

# Syntheses, Solid-state Structures and Catalytic Activity of Zinc Carboxylate Complexes in Lactide Polymerization

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 80<sup>th</sup> birthday

Three dinuclear zinc carboxylate complexes  $[L^{1-3}Zn(\mu, \eta^2-O_2CPh)]_2$  (**1**, **2**, **4**) containing either the bidentate *N,N'*-chelating  $\beta$ -diketiminato ligand  $RNC(Me)C(H)C(Me)NR$  ( $R = 2,6-iPr_2-C_6H_3$ ,  $L^1$ , complex **1**), the tridentate *O,N,N'*-chelating ligand  $OC(Me)C(H)C(Me)NCH_2CH_2NMe_2$  ( $L^2$ , complex **2**) or the bis-*N,N'*-chelating bis- $\beta$ -diketiminato ligand  $RNC(Me)C(H)C(Me)NNC(Me)-C(H)C(Me)NR$  ( $R = 2,6-iPr_2-C_6H_3$ ,  $L^3$ , complex **4**) were synthesized and characterized including single-crystal X-ray diffraction. Reaction of the neutral bis- $\beta$ -diketimine ( $L^3(H)_2$ ) with two equivalents of  $ZnMe_2$  leads to the expected heteroleptic dinuclear zinc complex  $L^3(ZnMe)_2$  **3** in 93% yield. Further reaction with benzoic acid  $PhCO_2H$  leads to complex **4**. Complex **2** forms a rather strong carboxylate-bridged dimer, whereas the carboxylate groups in complexes **1** and **4** act as asymmetrical bridges between both Zn atoms, pointing to the formation of a weakly bonded dimer. The zinc atoms in **1** and **4** are tetrahedrally coordinated, whereas in **2** the coordination number is increased to five due to the coordination of the pendant donor arm. The ring opening polymerization (ROP) of *rac*-lactide was investigated with the zinc complexes **1–4** and diazabicycloundec-7-ene (DBU) as a co-catalyst. Complexes **2** and **3** are active polymerization catalysts, which in the presence of DBU converted 200 equiv. of *rac*-lactide into polylactide within 10 min at ambient temperature. The analysis of the crude polymer showed that the lactide polymerization with catalyst **2** occurs *via* a slightly modified activated-monomer mechanism.

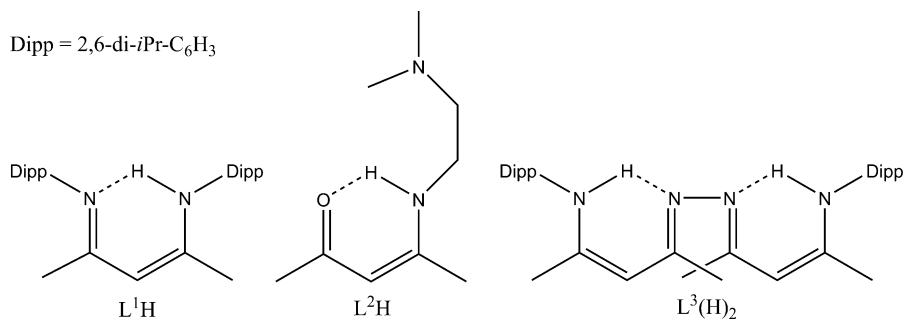
**Key words:** Zinc, Carboxylate, *N,N'* Ligands, *N,N,O* Ligands

## Introduction

In the last decade, monoanionic bidentate *N,N'*-chelating ligands such as  $\beta$ -diketiminato ligands ( $L^1$ ) [1–7] as well as monoanionic donor-functionalized multidentate [NNO] ( $L^2$ ) [8–15] [ONO] or [ONOO] ligands [16–18] have found widespread application in organometallic chemistry since they are easily accessible, and their steric and electronic properties can easily be adjusted by variation of the organic substituents (Scheme 1) [19]. Resulting main group metal and transition metal complexes have intensely been investigated in the ring opening polymerization (ROP) of cyclic esters such as lactide [20–24]. Coates *et al.* have investigated  $\beta$ -diketiminato zinc complexes in de-

tail, and they observed very high polymerization activities for weakly bonded dimeric  $\beta$ -diketiminato complexes [25–31]. As a consequence, dinucleating bis- $\beta$ -diketiminates, *i. e.* those of type  $L^3$  containing an N–N bond as well as those containing an organic spacer, in which the metal-metal distances can be adjusted by variation of the organic spacer, hence forcing the formation of cooperative effects between both metal atoms, have attracted growing interest, and high lactide polymerization activities have been reported [32–35].

We have a long-standing interest in *N,N*- and *N,O*-chelating zinc complexes containing  $\beta$ -diketiminato [36–40], amidinate [41–46], and amidate ligands [47]. Only recently, we became interested in the polymerization catalysis of cyclic esters and reported on



Scheme 1. Bidentate, tridentate and binuclear ligands (L<sup>1</sup>–L<sup>3</sup>) in their protonated forms.

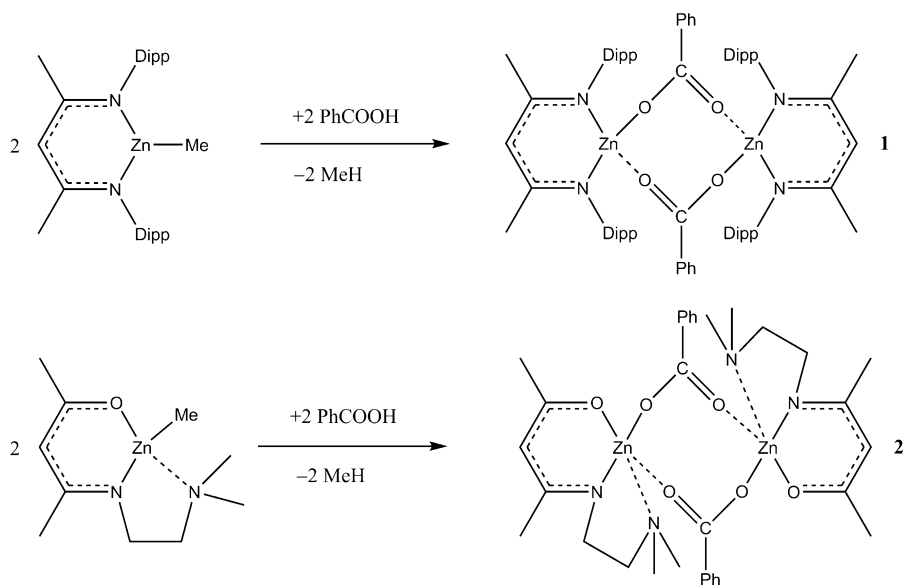
the use of cationic  $\beta$ -diketiminato zinc complexes as well as of neutral tridentate [NNO] zinc complexes containing donor-functionalized  $\beta$ -ketiminato ligands (L<sup>2</sup>) in the ROP of lactide [48, 49]. We now expanded our studies to the corresponding zinc carboxylate complexes containing bidentate  $\beta$ -diketiminato, tridentate [NNO] and dinucleating bis- $\beta$ -diketiminato substituents and report on their solid-state structures and their use in the ROP of lactide.

