DOI: 10.1002/zaac.200801382

Synthesis and Characterization of β-Diketiminate Zinc Complexes

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Dedicated to Professor Gerd Meyer on the Occasion of His 60th Birthday

Keywords: Zinc; β-Diketiminate; X-ray diffraction; Coordination chemistry; NMR spectroscopy

Abstract. Reactions of the monomeric β-diketiminate zinc complex MesNacNacZnMe (MesNacNac = $\{[2,6\text{-}(2,4,6\text{-}Me_3{-}C_6H_2)\text{-}N(Me)C)]_2CH\}$) with ROH (R = Me, Et, *i*Pr) yielded the corresponding zinc alkoxides $[MesNacNacZnOR]_2$ (R = Me **1**, Et **2**, *i*Pr **3**). In addition, the reaction of MesNacNacZnCl with various reducing agents such as potassium graphite, potassium, or sodium gave the Zn^{II} complex $[MesNacNac]_2Zn$ **4**. Compounds **1**−**4** were characterized by elemental analyses, mass and multinuclear (^1H, $^{13}C\{^1H\}$) NMR spectroscopy, and by single-crystal X-ray analysis.

Introduction

β-Diketiminato-ligands $\{(RN(R')C]_2CH\}$ have been demonstrated in the past to efficiently stabilize unusual low-valent [1], multiple-bonded [2], and cationic metal complexes [3]. One of the most striking features is that their steric demand can be precisely controlled by variation of the organic substituents R bound to the imine centre. β-Diketiminate zinc complexes, which are known for a long time [4], have received growing interest over the last decade. Amide and alkoxide complexes LZnX (X = NR_2, OR; L = β-diketiminato), in particular those containing the sterically demanding DippNacNac substituent (DippNacNac = $\{[(2,6\text{-}iPr_2{-}C_6H_3)N(Me)C)]_2CH\}$[5]), are very efficient living single-site catalysts for the ring-opening polymerization (ROP) of lactide [6] and the copolymerization of epoxides and carbon dioxide [7]. Moreover, the high potential of β-diketiminato-ligands to stabilize low-coordinate and low-valent compounds was demonstrated by the synthesis of the Zn−Zn bonded complex $DippNacNac_2Zn_2$ [8].

We became only recently interested in β-diketiminate zinc complexes and reported on the synthesis of several complexes of the type MesNacNacZnX (MesNacNac = $\{[(2,4,6\text{-}Me_3{-}C_6H_2)N(Me)C)]_2CH\}$, X = Cl, I, Me) [9] as well as the low-valent complex $MesNacNac_2Zn_2$ [10]. Herein, we report on the synthesis of β-diketiminate zinc alkoxides complexes of the type LZnOR (X = Me **1**, Et **2**, *i*Pr **3**) and $MesNacNac_2Zn$ (**4**), which was obtained from reduction reactions of MesNacNacZnX (X = Cl, I) with reducing agents such as sodium, potassium, and potassium graphite, respectively.

Experimental Section

General Procedure

Manipulations were performed in a glovebox under argon or with standard Schlenk techniques. Dry solvents were obtained from a solvent purification system (MBraun) and degassed prior to use. MesNacNacZnX (X = Me, Cl) [9] was prepared according to literature methods, alcohols were obtained from Acros and dried prior to use. A Bruker DMX300 spectrometer was used for NMR spectroscopy. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to internal C_6D_5H (^1H: δ = 7.154; ^{13}C: δ = 128.0). IR spectra were recorded with a Bruker Alpha-T FT-IR spectrometer. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were performed at the *Elementaranalyse Labor* of the University of Essen.

General synthesis of $\{[(2,4,6\text{-}Me_3{-}C_6H_2)N(Me)C)]_2CH\}ZnOR$ (R = Me 1, Et 2, *i*Pr 3): ROH (R = Me **1**, Et **2**, *i*Pr **3**, 5 mmol) was added at ambient temperature to MesNacNacZnMe (2.07 g, 5 mmol) dissolved in Et_2O (40 mL). After the gas evolution has stopped, the solution was stirred for additional 12 h. Colorless solids precipitate, which were isolated by filtration and recrystallized from solutions in toluene at −30 °C.

