O2'–Zn1–O1	–	119.03(10)	–	–
N1–Zn1–O2'	–	115.33(10)	–	–
O2–Zn1–O2'	–	80.70(10)	–	–
N1'–Zn1–N1	–	–	–	128.47(7)
N _{DMAP} –Zn1–N1	–	–	106.32(3)	–
N _{DMAP} –Zn1–C _{Et}	–	–	109.56(3)	–
N _{DMAP} –Zn1–O1	–	–	95.52(3)	–

[a] equal because of symmetry equivalence, [b] equal because of symmetry equivalence

The Zn atom in **2** is coordinated by a chelating MeNacac ligand to complete its slightly distorted tetrahedral coordination sphere (bond angles in the range from 80:70(10)° to 121:61(10)°). The six-membered ZnNC₃O ring is planar (r.m.s. deviation from best plane 0.0219 Å) and adopts a perpendicular orientation to the central Zn₂O₂ four-membered ring (angle between best planes 87.74(6)°). The latter ring is also planar (r.m.s. from best plane 0.0055 Å). The plane of the phenolate substituent is perpendicular

to both the four-membered (angle between best planes 85.42(9)°) and the six-membered ring (angle between best planes 89.88(9)°). The Zn–N and Zn–O bonds are substantially shorter compared to those in **1**, possibly resulting from strong intramolecular hydrogen bonds from the methyl groups of the phenolate to the heteroatoms of the MesNacac ligand.

3 crystallizes in the triclinic space group *P*-1 with the molecule placed on the general position (Fig. 3). The zinc atom (Zn1) is coordinated to the MeNacac ligand in the expected N,O-chelating mode as well as one additional ethyl group and one dmap molecule, resulting in a total coordination number of four.

Figure 3. Solid state structure of **3**, thermal ellipsoids are shown at 50% probability levels.

The most notable distortion of the tetrahedral environment of the zinc atom is its shift towards one of the planes of the tetrahedron (located 0.4872(5) Å off the N1/O1/C_{Et} plane) and the coordination mode at the zinc atom can thus rather be described as trigonal-bipyramidal with one empty coordination site. The zinc atom and the NC₃O backbone of the MeNacac ligand form a planar six-membered ring (r.m.s. deviation from best plane 0.0648 Å). The distortions necessarily lead to a range of bond angles significantly differing from the ideal tetrahedral angle (94.05(3) to 129.57(4)°). The Zn–N and Zn–O bond lengths in **3** agree very well with values previously observed for the only structurally characterized dmap-coordinated Zn ketimate complex dmap-Zn(Et)L, which crystallized with two independent molecules in the asymmetric unit and showed Zn–N_{DMAP} bond lengths of 2.123(3) and 2.117(3) Å, respectively.^[11] A CSD search for any type of Zn(dmap) complexes (46 hits, 68 bonds) revealed a mean bond length of 2.18(6) Å (range 1.986 to 2.177 Å). The Zn–O and Zn–N bond distances in **3** also agree very well with corresponding values observed for homo- and heteroleptic tridentate ketoimate zinc complexes.^[22a, 30]

5 crystallizes in the orthorhombic space group *Pbcn* (Fig. 4). The molecule occupies special position 4c and consequently shows two-fold rotational symmetry. The zinc atom is coordinated by two N,O-chelating MeNacac ligands, resulting in a tetrahedral environment at the zinc atom, which is distorted along the -4 axis since the endocyclic O–Zn–N bond angles (see Table 1) are

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restrained by the bite angle of the ligand. The six-membered ring is flat (r.m.s. deviation from best plane 0.0604 Å) and approximately perpendicular to its symmetry equivalent (88.54(3)° angle between best planes). The Zn-N and Zn-O bond lengths again match well those observed for **1** to **3** as well as with the mean values obtained from the CSD.

Figure 4. Solid state structure of **5**, thermal ellipsoids are shown at 50% probability levels. Symmetry generated part displayed in pale colors.