## Results and Discussion

Reactions of the heteroleptic methyl-substituted zinc complexes L<sup>1/2</sup>ZnMe with one equivalent of benzoic acid in dichloromethane at –30 °C occurred with

elimination of methane and subsequent formation of the corresponding dimeric zinc carboxylate complexes [L<sup>1</sup>Zn( $\mu$ , $\eta^2$ -O<sub>2</sub>CPh)]<sub>2</sub> **1** and [L<sup>2</sup>Zn( $\mu$ , $\eta^2$ -O<sub>2</sub>CPh)]<sub>2</sub> **2** (Scheme 2).

The <sup>1</sup>H NMR spectra (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C) of **1** and **2** showed the characteristic resonances of the [L<sup>1/2</sup>] ligands and those of the bridging carboxylate group (**1**:  $\delta$  = 7.80–8.24 ppm; **2**:  $\delta$  = 7.43–8.11 ppm), whereas the Zn–Me resonances of the starting complexes have fully disappeared. **1** and **2** adopt dimeric structures in CD<sub>2</sub>Cl<sub>2</sub> solution at ambient temperature, as was shown by pulsed-gradient spin echo (PGSE) NMR measurements. The hydrodynamic radii (**1**: 5.74 Å; **2**: 5.41 Å) are larger than that of dimeric [L<sup>2</sup>ZnCl]<sub>2</sub> (4.78 Å) [48]. These findings were verified



Scheme 2. Synthesis of **1** and **2**.

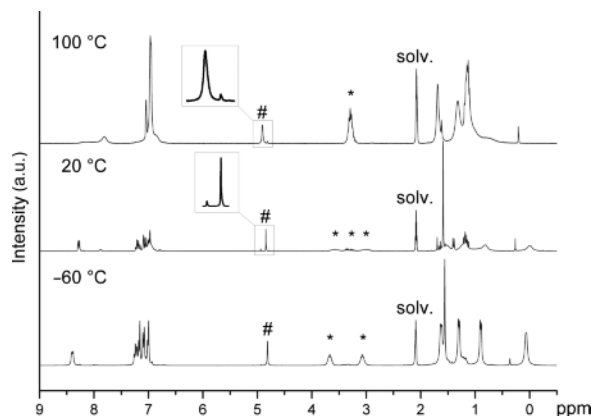


Fig. 1. Temperature-dependent  $^1\text{H}$  NMR spectroscopy study of **1** in  $[\text{D}_8]\text{toluene}$  in the temperature range from  $-80$  to  $100$  °C. Resonances of the methyl groups of the backbone (#) and the *i*-Pr (\*) are marked.

by a temperature-dependent  $^1\text{H}$  NMR spectroscopy study of **1** in  $[\text{D}_8]\text{toluene}$  in the temperature range from  $-80$  to  $100$  °C.

Complex **1** is predominantly dimeric below  $+20$  °C and almost monomeric at  $+100$  °C (Fig. 1). Two well separated septets for the *i*-Pr groups were detected at  $-60$  °C, whereas at  $20$  °C a third septet appeared, whose intensity was raising with increasing temperature. At the same time, a second singlet for the methyl

groups of the backbone appeared. Between  $+20$  and  $+80$  °C an equilibrium of both forms was observed. These results are comparable to those of the zinc acetate complex  $[\text{L}^1\text{Zn}-\mu,\eta^2\text{-OAc}]_2$ , which exhibited two sets of resonances at ambient temperature due to the presence of an equilibrium between the monomeric and dimeric form, and the relative intensity of the resonances was found to be temperature-dependent [29].  $[\text{L}^1\text{Zn}-\mu,\eta^2\text{-OAc}]_2$  was predominantly dimeric below  $-20$  °C and monomeric at  $+100$  °C.

Crystals of **1** and **2** suitable for single-crystal X-ray diffraction analyses were obtained from freshly prepared solutions in  $\text{CH}_2\text{Cl}_2$  upon storage at  $-30$  °C (Figs. 2 and 3). **1** crystallizes in space group  $P2_1/c$  with two independent molecules, and **2** crystallizes in  $P\bar{1}$ . All molecules are placed on centers of inversion. The crystal quality of **1** was rather low, and consequently the quantitative results of the structure determination should be critically accessed. The connectivity, however, can certainly be considered reliable.

In the solid state complexes **1** and **2** adopt dimeric carboxylate-bridged structures, resulting in the formation of non-planar eight-membered  $\text{Zn}_2(\text{O}_2\text{C})_2$  rings. The zinc atoms in **1** adopt slightly distorted tetrahedral coordination geometries, as is typical for four-coordinated zinc complexes. The Zn–N (Zn1–N1 1.987(2) Å, Zn1–N2 1.963(2) Å) and Zn–O bond lengths (Zn1–O1<sub>sub</sub> 1.953(2) Å, Zn1–O2<sub>sub</sub>