1: Yield 1.93 g (90 %), Mp: > 230 °C. Elemental Analysis $C_{48}H_{64}N_4O_2Zn_2$ (859.80 $g\cdot mol^{-1}$): found (calcd): H, 7.39 (7.50); C, 66.67 (67.05); N, 6.23 (6.52) %.

^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 1.50 (s, 6 H, β-CCH_3), 2.05 (s, 12 H, *o*-CH_3), 2.39 (s, 6 H, *p*-CH_3), 3.5 (s, 3 H, OCH_3), 4.76 (s, 1 H, γ-*CH*), 6.86 (s, 4 H, *m*-*H*). **^{13}C NMR** (75 MHz, C_6D_6, 25 °C): δ = 17.8 (*o*-CH_3), 20.9 (β-CCH_3), 22.7 (*p*-CH_3), 64.5 (OCH_3), 93.8 (γ-*C*), 129.1 (*m*-C), 131.6 (*o*-C), 132.1 (*p*-C), 145.2 (*ipso*-C), 167.5

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(β-C). **IR**: ν1543, 1521, 1454, 1378, 1259, 1202, 1148, 1079, 1013 cm^{-1}.

2: Yield 1.69 g (77 %), Mp: > 230 °C. Elemental Analysis $C_{50}H_{68}N_4O_2Zn_2$ (887.86 g·mol^{-1}): found (calcd): H, 7.64 (7.72); C, 67.42 (67.64); N, 6.30 (6.31) %.

^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): δ = 0.89 (m, 3 H, OCH$_2$*CH$_3$*), 1.39 (s, 6 H, β-C*CH$_3$*), 1.77 (s, 12 H, *o-CH$_3$*), 2.37 (s, 6 H, *p-CH$_3$*), 3.48 (m, 2 H, O*CH$_2$*CH$_3$), 4.70 (s, 1 H, γ-*CH*), 6.78 (s, 4 H, *m-H*) **^{13}C NMR** (75 MHz, [D$_8$]THF, 25 °C): δ = 18.6 (*o-CH$_3$*), 21.1 (OCH$_2$*C*H$_3$), 21.4 (β-C*C*H$_3$), 23.1 (*p*-CH$_3$), 61.7 (O*C*H$_2$CH$_3$), 94.4 (γ-*C*), 130.0 (*m*-C), 132.4 (*o*-C), 133.0 (*p*-C), 146.7 (*ipso*-C), 167.8 (β-C). **IR**: ν1544, 1523, 1403, 1261, 1202, 1148, 1021, 856 cm^{-1}.

3: Yield 1.8 g (78 %), Mp: > 230 °C. Elemental Analysis $C_{52}H_{72}N_4O_2Zn_2$ (915.91 g·mol^{-1}): found (calcd): H, 7.86 (7.92); C, 68.2 (67.67); N, 6.08 (6.12) %.

^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): δ = 0.86 (d, 6 H, CH(*CH$_3$*)$_2$), 1.41 (s, 6 H, β-C*CH$_3$*), 1.83 (s, 12 H, *o-CH$_3$*), 2.36 (s, 6 H, *p-CH$_3$*), 3.48 (m, 1 H, (*CH*)O), 4.77 (s, 1 H, γ-*CH*), 6.86 (s, 4 H, *m-H*). **^{13}C NMR** (75 MHz, [D$_8$]THF, 25 °C): δ = 19.3 (*o*-CH$_3$), 21.1 (β-C*C*H$_3$), 23.5 (*p*-CH$_3$), 28.2 (CH(*C*H$_3$)$_2$), 65.8 (O*C*H(CH$_3$)$_2$), 95.1 (γ-*C*), 130.0 (*m*-C), 132.7 (*o*-C), 133.2 (*p*-C), 146.9 (*ipso*-C), 168.1 (β-C). **IR**: ν1460, 1376, 1260, 1093, 1019, 799 cm^{-1}.