Polymerization studies. **1** – **5** were tested in ROP of *rac*-lactide (Table 2). Kinetic experiments were performed in CD₂Cl₂ or CDCl₃ at ambient temperature. **1** shows a rather slow activity in ROP of lactide compared to other catalysts containing β -diketiminato ligands. After 24 h only 13% were converted into the polymer, whereas a polymerization of 90% needs seven days (SI). In contrast, the homoleptic zinc catalyst **5** is slightly faster by converting 13% within 10 h, but the TOFs of both catalysts (**1** (**1**), **3** (**5**)) are rather disappointing. MALDI-TOF measurements show that the N,O-chelating MeNacac ligand of the homoleptic complex is able to open the lactide (Fig. S26) as was previously reported.^[31] The introduction of sterically more demanding 2,6-dimethylphenol ligand in **2** results in a significant activity increase, and **2** was found to convert 80% of *rac*-lactide into PLA within 66 minutes with $k_p = 1.167 \times 10^{-4} \text{ L s}^{-1} \text{ mmol}^{-1}$. Careful analysis of the MALDI-TOF spectra of the polymers obtained with catalysts **2** and **3** suggest that the polymerization reactions proceed through the well-known coordination insertion mechanistic (CIM) pathway. The initial step in the CIM pathway is the coordination of LA to the metal center through the carbonyl oxygen atom followed by insertion of the nucleophilic substituent of the metal complex to the activated carbonyl carbon atom of LA through simple nucleophilic attack followed by rearrangement and formation of an alkoxy intermediate. This alkoxy intermediate is the authentic, active species in the ROP and the chain propagation step proceeds via repeatedly coordination of LA to the metal center followed by insertion of alkoxy group by breaking the M-O bond. The above assumption also reflects the ROP results as summarized in table 2. The polymerization results reveal that catalyst **2** shows a higher reactivity than catalyst **1**, which is caused by the stronger nucleophilic nature of the 2,6-dimethylphenoxide ligand in **2** compared to the ethyl group in **1**. The less nucleophilic Et group hampers the formation of the active alkoxy intermediate species, resulting in a high molecular weight

(M_n) of 127.000 g/mol. Catalyst **2** is also more active compared to catalyst **3**, also resulting from the stronger nucleophilic nature of the dimethylphenoxide ligand compared to the dimethylamino pyridine base. Therefore, **2** again initiates the formation of the alkoxy intermediate much faster than **3**, resulting in a faster propagation of the polymer chain. The lack of reactivity in case of catalyst **5** in the ROP of lactide results from the poor nucleophilicity of the N,O-chelating ketoiminato ligands.

The analysis of the polymerization results (table 2) also showed that a moderate correlation between observed molecular weight (M_n) and theoretical molecular weight exist for catalyst **2** and **3**, whereas the observed molecular weight obtained with catalyst **1** ($M_n = 127.000 \text{ g/mol}$) was found to be much higher than the theoretical molecular weight ($M_{n,theo}$: 28.800 g/mol for 100 % conversion). This finding proves that a smaller number of active alkoxy intermediate species are produced during the polymerization reaction with catalyst **1**, hence resulting in an elongated reaction time for achieving high conversion as well as in the growth of significantly longer polymer chains. This finding clearly originates from the presence of the less nucleophilic Et group, which is a rather poor initiator in ROP of cyclic ethers.

However, compared to the dinuclear zinc catalyst from Williams *et al.*, which represents the fastest catalyst so far, complex **2** is 250 times slower.^[10a]

Table 2. Ring-opening polymerization mediated by **1** - **3** and **5**.^[a]

cat. ^[a]	Time [min]	conv. [%] ^[c]	TOF [h ⁻¹]	M_n [g mol ⁻¹] ^[c]	PD ^[d]	$k_{app} \times 10^{-5} \text{ s}^{-1}$	k_p [L s ⁻¹ mmol ⁻¹]
1 ^[a]	7 days	90	1	127000	2.0	0.028	3.922×10^{-8}
2 ^[b]	66	80	73	19300	1.8	67.5	1.167×10^{-4}
3 ^[b]	114	88	46	15000	1.8	30.5	0.523×10^{-4}
5 ^[a]	600	13	3	16300	1.8	0.163	2.283×10^{-7}

[a] [LA] / [cat] 200:1, in 0.7 mL CD₂Cl₂ at RT, subl. *rac*-LA; [b] [LA] / [cat] 100:1, in 0.6 mL CDCl₃ at RT, subl. *rac*-LA; [c] determined by ¹H-NMR; [d] $PD = M_w/M_n$ as determined by GPC (in THF), $M_{n,theo}$: 28 800 g mol⁻¹ for 100 % conversion ([LA]/[cat] 200:1) and 14 400 g mol⁻¹ for 100 % conversion ([LA]/[cat] 100:1).