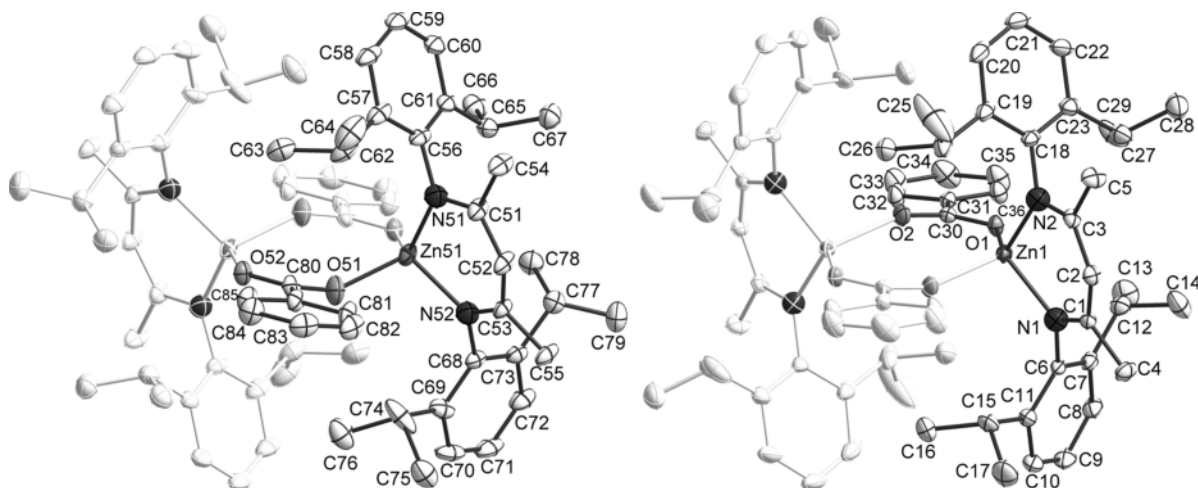


Fig. 2. Molecular structure of **1** in the solid state; hydrogen atoms and the disordered solvent molecule have been omitted for clarity, displacement ellipsoids are drawn at the 50% probability level. The orientation of the two independent molecules does not resemble their arrangement in the asymmetric unit. Symmetry-generated parts of the molecules are drawn in light grey [ $-x+1, -y+1, -z$ , or  $-x, 1-y, 1-z$  (second molecule)].

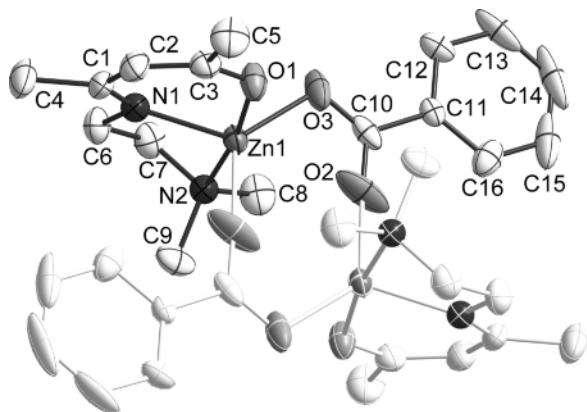


Fig. 3. Molecular structure of **2** in the solid state; hydrogen atoms and the solvent molecule have been omitted for clarity, displacement ellipsoids are drawn at the 50% probability level. The symmetry-generated part of the molecule is drawn in light grey ( $-x+1, -y+1, -z+1$ ).

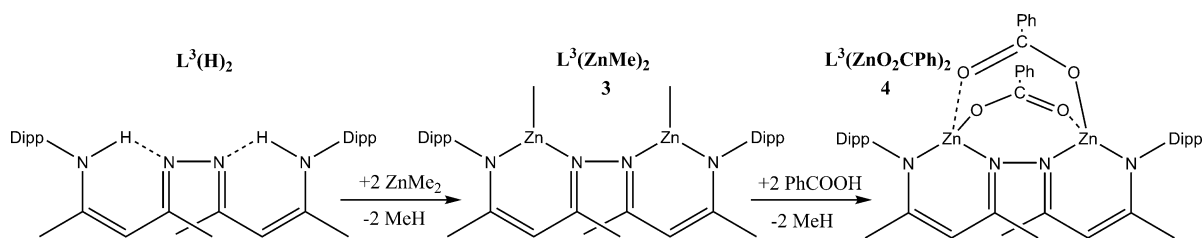
1.986(2) Å) of **1** are comparable to those reported for related dimeric  $\beta$ -diketiminato zinc acetate complexes  $[L^1Zn(\mu, \eta^2-O_2CMe)_2]_2$  [25–31], in which the Zn–N bond lengths range from 1.918 to 2.114 Å with a mean value of 1.970(34) Å, while the Zn–O bond lengths range from 1.903 to 2.014 Å with a mean value of 1.970(18) Å [50]. In contrast, the monomeric zinc carbamate complex  $L^1ZnO_2CN(iPr)_2$  showed significantly elongated Zn–O bonds (2.028(2), 2.041(1) Å), while the Zn–N bond lengths (1.935(1), 1.952(1) Å) are comparable to those of **1** [51]. Comparable findings were observed for the carbonate-bridged  $\beta$ -diketiminato zinc complex  $[L^1ZnO_2COiPr]_2$  (Zn–N 1.97(2), 1.96(2) Å; Zn–O 2.027(8), 1.939(8) Å [25]).

The zinc atoms in **2** are fivefold coordinated due to the presence of the amine donor of the NNO ligand (Fig. 3). In contrast, several zinc complexes containing tridentate ketoiminato ligands as recently reported by Fritsch *et al.* adopt monomeric structures in the solid state with fourfold-coordinated Zn atoms [52, 53]. The

carboxylate groups form symmetrical bridges between the two zinc atoms, resulting in almost identical Zn–O bond lengths (Zn1–O2<sub>sub</sub> 2.042(2) Å, Zn1–O3<sub>sub</sub> 2.049(2) Å), which are comparable to the Zn1–O1<sub>ring</sub> bond length of 2.025(2) Å in **2** but slightly elongated compared to those of **1** due to the increased coordination number. As expected the Zn1–N2 bond toward the donor side arm (2.243(2) Å) is significantly longer than the Zn1–N1 bond (2.016(2) Å). The C–O bond lengths in **1** (C30–O1 1.271(3) Å, C30–O2 1.251(3) Å) and **2** (C10–O2 1.243(3) Å, C10–O3 1.247(3) Å) are in between those observed for C–O single and C=O double bonds due to  $\pi$  delocalization within the O–C–O unit as it is typical in carboxylate complexes. The Zn···Zn separation in **1** (4.334(1) Å) is significantly elongated compared to that observed in **2** (3.705(1) Å), even though the Zn atoms in **2** show a higher coordination number (5 vs. 4). This finding clearly reflects the higher steric demand of the  $\beta$ -diketiminato ligand compared to the less bulky amidinato ligand. Zn···Zn separations previously reported for dimeric  $\beta$ -diketiminato zinc acetates range from 3.807 (RNC(Me)C(H)C(Me)NR (R = 2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)) [30] to 4.245 Å ( $[L^1Zn(\mu, \eta^2-OAc)_2]_2$ ) [30, 54].