{[(2,4,6-Me$_3$−C$_6$H$_2$)N(Me)C)]$_2$CH}$_2$Zn (4): A solution of sodium naphtalenide (5 mmol) in THF was added dropwise to MesNacNacZnCl (2.16 g, 5 mmol) dissolved in THF (20 mL). The suspension was stirred at ambient temperature for 12 h and then filtered. The extract was reduced in volume and stored for 48 h at −30 °C. Compound **4** was obtained in form of colorless crystals.

4: Yield 1.8 g (78 %), Mp: > 230 °C. Elemental Analysis $C_{46}H_{58}N_4Zn$ (732.36 g·mol^{-1}): found (calcd): H, 7.92 (7.98); C, 75.14 (75.44); N, 7.48 (7.65) %.

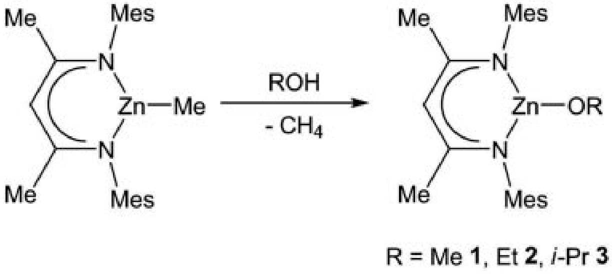
^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ = 1.52 (s, 6 H, β-C*CH$_3$*), 1.96 (s, 12 H, *o-CH$_3$*), 2.22 (s, 6 H, *p-CH$_3$*), 4.80 (s, 1 H, γ-*CH*), 6.70 (s, 4 H, *m-H*). **^{13}C NMR** (75 MHz, C$_6$D$_6$, 25 °C): δ = 18.2 (*o*-CH$_3$), 20.6 (β-C*C*H$_3$), 23.4 (*p*-*C*H$_3$), 94.1 (γ-*C*), 128.6 (*m*-C), 131.7 (*o*-C), 132.7 (*p*-C), 141.5 (*ipso*-C), 160.8 (β-C). **IR**: ν1552, 1515, 1453, 1398, 1258, 1148, 1007, 854, 779.

X-ray Structure Solution and Refinement of 1−4

Crystallographic data of **1**−**4** are given in Table 2. Figure 1, Figure 2 and Figure 4 show ORTEP diagrams of the solid-state structures of **2**−**4**, Figure 3 the reduced structure of **1** and Figure 5 the reduced structure of **4**. Single crystals of **1**−**4** were obtained from solutions in THF (**1**, **2**, **4**) and benzene (**3**) at −30 °C. Data were collected on a Bruker-AXS SMART APEX CCD. The structures were solved by Direct Methods (SHELXS-97) [11] and refined by full-matrix least-squares on F^2 (SHELXL-97) [12]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model. Multi-scan absorption corrections were applied. Crystallographic data of the structures (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-711909 (**1**), CCDC-711910 (**2**), CCDC-711911 (**3**), and CCDC-711912 (**4**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-Mail for inquiry: fileserv@ccdc.cam.ac.uk; E-Mail for deposition: deposit@ccdc.cam.ac.uk).

Results and Discussion

Equimolar amounts of MesNacNacZnMe and ROH react at ambient temperature with smooth evolution of methane and subsequent formation of the corresponding alkoxides MesNacNacZnOR (R = Me **1**, Et **2**, *i*Pr **3**) in high yield (Scheme 1).



Scheme 1. Synthesis of β-diketiminate zinc alkoxides by methane elimination reaction.

Compounds **1**−**3** were obtained as colorless crystalline solids after recrystallization from solutions in toluene at −30 °C. ^{1}H and ^{13}C NMR spectra of **1**−**3** show the expected resonances due to the MesNacNac ligand and the OR groups in the expected 1:1 intensities, whereas the resonances of the Zn−Me group has disappeared.

Single crystals of **1**−**3** suitable for X-ray structure determinations were obtained from solutions in THF (**1**, **2**) and benzene (**3**), respectively, at −30 °C. The molecular structures of **2** and **3** are shown in Figure 1 and Figure 2.