Since we recently observed a beneficial influence of additional Lewis bases such as dmap on the catalytic activity of ketoiminato zinc catalyst,^[11] we also investigated the activity of the dmap-coordinated complexes **3** and **4**. Complex **3** converts 88% of *rac*-lactide into PLA within 114 minutes resulting in a k_p value of $0.523 \times 10^{-4} \text{ L s}^{-1} \text{ mmol}^{-1}$. Waymouth *et al.* have been reported the subsiding mechanism using dmap as initiator.^[32] Sole dmap is almost inactive in ROP, hence the strong activity increase upon addition of dmap to **1** points to a cooperative beneficial effect.^[33] Comparable results were expected for the phenoxy-substituted derivatives **2** and **4**, but due to the very poor solubility of **4** in common organic solvents, **4** could only be investigated in bulk polymerization reactions, and the results are therefore not directly comparable with those obtained for **1** - **3** and **5**. However, these studies proved that **4** is rather active in bulk polymerization requiring much higher temperatures, converting 93 % lactide to PLA within 20 minutes (SI).

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Figure 5 shows the lactide polymerization kinetics for **2** and **3**.

Figure 5. Plot of ring-opening polymerization (ROP) of lactide with complex **2** (blue) and **3** (red): semi-logarithmic plot of the polymerizations of *rac*-LA [LA]:[Init.] = 100:1, 25 °C, CDCl₃; conversion rate determined by ¹H NMR spectroscopy.

While the logarithmic conversion of **3** against the time shows a linear fit, an induction phase for the polymerization using complex **2** is observed. The inducing phase is probably caused by the dissociation of the dinuclear complex. The activity and the mechanism of other dimeric species is under current investigation. Once the dissociation has occurred, both zinc centers are active to control the polymerization. The obtained molecular weights of the polymer fit well to the calculated masses under the assumption that one phenolate and one zinc atom initiate and control the polymerization. For clarifying the subsiding mechanism end-group analysis by MALDI-TOF have been performed. The results maintained that dmap in complex **3** and the phenolate in complex **2** are bound at the chain end of the polymer. In the polymerization reaction, dmap and the phenolate open the lactide ring and therefore a coordination insertion mechanism is proposed. The tested complexes **2** and **3** show characteristics of a well-defined catalyst. However, complexes **1** and **5** show a slower activity. The molecular weights for polymers obtained with **1** are much higher than the theoretical values. The broad polydispersity of the resulting polymer obtained with catalyst **1** indicates that transesterification reactions occur during the ROP.

Pulsed-gradient spin echo (PGSE) measurements were performed to investigate the structures of **1** - **3** in CH₂Cl₂ and THF solution (Table 3), respectively. In non-coordinating CH₂Cl₂, the hydrodynamic radius of **1** is smaller than that of **3**, which indicates that both molecules adopt monomeric structures in solution, and the larger hydrodynamic radius of **3** results from the coordination of the strong Lewis base dmap. In contrast, the hydrodynamic radii of **2** in dichloromethane and in THF are significantly larger, indicating the formation of dimeric molecules in solution as was observed in the solid state.

Table 3. PGSE measurements of **1** - **3**.^[a]

Solvent	1	2	3
CH ₂ Cl ₂	3.309	5.242	4.079
THF	3.692	5.521	3.762

[a] Measurements were performed at 25 °C.

According to these NMR studies, the inducing phase in the ROP of lactide using complex **2** may be caused by the dissociation of dimeric **2** into the monomeric complex. The monomeric complex then rapidly polymerizes lactide due to the strong nucleophilic nature of the 2,6-dimethylphenoxide ligand, which readily attacks the electrophilic carbon center of the coordinated lactide. In contrast, **1** and **3**, which are expected to be monomeric in solution under ROP conditions, are less active in lactide polymerization due to the less nucleophilic nature of the Et substituent compared to the 2,6-dimethylphenoxide ligand in **2**.

Conclusions

One homoleptic and four heteroleptic zinc ketoiminate complexes were synthesized and four of them were characterized by single crystal X-ray analysis. The complexes were investigated for the ROP of lactide and the heteroleptic complexes **2** and **3** containing an additional phenoxide or Lewis base substituent at the Zn atom turned out to be much more active catalysts compared to **1** and **5**, respectively. Moreover, the beneficial effect of the addition of the external Lewis base dmap on the catalytic activity was revealed. The complexes convince by their simple synthesis and their high catalytic performance.