Reaction of the neutral bis- $\beta$ -diketimine ( $L^3(H)_2$ ) with two equivalents of  $ZnMe_2$  occurred with alkane elimination and formation of the expected heteroleptic dinuclear zinc complex  $L^3(ZnMe)_2$  **3** in high yield (93%). Further treatment of **3** with two equivalents of benzoic acid in dichloromethane at  $-30^\circ C$  yielded the corresponding dinuclear zinc carboxylate complex  $[L^3(ZnO_2C(C_6H_5))_2]_2$  **4** (Scheme 3). The <sup>1</sup>H NMR spectra of **3** and **4** showed the expected resonances of the  $[L^3]$  ligand and of the Zn–Me groups ( $\delta = -0.98$  ppm, **3**) and the Zn–carboxylate groups ( $\delta = 7.35$ – $7.89$  ppm, **4**).

Colorless single crystals of **3** were obtained from a solution in *n*-pentane (Fig. 4). The Zn–N (Zn1–N1 1.941(1) Å, Zn1–N2 1.960(1) Å, Zn2–N3 1.969(1) Å,



Scheme 3. Synthesis of **3** and **4**.

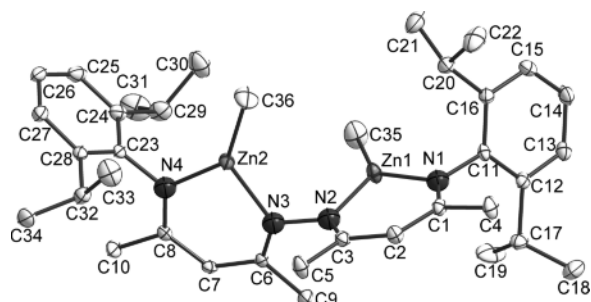


Fig. 4. Molecular structure of **3** in the solid state; hydrogen atoms have been omitted for clarity, displacement ellipsoids are drawn at the 50% probability level.

Zn2–N4 1.942(1) Å) and Zn–C (Zn1–C35 1.941(2), Zn2–C36 1.944(2) Å) bond lengths are comparable to those reported by Harder *et al.* for the corresponding Et-substituted complex  $L^3(\text{ZnEt})_2$  [34]. The  $\beta$ -diketimate units within the ligand are perpendicularly oriented with respect to each other (angle between least-squares planes: **3**: 76.5(1);  $L^3(\text{ZnEt})_2$ : 87.1(1) [34]) as it was also observed in other metal complexes containing  $L^3$  [55], leading to a Zn...Zn distance of 3.867(1) Å, which is slightly shorter compared to that observed for  $L^3(\text{ZnEt})_2$  (3.968(1) Å) [34]. Moreover, the Zn–C and Zn–N bond lengths of **3** are comparable to those observed in monometallic  $\beta$ -diketimate  $L^1\text{ZnMe}$  complexes (Zn–N 1.948(2), 1.943(2) Å; Zn–C 1.941(3) Å) [56] and in base-stabilized  $\beta$ -diketimate (base) $L^1\text{ZnMe}$  (base = dmap, *t*BuPyr) complexes [49].

Single crystals of **4** were obtained from a solution in methylene chloride upon storage at  $-30^\circ\text{C}$  (Fig. 5). The bonding parameters within the bis- $\beta$ -diketimate ligand in **4** are almost identical to those observed for **3**,  $L^3(\text{ZnEt})_2$  [34] and for comparable Mg hydride complexes [55]. The carboxylate groups also adopt unsymmetrical-bridging positions between both zinc atoms as was observed for **1**, but the Zn–O bond lengths (Zn1–O1 1.997(2) Å, Zn1–O2 1.930(2) Å) differ even more than in **1**. The different Zn–O bond lengths in **4** clearly result from the fixed geometry of the bis- $\beta$ -diketimate ligand. The zinc atoms in **4** adopt slightly distorted tetrahedral coordination geometries as was expected for fourfold-coordinated zinc atoms. Compared to **3**, the Zn–N bond lengths are almost identical (Zn1–N1 1.940(2) Å, Zn1–N2 1.956(2) Å), whereas the presence of the bridging carboxylate groups results in a significantly shorter

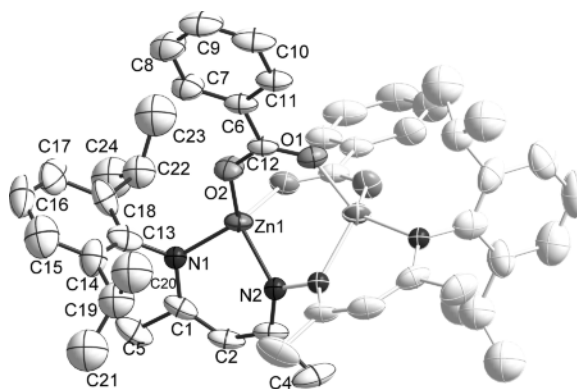


Fig. 5. Molecular structure of **4** in the solid state; hydrogen atoms and the second orientation of the ligand have been omitted for clarity, displacement ellipsoids are drawn at the 50% probability level. The symmetry-generated part of the molecule is drawn in light grey ( $-x+1, y, -z+1/2$ ).

Zn...Zn distance of 3.201(1) Å compared to 3.867(1) Å observed for  $L^3(\text{ZnMe})_2$  **3**. The C–O bond lengths within the carboxylate bridge (C12–O1 1.248(3) Å, C12–O2 1.258(3) Å) are identical to those observed for **1** and **2**.

### Polymerization studies

The ring opening polymerization activity of the zinc complexes **1–4** toward *rac*-lactide was investigated in  $\text{CD}_2\text{Cl}_2$  solution at ambient temperature. Moreover, these studies were expanded to mixtures of **2–3** and the strong Lewis base diazabicycloundec-7-ene (DBU) as co-catalyst. Polymerization activities were measured using NMR spectroscopy. Of particular interest was the influence of the pendant donor arm ( $L^2$ ) in the dimeric carboxylate-bridged structures **1** and **2** and the role of the bridging carboxylate groups in the dinuclear zinc complexes **3** and **4**.