1 and **2** crystallize in the triclinic space group $P\bar{1}$ with two molecules in the unit cell, whereas **3** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. **1**−**3** adopt dimeric structures in the solid state with bridging OR groups, forming centrosymmetric four-membered Zn_2O_2 rings. As a consequence, the zinc atoms in **1**−**3** adopt distorted tetrahedral coordination spheres as was observed previously for complexes of the type {[(2,6-*i*Pr$_2$−C$_6$H$_3$)N(Me)C)]$_2$CH}ZnOR. Only {[(2,6-*i*Pr$_2$−C$_6$H$_3$)N(Me)C)]$_2$CH}ZnO*t*-Bu containing the sterically slightly more hindered *tert*-butoxy substituent is monomeric in the solid state [6a]. The β-diketiminato cores in **1**−**3** are almost planar with the sum of bond angles at N1, N2, C1 and C3 ranging from 359.9 to 360°. Moreover, the N−C and C−C bonds lengths of **1** and **2** within the six-membered ring are almost equal. They are in between typical values observed for single and double bonds, indicating a delocalized π-electron system. In contrast, the C−C bond lengths within the backbone of the β-diketiminato core of **3** [C1−C2 1.422(13), C2−C3 1.383(12) Å] differ significantly, indicating a disturbed π-electron system, which most likely results from the larger repulsive interac-

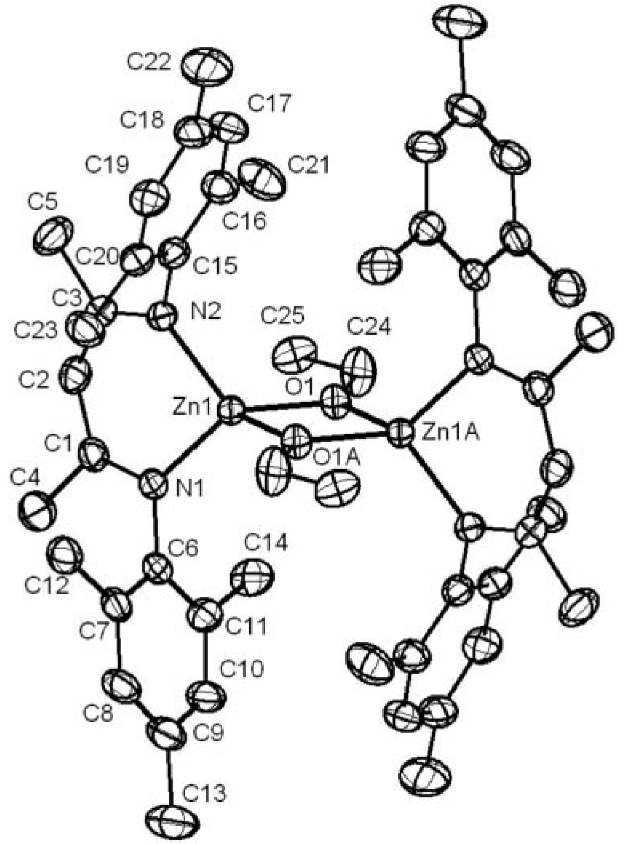


Figure 1. Molecular structure and atom numbering scheme of **2**; thermal ellipsoids are drawn at the 30 % probability level. The THF molecule and the hydrogen atoms have been omitted for clarity.