Experimental Section

Reactions were performed in purified Ar atmosphere using standard Schlenk and glovebox techniques. Solvents were carefully dried over and degassed prior to use. Deuterated solvents were stored over activated molecular sieves (4 Å). Karl Fischer titration of the dry solvents showed values below 2 ppm. The ketoimine LH was prepared by literature method.^[34] 2,6-dimethylphenol and dmap (Acros) were sublimed before use.

MALDI-TOF mass spectrometry: The end group analysis was performed by MALDI-TOF on a Bruker ultrafleXtreme equipped with a 337 nm smartbeam laser in the reflective mode. THF solutions of trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malono-nitrile (DCTB) (5 µL of a 20 mg/mL solution), sodium trifluoroacetate (0.1 µL of a 10 mg/mL solution), and analyte (5 µL of a 10 mg/mL) were mixed and a droplet thereof applied on the sample target. Protein 1 calibration standard is the name of the protein mixture used for calibration. For spectra 4000 laser shots with 24 % laser power were collected. The laser repetition rate was 1000 Hz. The homopolymer analysis was performed using Polymerix software (Sierra Analytics).

¹H (300 MHz) and ¹³C{¹H} (75.5 MHz) NMR (δ in ppm) spectra were recorded using a Bruker Avance 300 or a Bruker Avance III (¹H, 400 MHz) spectrometer and the spectra were referenced to internal THF-d₈ (¹H: δ = 1.72, 3.58; ¹³C: 67.21, 25.31), CDCl₃ (¹H: δ = 7.26) and CD₂Cl₂ (¹H: δ = 5.32; ¹³C: 53.84). Microanalyses were performed at the elemental analysis laboratory of the University of Duisburg-Essen. IR Spectra were recorded on an ALPHA-T FTIR spectrometer equipped with a single reflection ATR

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sampling module. The spectrometer was placed in a glovebox to avoid hydrolysis and oxidation reactions.

Gel Permeation Chromatography (GPC): The average molecular weights and the weight of the obtained polylactide samples were determined by gel permeation chromatography (GPC) in THF as mobile phase at a flow rate of 1 mL/min. The utilized GPCmax VE-2001 from Viscotek is a combination of an HPLC pump, two Malvern Viscotek T columns (porous styrene divinylbenzene copolymer) with a maximum pore size of 500 and 5000 Å and a refractive index detector (VE-3580) and a viscometer (Viscotek 270 Dual Detector). Universal calibration (polystyrol as standard) was applied to evaluate the chromatographic results.

Polymerizations experiments in solution were performed at room temperature with sublimed *rac*-lactide and the corresponding catalyst in a molar ratio of either 200:1 (144.13 mg, 1 mmol *rac*-lactide, 0.005 mmol **1** & **5**) in 0.7 mL CD₂Cl₂ (**1**, **5**) or in a molar ratio of 100:1 (50 mg, 0.347 mmol *rac*-lactide, 0.0035 mmol **2** & **3**) in 0.6 mL CDCl₃ (**2**, **3**), respectively. The bulk polymerization experiment with **4** was performed at 140 °C in a molar ratio of either 200:1 with the same amounts as in solution. The polymer was dried in vacuum and the conversion rate was determined from the ¹H NMR spectra by integration of methyl protons of the monomer (δ = 1.53 ppm) versus the methyl protons of the polymer (δ = 1.47 ppm).

Synthesis of 1: A solution of LH (282.9 mg, 2.5 mmol) in 10 mL of THF was added to a solution of ZnEt₂ (2.5 mL, 1M/L in hexanes) in 10 mL of THF at -60 °C. After stirring for 12 h, the solvent was removed in vacuum, yielding a colorless crystalline solid, that was recrystallized from a solution in 5 mL of THF at -30 °C. Yield: 412 mg (80%). M.p.: 137 °C. Anal. calc. for C₈H₁₅NOZn: C 46.51, H 7.32, N 6.78; found: C 46.30, H 7.29; N 6.92 %. ¹H NMR (THF-d₈, 25 °C): δ = 0.11 (q, ³J_{HH} = 8.1 Hz, 2H, ZnCH₂CH₃), 1.21 (t, ³J_{HH} = 8.1 Hz, 3H ZnCH₂CH₃), 1.80 (s, 3H, CCH₃), 1.87 (s, 3H, CCH₃), 3.07 (s, 3H, NCH₃), 4.76 (s, 1H, CH). ¹³C NMR (THF-d₈, 25 °C): δ = 6.40 (ZnCH₂CH₃), 10.65 (ZnCH₂CH₃), 18.03 (CCH₃), 24.63 (CCH₃), 35.51 (NCH₃), 99.93 (CH), 170.03 (CN), 179.54 (CO). IR: ν 2849, 1612, 1531, 1384, 1262, 1210, 995, 926, 855, 781, 679, 641, 606, 572, 503, 434.