The zinc carboxylate complexes **1** and **4** do not show any polymerization activity toward *rac*-lactide. The inactivity of **1** was rather surprising since the comparable dimeric zinc acetate complex  $[\text{L}^1\text{Zn}-\mu, \eta^2\text{-O}_2\text{CMe}]_2$  was found to be catalytically active in the ROP of *rac*- and *meso*-lactide, even though only polymers with broad polydispersities and low molecular weights have been obtained [24]. In contrast, the dimeric zinc carboxylate complex **2** containing the pendant donor arm as well as the dinuclear zinc methyl compound **3** were found to be active in *rac*-lactide polymerization at am-



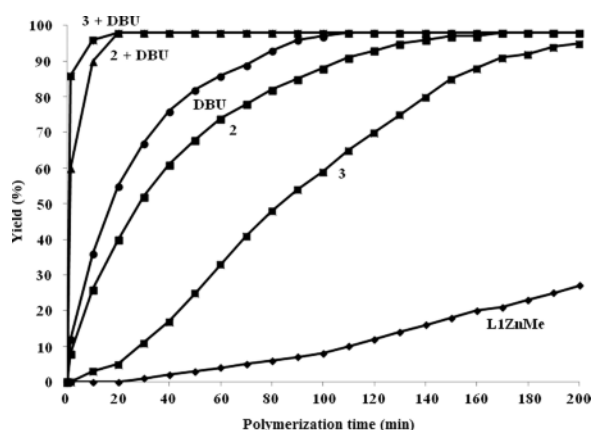


Fig. 6. Lactide polymerization kinetics in dichloromethane at ambient temperature [lactide to catalyst ratio: 200] [ $c_{\text{cat}}: 8.3 \times 10^{-3} \text{ mol L}^{-1}$ ] **2** [ $\text{L}^2\text{ZnO}_2\text{C}(\text{C}_6\text{H}_5)$ ] and **3** [ $\text{L}^3(\text{ZnMe})_2$ ] (+ co-catalyst DBU) compared to the mononuclear catalyst  $\text{L}^1\text{ZnMe}$  and DBU. [ $\text{L}^1\text{ZnO}_2\text{C}(\text{C}_6\text{H}_5)$ ] (**1**) and [ $\text{L}^3(\text{ZnO}_2\text{C}(\text{C}_6\text{H}_5))_2$ ] (**4**) do not show any activity in solution at ambient temperature within 600 min.

bient temperature. Since the catalytic activity of the mononuclear zinc methyl complex  $\text{L}^1\text{ZnMe}$  is roughly half of that of **3**, cooperative effects between the two zinc atoms in **3** can be ruled out. The catalytic activity of the zinc complexes **2** and **3** can be further increased by the addition of the external Lewis base DBU. Mixtures of **2**/DBU and **3**/DBU were found to polymerize 200 parts of lactide within 10 min in  $\text{CD}_2\text{Cl}_2$  at ambient temperature (Fig. 6).

$^1\text{H}$  NMR analyses of the crude polymerization products showed resonances due to the starting zinc complexes **2** and **3**.  $P_i$  values as determined by homonuclear decoupled  $^1\text{H}$  NMR spectra showed predominantly atactic polymers.  $M_w$  and polydispersity index (PDI) values were determined by gel permeation chromatography (see Table 1).

Note that no bimodal molecular weight distributions were detected. MALDI-TOF MS analyses of the crude polymerization product as-obtained with catalyst **2** (lactide/catalyst = 20 : 1) showed the presence of cyclic and linear  $n \times 72 \text{ g mol}^{-1}$  polylactide fragments with OH/OH end groups, resulting from the hydrolytic workup of the crude polymer. No lactide-carboxylate fragments were detected in the spectra, as would be expected for a coordination/insertion polymerization mechanism (CIM). These findings point to a modified activated-monomer mechanism (AMM), in which the lactide is first coordinated to a metal center

Table 1. Molecular weight and polydispersity index of the resulting polylactide as obtained from polymerization reactions in solution at room temperature [ $c_{\text{cat}}: 8.3 \times 10^{-3} \text{ mol L}^{-1}$ ].

| Catalyst  | Time (min) | conv. <sup>a</sup> (%) | $M_w^b$ ( $10^4 \text{ g mol}^{-1}$ ) | PDI <sup>c</sup> | $P_i^d$ |
|---|------------|------------------------|---------------------------------------|------------------|---------|
| <b>1</b> $\text{L}^1\text{ZnO}_2\text{CPh}$     | –          | –                      | –                                     | –                | –       |
| <b>2</b> $\text{L}^2\text{ZnO}_2\text{CPh}$     | 120        | 93                     | 8.6                                   | 1.9              | 0.63    |
| <b>3</b> $\text{L}^3(\text{ZnMe})_2$            | 180        | 92                     | 10.0                                  | 1.6              | 0.64    |
| <b>4</b> $\text{L}^3(\text{ZnO}_2\text{CPh})_2$ | –          | –                      | –                                     | –                | –       |
| <b>2</b> + DBU                                  | 10         | 90                     | 3.4                                   | 1.5              | 0.31    |
| <b>3</b> + DBU                                  | 10         | 96                     | 5.8                                   | 1.6              | 0.57    |
| DBU (ref. [48])                                 | 80         | 93                     | 16.2                                  | 1.9              | 0.30    |
| $\text{L}^1\text{ZnMe}$                         | 600        | 88                     | 8.2                                   | 1.2              | 0.88    |

<sup>a</sup> Estimated from  $^1\text{H}$  NMR integration of the relative intensities of the OCHMe resonance and the residual *rac*-lactide and polylactide resonances in  $\text{CD}_2\text{Cl}_2$ ; <sup>b</sup> determined by GPC analysis in THF at 23 °C. <sup>c</sup>  $\text{PDI} = M_w/M_n$ ; <sup>d</sup> determined by analysis of the OCHMe resonances of selectively homonuclear decoupled  $^1\text{H}$  NMR spectra.

and then activated by an external alcohol, as was previously observed for zinc amidinate complexes [48]. The hemilabile pendant donor arm plays a key role for the polymerization activity of the zinc complex **2**. The lactide monomer coordinates to the electrophilic Zn atom in complex **2** by replacement of the pendant amine arm. The pendant dimethylamine base or the external stronger base (DBU) then attacks the electrophilic carbonyl atom of the coordinated lactide.

## Conclusion

Mono- and dinuclear zinc methyl complexes  $\text{L}^1\text{ZnMe}$ ,  $\text{L}^2\text{ZnMe}$  and  $\text{L}^3(\text{ZnMe})_2$  react with benzoic acid with alkane elimination and subsequent formation of the dimeric zinc carboxylate complexes ( $\text{L}^{1/2}\text{ZnO}_2\text{CPh})_2$  **1** and **2** and the bis- $\beta$ -diketiminato zinc carboxylate [ $\text{L}^3(\text{ZnO}_2\text{CPh})_2$ ] **4**. While the Zn–O bond lengths of the bridging carboxylate units are identical (**2**) or differ only slightly (**1**), they differ more significantly in **4** due the fixed geometry of the bis- $\beta$ -diketiminato ligand. The zinc atoms in **1** and **4** are tetrahedrally coordinated, whereas those in complex **2** are additionally coordinated by the hemilabile donor sidearm leading to a fivefold-coordination. The Zn–Zn distance in the carboxylate complex **4** is significantly shorter than that observed in **3**. Complexes **2** and **3** are active *rac*-lactide polymerization catalysts, in particular in the presence of the strong Lewis base DBU. In case of the zinc complex **2** the catalysis proceeded

via a slightly modified activated-monomer mechanism (AMM) as was shown by MALDI-TOF MS analysis of the resulting polymer.