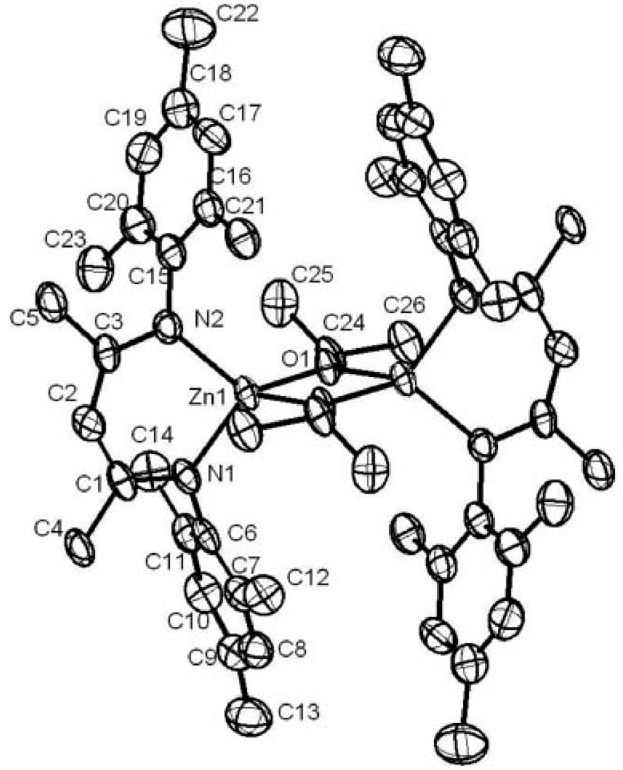


Figure 2. Molecular structure and atom numbering scheme of **3**; thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms and disordered benzene molecule have been omitted for clarity.

tions between the sterically encumbered MesNacNac substituent and the *i*Pr group.

The repulsive interactions between the MesNacNac substituent and the OR groups steadily increase with increasing steric demand of the alkoxy group as was expected. This can clearly be seen when comparing the deviation of the six-membered ZnN_2C_3 metallacycle from planarity. The tetracoordinate zinc atom in **1** has moved out of the plane by 0.419(3) Å, resulting in a *boat-type* conformation (see Figure 3). This value significantly increases up to 0.524(3) Å (**2**) and 0.592(3) Å (**3**), respectively. Comparable findings have been previously observed for DippNacNacZn*t*Bu(THF) and DippNacNacZnPh complexes [5d]. In addition, the increasing steric demand of the alkoxy substituent is reflected by a steady increase of the Zn−N bond lengths [average values 1.973 (**1**), 1.980 (**2**), 1.993 Å (**3**)]. Only $\{[(2,6\text{-}i\text{Pr}_2{-}\text{C}_6\text{H}_3)\text{N(Me)C})]_2\text{CH}\}\text{ZnO}i\text{-Pr}$, which contains the sterically most demanding Dipp substituent [6f], shows significantly longer Zn−N bond lengths [2.074(4), 2.054(4) Å]. In contrast, the Zn−O and Zn−N bond lengths, the endocyclic N−Zn−N, O−Zn−O and Zn−O−Zn bond angles as well as the bonding parameters of the MesNacNac ligand of **1**−**3** are very similar (see Table 1) and do not show any remarkable structural

Table 1. Selected bond lengths /Å and angles /° of **1**−**4**.

	1	**2**	**3**	**4**
Zn1−N1	1.977(3)	1.981(3)	1.990(7)	2.039(2)
Zn1−N2	1.969(3)	1.978(3)	1.995(7)	2.017(2)
Zn1−O1	1.951(3)	1.987(3)	1.952(5)	
Zn1−O1A	1.983(3)	1.949(3)	2.005(5)	
N1−C1	1.325(5)	1.326(5)	1.339(10)	1.332(2)
N1−C6	1.433(5)	1.435(5)	1.451(11)	1.441(2)
N2−C3	1.340(5)	1.321(5)	1.347(11)	1.330(2)
N2−C15	1.439(5)	1.439(5)	1.437(12)	1.439(2)
C1−C2	1.394(5)	1.393(7)	1.422(13)	1.403(3)
C2−C3	1.406(5)	1.403(6)	1.383(12)	1.403(3)
N1−Zn1−N2	98.3(2)	97.5(2)	96.1(3)	95.0(1)
N1−Zn1−O1	118.1(2)	117.4(2)	124.1(3)	
N2−Zn1−O1	125.6(2)	118.3(2)	122.2(3)	
O1−Zn1−O1A	81.3(2)	82.4(2)	81.1(2)	
Zn1−O1−Zn1A	98.7(2)	97.6(2)	98.9(2)	
Zn1−N1−C1	119.8(2)	118.5(3)	119.6(6)	117.0(2)
Zn1−N1−C6	121.2(2)	122.8(3)	124.8(5)	127.5(2)
Zn1−N2−C3	118.9(2)	119.1(3)	118.4(7)	119.1(2)
Zn1−N2−C15	123.7(2)	122.2(3)	123.5(6)	123.6(2)
C1−N1−C6	118.9(3)	118.7(4)	115.6(7)	115.3(2)
C3−N2−C15	117.3(3)	118.6(3)	118.1(8)	117.3(2)
N1−C1−C2	124.2(3)	124.6(4)	123.6(9)	124.8(2)
N2−C3−C2	124.9(3)	123.9(4)	124.9(9)	124.1(2)
C1−C2−C3	129.4(4)	129.5(4)	129.0(8)	128.7(2)
C2−C1−C4	116.1(4)	116.2(4)	116.4(8)	115.3(2)
C2−C3−C5	116.1(3)	116.9(3)	116.6(8)	115.9(2)