Synthesis of 2: A solution of 2,6-Dimethylphenol (179.12 mg, 1.47 mmol) in 10 mL of THF was dropwise added to a cooled (-90 °C) solution of **1** (300 mg, 1.47 mmol) in 10 mL of THF. The solution was slowly warmed to ambient temperature and stirred for additional 2 h. The solvent was evaporated in vacuum and the resulting crystalline solid was re-crystallized from a solution in 5 mL of THF at -30 °C. Yield: 370 mg (84%) of **3** as powder. M.p.: 178 °C. Anal. calc. for C₁₄H₁₉NO₂Zn: C 56.30, H 6.41, N 4.69; found: C 55.98, H 6.61; N 4.62%. ¹H NMR (CD₂Cl₂, 25 °C): δ = 1.85 (s, 3H, CCH₃), 1.86 (s, 3H, CCH₃), 2.38 (s, 6H, *o*-CH₃), 3.23 (s, 3H, NCH₃), 4.79 (s, 1H, CH), 6.65 (t, ³J_{HH} = 7.4 Hz, 1H, *p*-CH), 6.92 (d, ³J_{HH} = 7.4 Hz, 2H, *m*-CH). ¹³C NMR (CD₂Cl₂, 25 °C): δ = 17.42 (*o*-CCH₃), 21.96 (CCH₃), 27.85 (CCH₃), 39.08 (NCH₃), 97.41 (CH), 119.67 (*p*-CH), 128.86 (*m*-CH), 176.69 (CN), 183.98 (CO). IR (neat): ν 2961, 1591, 1509, 1461, 1417, 1392, 1381, 1369, 1262, 1229, 1209, 1158, 1092, 1015, 998, 936, 917, 860, 837, 799, 770, 751, 687, 643, 599, 579, 522, 488, 458.

Synthesis of 3: DMAP (179.1 mg, 1.47 mmol) was added to a solution of **1** (300 mg, 1.47 mmol) in 15 mL of THF and stirred at ambient temperature for 1h. The solvent was then removed in vacuum and the resulting crystalline solid was re-crystallized from a solution in 5 mL of toluene at -30 °C. Yield 455 mg (95%). M.p.: 101 °C. Anal. calc. for C₁₅H₂₅N₃OZn: C 54.80, H 7.67, N 12.78, found: C 53.40, H 7.73; N 13.10%. ¹H NMR (CD₂Cl₂, 25 °C): δ = 0.09 (q, ³J_{HH} = 8.1 Hz, 2H ZnCH₂CH₃), 1.23 (t, ³J_{HH} = 8.1 Hz, 3H, ZnCH₂CH₃), 1.84 (s, 3H, CCH₃), 1.85 (s, 3H, CCH₃), 2.98 (s, 3H, NCH₃), 3.01 (s, 6H, N(CH₃)₂), 4.71 (s, 1H, CH), 6.52 (d, ³J_{HH} = 5.3 Hz, 2H, *m*-CH_{DMAP}), 7.96 (d, ³J_{HH} = 5.3 Hz, 2H, *o*-CH_{DMAP}). ¹³C NMR (CD₂Cl₂, 25 °C): δ = -3.78 (ZnCH₂CH₃), 13.97 (ZnCH₂CH₃), 21.13 (CCH₃), 27.85 (CCH₃), 38.26 (NCH₃), 39.50 (N(CH₃)₂), 96.21 (CH), 107.13 (*m*-CH_{DMAP}), 148.70 (*o*-CH_{DMAP}), 155.58 (CN(CH₃)₂), 171.88 (CN), 181.25 (CO). IR (neat): ν 2843, 1600, 1504, 1419, 1389, 1269, 1223, 1068, 110, 937, 800, 754, 576, 523, 490, 430.