## Experimental Section

The air- and moisture-sensitive compounds were handled under inert gas atmosphere (argon, < 0.3 ppm O<sub>2</sub>) using standard vacuum techniques and a glove box (MBraun Unilab V2.0). Solvents were carefully dried over CaH<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>) or Na-K alloy (pentane, hexane), degassed and stored in teflon-sealed glass vessels over molecular sieve. L<sup>1</sup>ZnMe [56], L<sup>2</sup>ZnMe [48], and L<sup>3</sup>(H)<sub>2</sub> [34], were synthesized according to literature methods. <sup>1</sup>H and <sup>13</sup>C spectra were recorded with a Bruker Avance 300 spectrometer and are referenced to internal CD<sub>2</sub>Cl<sub>2</sub> (<sup>1</sup>H: δ = 5.36 ppm, <sup>13</sup>C: δ = 53.4 ppm). Homonuclear-decoupled <sup>1</sup>H NMR spectra were obtained by analysis of the OCHMe resonances with a Bruker Avance III HD 600 spectrometer. IR spectra were recorded with a Bruker FT-IR spectrometer with attenuated total reflection and analyzed by the OPUS software. Elemental analyses were performed at the Labor für Elementaranalyse of the University of Duisburg-Essen. GPC data, the average molar mass (*M*<sub>n</sub>) and molar mass distribution (*M*<sub>w</sub>/*M*<sub>n</sub>) were obtained by gel permeation chromatography (GPC) in THF at 23 °C (flow rate 1 mL min<sup>-1</sup>). The Column (PSS-SDV analytical linear XL 10 μm) were used with a refractive index detector (Agilent Technologies 1200 Series PSS) and calibrated with a polystyrene standard-Kit (PSS-Kit, Poly(styrene) high; Mp 682–1,670,000 D; 12 × 1 g; Lot No.: PSS-pskith). Kuhn-Mark-Houwink parameters for polystyrene standards were used (KPS = 0.011 mL<sup>-1</sup>, α<sub>PS</sub> = 0.725). The polymer samples were dissolved in THF (1 mg mL<sup>-1</sup>) at 23 °C. MALDI-TOF-MS analysis was performed on a Bruker Autoflex III, 200 Hz, Smart beam laser 355 nm. The polymer samples were dissolved in THF, and potassium trifluoroacetate was used as cationization agent. The matrix is 2,5-dihydroxybenzoic acid.

### L<sup>1</sup>ZnO<sub>2</sub>C(C<sub>6</sub>H<sub>5</sub>) (1)

L<sup>1</sup>ZnMe (0.50 g, 1.0 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and cooled to -30 °C. A solution of benzoic acid (0.12 g, 1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added dropwise, immediately resulting in a smooth gas evolution, and the resulting mixture was stirred for 2 h upon warming to ambient temperature. The solvent was removed *in vacuo*, and the resulting solid was dissolved in 5 mL of THF and stored at -30 °C. Colorless crystals of **1** were obtained within 24 h (0.37 g, 61%; m. p. 240 °C). – C<sub>36</sub>H<sub>46</sub>N<sub>2</sub>O<sub>2</sub>Zn (604.14): calcd. C 71.6, H 7.7, N 4.6; found C 66.1, H 7.8, N 3.9. – <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ = 1.23 (d,

<sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.27 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.83 (s, 6H, β-CCH<sub>3</sub>), 3.22 (sept, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 5.08 (s, 1H, γ-CH), 7.20–7.60 (6H, *m/p*-H), 7.80–8.24 (5H, CH<sub>(Aryl)</sub>) ppm. – <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ = 23.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.6 (β-CCH<sub>3</sub>), 23.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 94.4 (γ-C), 123.5 (*m*-C), 125.7 (*p*-C), 127.8 (CH<sub>(Aryl)</sub>), 130.0 (CH<sub>(Aryl)</sub>), 131.5 (CH<sub>(Aryl)</sub>), 134.5 (C<sub>q</sub>), 142.4 (*o*-C), 144.5 (*i*-C), 169.7 (β-CCH<sub>3</sub>) 174.2 (C<sub>q</sub>) ppm. – ATR-IR: ν = 3057, 2961, 2926, 2866, 1609, 1546, 1436, 1408, 1316, 1258, 1177, 1090, 1014, 859, 793, 758, 714, 679, 489, 390 cm<sup>-1</sup>.

### L<sup>2</sup>ZnO<sub>2</sub>C(C<sub>6</sub>H<sub>5</sub>) (2)

L<sup>2</sup>ZnMe (0.50 g, 2.0 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and cooled to -30 °C. A solution of benzoic acid (0.24 g, 2.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added dropwise, immediately resulting in a smooth gas evolution. The clear solution was slowly warmed to ambient temperature and stirred for another 2 h. The solution was concentrated to 5 mL and stored at -30 °C. Colorless crystals of **2** were obtained within 24 h (0.52 g, 73%; m. p. 194 °C). – C<sub>16</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>Zn (355.73): calcd. C 54.0, H 6.2, N 7.9; found C 54.0, H 6.2, N 8.3. – <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ = 2.03 (s, 3H, C<sub>β</sub>CH<sub>3</sub>), 2.16 (s, 3H, C<sub>δ</sub>CH<sub>3</sub>), 2.46 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.80 (t, <sup>3</sup>J<sub>HH</sub> = 5.6 Hz, 2H, CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>), 3.46 (t, <sup>3</sup>J<sub>HH</sub> = 5.6 Hz, 2H, C<sub>β</sub>NCH<sub>2</sub>), 4.93 (s, 1H, C<sub>γ</sub>H), 7.43–8.11 (5H, CH<sub>(Aryl)</sub>) ppm. – <sup>13</sup>C NMR (150.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ = 23.0 (C<sub>β</sub>CH<sub>3</sub>), 27.5 (C<sub>δ</sub>CH<sub>3</sub>), 45.5 (N(CH<sub>3</sub>)<sub>2</sub>), 45.6 (CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>), 59.2 (C<sub>β</sub>NCH<sub>2</sub>), 96.4 (C<sub>γ</sub>), 128.4 (CH<sub>(Aryl)</sub>), 130.6 (CH<sub>(Aryl)</sub>), 131.9 (CH<sub>(Aryl)</sub>), 135.2 (C<sub>q</sub>), 172.1 (C<sub>β</sub>N), 174.1 (C<sub>q</sub>), 182.9 (C<sub>δ</sub>O) ppm. – ATR-IR: ν = 3064, 2999, 2914, 2833, 2788, 1616, 1566, 1509, 1458, 1399, 1342, 1261, 1025, 935, 845, 715, 676, 561, 426 cm<sup>-1</sup>.