differences relative to other β-diketiminate zinc alkoxide complexes containing $\{[(2,6\text{-}Me_2{-}C_6H_3)N(Me)C)]_2CH\}$ [7b], $\{[(2,6\text{-}Et_2{-}C_6H_3)N(Me)C)]_2CH\}$ [7c, 13], and $\{[(2,6\text{-}Pr_2{-}C_6H_3)N(Me)C)]_2CH\}$ [13] substituents, respectively.

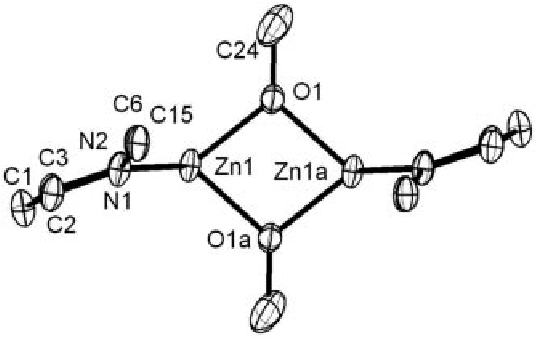
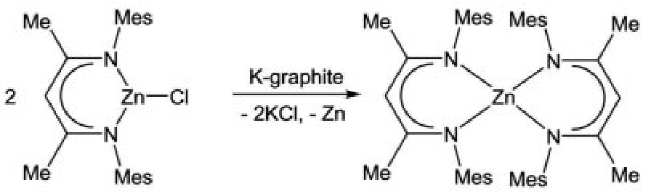


Figure 3. Reduced molecular structure and atom numbering scheme of **1** showing the *boat-type* conformation of the β-diketiminato groups; thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms, Dipp groups and *t*Bu groups except for the α carbon atoms have been omitted for clarity.

Due to our long term interest in low-valent metal complexes, we became also interested in complexes of the type R_2Zn_2, containing a central Zn−Zn bond with the zinc atoms in the formal oxidation state +1. Complexes of this type are known since the epoch-making synthesis of decamethyldizincocene $Cp^*{}_2Zn_2$ by *Carmona* et al. in 2004 [14]. Since then, some other low-valent organozinc complexes have been structurally characterized [8, 15]. They were typically prepared by *Wurtz-analogous* coupling reactions of the corresponding halide-substituted compounds RMX (X = Cl, Br, I) containing sterically encumbered organic substituents. Therefore, we investigated reactions of MesNacNacZnX (X = Cl, I) with several reducing agents such as sodium, potassium, sodium naphthalenide and potassium graphite. However, only the Zn^{II} complex $MesNacNac_2Zn$ **4** could be isolated from these reactions. The formation of **4** can be rationalized by a disproportionation reaction of $MesNacNac_2Zn_2$, which is most likely formed *in situ* as a reaction intermediate during the reduction reaction. However, the low-valent organozinc complex is not stable under these specific reaction conditions and consequently undergoes disproportionation reaction with subsequent formation of elemental zinc and **4** (Scheme 2) [16].