Synthesis of 4: A solution of DMAP (34.3 mg, 0.28 mmol) in 5 mL of THF was added to a solution of **2** (83.8 mg, 0.28 mmol) in 5 mL of THF and stirred at ambient temperature. The resulting white precipitate was isolated by filtration. Yield 101 mg (91%). ¹H NMR (CD₂Cl₂, 25 °C): δ = 1.89 (s, 3H, CCH₃), 1.91 (s, 3H, CCH₃), 2.14 (s, 6H, *o*-CH₃), 2.99 (s, 6H, N(CH₃)₂), 3.04 (s, 3H, NCH₃), 4.82 (s, 1H, CH), 4.71 (s, 1H, CH), 6.34 (t, ³J_{HH} = 6.7 Hz, 1H, *p*-CH), 6.55 (d, ³J_{HH} = 5.3 Hz, 2H, *m*-CH_{DMAP}), 6.82 (d, ³J_{HH} = 7.1 Hz, 2H, *m*-CH), 8.07 (d, ³J_{HH} = 5.2 Hz, 2H, *o*-CH_{DMAP}). ¹³C NMR (CD₂Cl₂, 25 °C): δ = 17.78 (*o*-CCH₃), 21.36 (CCH₃), 27.55 (CCH₃), 38.07 (NCH₃), 39.43 (N(CH₃)₂), 96.75 (CH), 107.13 (*m*-CH_{DMAP}), 114.05 (*p*-CH), 126.87 (*m*-CH), 128.03 (*o*-CH), 148.69 (*o*-CH_{DMAP}), 155.72 (CN(CH₃)₂), 164.43 (*ipso*-C), 174.93 (CN), 182.80 (CO). M.p.: 198 °C (dec.). Anal. calc. for C₁₅H₂₅N₃OZn: C 59.93, H 6.95, N 9.98, found: C 59.20, H 7.09, N 10.40%. IR (neat): ν 2824, 1507, 1458, 1326, 1016, 757, 523, 435.

Synthesis of 5: A solution of LH (265.8, 5 mmol) in THF was added to a solution of ZnEt₂ (2.5 mL, 1M/L in hexanes) in THF at ambient temperature and the resulting solution was stirred for 30 minutes. The solvent was removed in vacuum, yielding a colorless crystalline solid, which was recrystallized from THF at -30 °C. Yield: 612 mg (85%). M.p.: 162 °C. Anal. calc. for C₁₂H₂₀N₂O₂Zn: C 49.75, H 6.96, N 9.67; found: C 49.50, H 7.07; N 9.80%. ¹H NMR (THF-d₈, 25 °C): δ = 1.82 (s, 3H, CCH₃), 1.91 (s, 3H, CCH₃), 2.96 (s, 3H, NCH₃), 4.77 (s, 1H, CH). ¹³C NMR (THF-d₈, 25 °C): δ = 18.11 (CCH₃), 24.64 (CCH₃), 34.90 (NCH₃), 93.89 (CH), 171.98 (CN), 180.58 (CO). IR (neat): ν 1589, 1501, 1422, 1386, 1270, 1224, 1089, 995, 938, 757, 681, 453.

Single crystal X-ray analyses. The crystals were mounted on nylon loops in inert oil. Data were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (monochromated MoK α radiation, λ = 0.71073 Å) at 100(2) K. The structures were solved by Direct Methods (SHELXS-97)^[35] and refined anisotropically by full-matrix least-squares on *F*² (SHELXL-2014).^[36] Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups. In **2** the THF is disordered over three different positions with a total occupancy of about 0.75. SADI restraints were employed for all 1,2 and 1,3 distances. RIGU, DELU, and SIMU restraints were applied to the ADP of all solvent atoms and an additional ISOR restraint to the ADP of the solvents' O atoms. Removing the solvent contribution to the electron density with SQUEEZE^[37] slightly improved the R-values, however since the solvent positions were recognizable and (with vast use of restraints) refinable we chose to discard this model.

The crystallographic data of **1** - **3** and **5** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1569530 (**1**), CCDC-1569531 (**2**), CCDC-1569532 (**3**) and CCDC-1569533 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information. A CIF file giving X-ray crystallographic data of **1** - **3** and **5**. ¹H, ¹³C NMR and IR spectra of **1** - **5** as well as crystallographic details of **1** - **3** and **5** are given. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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COMMUNICATION

Five homo- and heteroleptic zinc ketoiminate complexes containing the sterically less demanding N,O-chelating MeNacac ligand are synthesized and their structures in solution and in the solid state investigated. In addition, their technical application as catalysts in ring-opening polymerization (ROP) of *rac*-lactide in CDCl₃ solution at ambient temperature was studied.

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