### L<sup>3</sup>(ZnMe)<sub>2</sub> (3)

A solution of L<sup>3</sup>(H)<sub>2</sub> (1.03 g, 2.0 mmol) in toluene (10 mL) was added to a solution of ZnMe<sub>2</sub> (3.5 mL, 1.2 M in toluene, 4.2 mmol) at -30 °C, and the yellowish solution was stirred for 5 h at ambient temperature. The solvent was removed *in vacuo* and the resulting solid was dissolved in 5 mL of *n*-pentane. The solution was stored at -30 °C, yielding colorless crystals of **3** within 24 h (1.25 g, 93%; m. p. 187 °C). – C<sub>36</sub>H<sub>54</sub>N<sub>4</sub>Zn<sub>2</sub> (673.59): calcd. C 64.2, H 8.1, N 8.3; found C 65.1, H 8.2, N 8.4. – <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ = -0.98 (s, 6H, ZnCH<sub>3</sub>), 1.06 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.11 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.17 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.22 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.69 (s, 6H, CH<sub>3</sub>CN), 2.04 (s, 6H, CH<sub>3</sub>CN), 2.97 (sept, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.97 (sept, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.82 (s, 2H, C<sub>γ</sub>H) 7.19 (6H, *m/p*-H) ppm. – <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):

$\delta = -17.8$  (ZnCH<sub>3</sub>), 21.7 (CH<sub>3</sub>CN), 23.4 (CH<sub>3</sub>CN), 23.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 92.8 (C<sub>γ</sub>), 123.8 (CH<sub>(N-Aryl)</sub>), 124.0 (CH<sub>(N-Aryl)</sub>), 125.8 (CH<sub>(N-Aryl)</sub>), 142.4 (C<sub>q</sub>), 142.5 (C<sub>q</sub>), 145.1 (C<sub>q</sub>), 166.3 (C<sub>q</sub>), 166.4 (C<sub>q</sub>) ppm. – ATR-IR:  $\nu = 3060, 2956, 2921, 2865, 2834, 1605, 1540, 1519, 1441, 1360, 1317, 1255, 1189, 1163, 1100, 1054, 1019, 950, 923, 858, 796, 759, 739, 709, 654, 550, 432$  cm<sup>-1</sup>.

### L<sup>3</sup>(ZnO<sub>2</sub>C(C<sub>6</sub>H<sub>5</sub>))<sub>2</sub> (**4**)

A solution of benzoic acid (0.24 g, 2.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added dropwise to a solution of L<sup>3</sup>(ZnMe)<sub>2</sub> (0.67 g, 1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) at  $-30$  °C. The resulting yellowish solution was slowly warmed to ambient temperature and stirred for another 2 h. The solution was concentrated to 5 mL and stored at  $-30$  °C, yielding colorless crystals of **4** within 24 h (0.79 g, 89%; m. p. 193 °C).

– C<sub>48</sub>H<sub>58</sub>N<sub>4</sub>O<sub>4</sub>Zn<sub>2</sub> (885.75): calcd. C 65.1, H 6.6, N 6.3; found C 62.4, H 6.6, N 5.6. – <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta = 1.24$  (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.28 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.31 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.35 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.72 (s, 6H, CH<sub>3</sub>CN), 1.99 (s, 6H, CH<sub>3</sub>CN), 3.17 (sept, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.72 (sept, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.61 (s, 2H, C<sub>γ</sub>H), 7.26 (6H, *m/p*-H), 7.35–7.89 (10H, CH<sub>(Aryl)</sub>) ppm. – <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta = 20.0$  (CH<sub>3</sub>CN), 23.1 (CH<sub>3</sub>CN), 23.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 90.9 (C<sub>γ</sub>), 123.8 (CH<sub>(N-Aryl)</sub>), 124.1 (CH<sub>(N-Aryl)</sub>), 125.7 (CH<sub>(N-Aryl)</sub>), 128.4 (CH<sub>(Aryl)</sub>), 130.7 (CH<sub>(Aryl)</sub>), 132.5 (CH<sub>(Aryl)</sub>), 134.4 (C<sub>q</sub>), 143.0 (C<sub>q</sub>), 143.4 (C<sub>q</sub>), 144.8 (C<sub>q</sub>), 167.8 (C<sub>q</sub>), 168.2 (C<sub>q</sub>), 174.3 (C<sub>q</sub>) ppm. – ATR-IR:  $\nu = 3058, 2959, 2924, 2866, 1606, 1569, 1508, 1401, 1354, 1317, 1256, 1100, 1022, 917, 796, 714, 676, 475, 434, 395$  cm<sup>-1</sup>.

Table 2. Crystal structure data for **1–4**.