Scheme 2. Synthesis of the bis-β-diketiminate zinc complex **4** by reduction reaction.

Single crystals of **4** were obtained from a solution in THF at −30 °C. Compound **4** crystallizes in the monoclinic space group *C*2/*c* with four molecules in the unit cell (Figure 4).

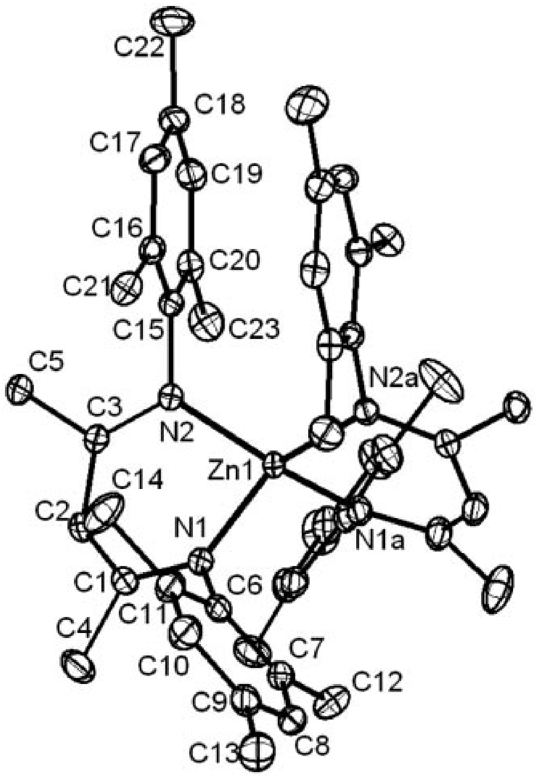


Figure 4. Molecular structure and atom numbering scheme of **4**; thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms and disordered thf molecule have been omitted for clarity.

The central zinc atom in **4** adopts a distorted tetrahedral coordination sphere with the endocyclic N1−Zn−N2 bond angle [94.98(6)°] being significantly smaller than the exocyclic N−Zn−N bond angles [N1−Zn1−N1a 113.26(9), N1−Zn1−N2a / N2−Zn1−N1a 116.27(6), N2−Zn1−N2a (122.45(8)°]. The β-diketiminato core significantly deviates from planarity as can clearly be seen in Figure 5.

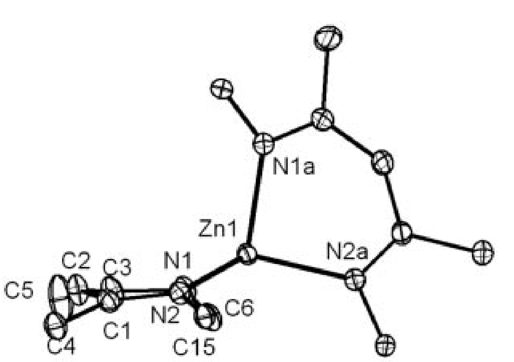


Figure 5. Reduced molecular structure and atom numbering scheme of **4** showing the *boat-type* conformation of the β-diketiminato groups; thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms and Dipp groups except for the α carbon atoms have been omitted for clarity.

Table 2. Crystallographic details of **1**−**4**.

	1	**2**$^{d)}$	**3**$^{e)}$	**4**$^{f)}$
emp. form.	$C_{48}H_{64}N_4O_2Zn_2$	$C_{50}H_{68}N_4O_2Zn_2 \cdot x(\text{thf})$	$C_{52}H_{72}N_4O_2Zn_2 \cdot x(C_6H_6)$	$C_{50}H_{66}N_4Zn \cdot x(\text{thf})$
mol. mass	429.89	455.94	496.99	876.54
cryst syst.	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$C2/c$
a /Å	8.739(3)	11.3832(11)	12.6294(9)	16.9305(12)
b /Å	10.633(5)	11.4399(12)	11.3811(8)	15.9803(12)
c /Å	13.575(6)	12.4482(13)	21.1965(16)	19.9972(15)
α /Å	67.746(10)	96.021(2)		
β /Å	80.283(19)	90.778(2)	90.304(6)	98.958(4)
γ /Å	77.155(14)	114.759(2)		
V /Å^3	1133.3(9)	1460.9(3)	3046.7(4)	5344.3(7)
Z	2	2	4	4
T /K	193(1)	296(1)	296(1)	173(1)
radiation (λ /Å)	Mo-K_α (0.71073)	Mo-K_α (0.71073)	Mo-K_α (0.71073)	Mo-K_α (0.71073)
μ /mm^{-1}	1.099	0.857	0.826	0.499
$D_{\text{calcd.}}$ /g·cm^{-3}	1.260	1. 360	1.084	1.089
$2\theta_{\max}$ /°	48	50	46	54
cryst dim. /mm	0.24 × 0.20 × 0.12	0.24 × 0.18 × 0.15	0.18 × 0.15 × 0.12	0.28 × 0.12 × 0.08
no. reflns	23525	12139	42665	90638
unique	3604	4946	4298	5663
R_{merg}	0.0577	0.0574	0.2376	0.0731
param./restraints	254 / 0	282 / 0	326 / 0	277 / 0
$R1^{a)}$	0.0412	0.0564	0.0791	0.0420
$wR2^{b)}$	0.0990	0.1594	0.2617	0.1185
goodness of fit$^{c)}$	1.053	0.991	1.021	1.043
final max/min. $\Delta\rho$ /e·Å^{-3}	0.311 / −0.536	0.486 / −0.261	0.433 / −0.465	0.339 / −0.377

a) $R1 = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$ (for $I > 2\sigma\ (I)$). b) $wR2 = \{\Sigma\ [w(F_o{}^2 - F_c{}^2)^2]/\Sigma\ [w(F_o{}^2)^2]\}^{1/2}$. c) Goodness of fit $= \{\Sigma\ [w(|F_o{}^2| - |F_c{}^2|)^2]/(N_{\text{observns}} - N_{\text{params}})\}^{1/2}$. d) THF molecule refined with reduced SOF 0.5. e) Benzene atoms C(31)−C(36) disordered over two sites with SOF 0.5 together with the riding hydrogen atoms. f) Refinement with corrected reflection data after PLATON/squeeze run based on data calculated by omitting highly disordered benzene molecule but keeping mostly ordered THF molecule (ref. A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, C-34). The alternative original refinement of the untreated reflection data set produces three different Fourier peaks with ~1.8 e·Å^{-3} caused by a highly disordered benzene molecule positioned around Wyckoff letter '*c*'. The refinement with these three peaks as carbon atoms with SOF 0.5 results in $R1 = 0.0501$.

The zinc atom has moved out of the plane by 0.680(3) Å, which is an even larger deviation than the value observed for complex **3**. The sum of bond angles at N1, N2, C1 and C3 is almost 360°. The N−C [N1−C1 1.332(2), N2−C3 1.330(2) Å] and C−C bonds lengths [C1−C2 1.403(3), C2−C3 1.403(3) Å] of the β-diketiminato core are equal, indicating a delocalized π-electron system. Comparable structural parameters have been previously observed in comparable bis-ligates $\{[(R)N(Me)C]_2CH\}_2Zn$ (R = 2-*i*Pr−C_6H_4, 2,6-Et_2−C_6H_3) [7c] and $\{[(R)N(Me)C]_2CH\}_2M$ (M = Mg, Ca, Sr, Ba; R = *i*Pr, *t*Bu, 2-*i*Pr-C_6H_4, 2,6-*i*Pr_2−C_6H_3) [17].

Conclusion

Three dimeric β-diketiminato zinc alkoxides MesNacNacZnOR have been prepared by methane elimination reaction between MesNacNacZnMe and alcohols ROH. In addition, reduction reaction of MesNacnacZnX with various reducing agents only gave the biscomplex $(\text{MesNacNac})_2Zn$, most likely due to a disproportionation reaction.

Acknowledgement

We gratefully acknowledge financial support by the *Deutsche Forschungsgemeinschaft* (DFG).

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Received: January 1, 2009