|  | <b>1</b>   | <b>2</b>  | <b>3</b>   | <b>4</b>  |
|--|--|---|--|---|
| Empirical formula  | C <sub>74</sub> H <sub>95</sub> N <sub>4</sub> O <sub>4.50</sub> Zn <sub>2</sub> | C <sub>34</sub> H <sub>48</sub> Cl <sub>4</sub> N <sub>4</sub> O <sub>6</sub> Zn <sub>2</sub> | C <sub>36</sub> H <sub>54</sub> N <sub>4</sub> Zn <sub>2</sub>       | C <sub>48</sub> H <sub>58</sub> N <sub>4</sub> O <sub>4</sub> Zn <sub>2</sub> |
| <i>M</i> <sub>r</sub>  | 1243.27  | 881.30  | 673.57   | 885.72  |
| Crystal size, mm   | 0.380 × 0.350 × 0.220  | 0.280 × 0.250 × 0.180   | 0.4 × 0.3 × 0.3  | 0.320 × 0.240 × 0.180   |
| <i>T</i> , K   | 100(1)   | 180(1)  | 179(1)   | 193(1)  |
| Crystal system   | monoclinic   | triclinic   | monoclinic   | monoclinic  |
| Space group  | <i>P</i> 2 <sub>1</sub> / <i>c</i>   | <i>P</i> $\bar{1}$  | <i>P</i> 2 <sub>1</sub> / <i>n</i>                                   | <i>C</i> 2/ <i>c</i>  |
| <i>a</i> , Å   | 19.0166(8)   | 9.0298(13)  | 15.067(2)  | 19.6071(14)   |
| <i>b</i> , Å   | 19.3766(8)   | 10.3037(15)   | 16.339(3)  | 9.1261(6)   |
| <i>c</i> , Å   | 18.6455(8)   | 11.8916(17)   | 15.393(3)  | 28.449(2)   |
| $\alpha$ , deg   | 90   | 75.143(5)   | 90   | 90  |
| $\beta$ , deg  | 101.6110(10)   | 68.192(5)   | 101.521(5)   | 108.932(3)  |
| $\gamma$ , deg   | 90   | 86.895(5)   | 90   | 90  |
| <i>V</i> , Å <sup>3</sup>  | 6729.8(5)  | 991.8(3)  | 3713.2(10)   | 4815.2(6)   |
| <i>Z</i>   | 4  | 1   | 4  | 4   |
| <i>D</i> <sub>calcd.</sub> , g cm <sup>-3</sup>                          | 1.23   | 1.48  | 1.21   | 1.22  |
| $\mu$ (MoK $\alpha$ ), mm <sup>-1</sup>                                  | 0.8  | 1.5   | 1.3  | 1.0   |
| Transmissions  | 0.75–0.61  | 0.75–0.58   | 0.75–0.56  | 0.75–0.63   |
| <i>F</i> (000), <i>e</i>   | 2652   | 456   | 1432   | 1864  |
| Index ranges   | $-28 \leq h \leq 26$<br>$-28 \leq k \leq 28$<br>$-27 \leq l \leq 27$             | $-12 \leq h \leq 12$<br>$-13 \leq k \leq 14$<br>$-16 \leq l \leq 16$                          | $-20 \leq h \leq 20$<br>$-22 \leq k \leq 22$<br>$-21 \leq l \leq 21$ | $-26 \leq h \leq 25$<br>$-12 \leq k \leq 12$<br>$-37 \leq l \leq 38$          |
| $\theta$ <sub>max</sub> , deg  | 31.736   | 29.221  | 29.537   | 29.202  |
| Reflections collected  | 209 274  | 20 885  | 76 278   | 42 007  |
| Independent reflections  | 22 698   | 5306  | 10 110   | 6484  |
| <i>R</i> <sub>int</sub>  | 0.0451   | 0.0308  | 0.0473   | 0.0306  |
| Refined parameters   | 768  | 230   | 393  | 290   |
| <i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup> | 0.0670   | 0.0363  | 0.0285   | 0.0495  |
| <i>wR</i> <sub>2</sub> [all data] <sup>a</sup>                           | 0.1828   | 0.1019  | 0.0823   | 0.1279  |
| Goof <sup>b</sup>  | 1.129  | 1.037   | 1.131  | 1.126   |
| $\Delta\rho$ <sub>final</sub> (max/min), e Å <sup>-3</sup>               | 1.256/–0.977   | 0.780/–0.531  | 0.429/–0.571   | 0.671/–0.650  |

<sup>a</sup>  $R(F) = \Sigma |F_o| - |F_c| / \Sigma |F_o|$ ;  $wR(F^2) = [\Sigma \{w(F_o^2 - F_c^2)^2\} / \Sigma \{w(F_o^2)^2\}]^{0.5}$ ;  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$  mit  $P = [F_o^2 + 2F_c^2]/3$ , *a* and *b* constants chosen by programme; <sup>b</sup> Goof =  $[\Sigma \{w(F_o^2 - F_c^2)^2\} / (n - p)]^{0.5}$  with *n* data and *p* parameters.



*X-Ray structure determinations*

Crystallographic data of **1–4**, which were collected on a Bruker AXS APEX2 diffractometer (MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å) at 100(1) K (**1**), 180(1) K (**2**), 179(1) K (**3**), and 193(1) K (**4**), are summarized in Table 2, and selected bond lengths and angles are given in Table 3. The solid-state structures of **1–4** are shown in Figs. 2–5. The structures were solved by Direct Methods (SHELXS-97 [57, 58]) and refined anisotropically by full-matrix least-squares on  $F^2$  (SHELXL-97) [58, 59]. Semi-empirical absorption corrections were applied based on multi-scans of equivalent reflections (Bruker AXS APEX2). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model or rigid methyl groups. Crystals of complex **1** contain a THF molecule which is disordered over a center of inversion. Its atoms could not be refined anisotropically in a satisfactory manner. Complex **2** crystallized as a dichloromethane solvate. The diisopropylphenyl ligand of **4** was disordered over two positions. Its phenyl ring was constrained to form a regular hexagon, and distance restraints were applied to the isopropyl groups which could only be refined isotropically [59].

CCDC 1008546 (**1**), 1008539 (**2**), 1008535 (**3**), and 1008545 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from

Table 3. Selected bond lengths (Å) and angles (deg) for **1**, **2**, **3**, and **4**.

|  | <b>1</b> | <b>2</b> | <b>3</b> | <b>4</b> |
|--|----------|----------|----------|----------|
| Zn1–N1                                   | 1.987(2) | 2.016(2) | 1.941(1) | 1.940(2) |
| Zn1–N2                                   | 1.963(2) | –        | 1.958(1) | 1.956(2) |
| Zn1–O1                                   | –        | 2.025(2) | –        | –        |
| Zn1–O1 <sub>sub</sub>                    | 1.953(2) | 2.042(2) | –        | 1.997(2) |
| Zn1–O2 <sub>sub</sub>                    | 1.986(2) | 2.049(2) | –        | 1.930(2) |
| Zn1–N <sub>donor</sub>                   | –        | 2.243(2) | –        | –        |
| Zn1–C35                                  | –        | –        | 1.941(2) | –        |
| Zn1–Zn2                                  | 4.311(2) | 3.705(1) | 3.867(1) | 3.201(1) |
| N1–Zn1–N2                                | 99.3(1)  | –        | 94.5(1)  | 94.7(1)  |
| N1–Zn1–O1                                | –        | 91.3(1)  | –        | –        |
| N1–Zn1–N <sub>donor</sub>                | –        | 81.5(1)  | –        | –        |
| N1–Zn1–O1 <sub>sub</sub>                 | 117.3(1) | 104.9(1) | –        | 115.1(1) |
| N1–Zn1–O2 <sub>sub</sub>                 | 101.2(1) | 125.7(1) | –        | 119.0(1) |
| N1–Zn1–C35                               | –        | –        | 136.4(1) | –        |
| O1 <sub>sub</sub> –Zn1–O2 <sub>sub</sub> | 108.1(1) | 129.4(1) | –        | 103.2(1) |

The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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