Synthesis and Characterization of β -Diketimate Zinc Complexes**

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Abstract. The monomeric β -diketimate zinc complex (Mes)NacNacZnMe **1** (MesNacNac = {[2,6-(2,4,6-Me₃-C₆H₂)N(Me)C]₂CH}) was obtained in almost quantitative yield from the reaction of ZnMe₂ with (Mes)NacNacH. Reaction of **1** with either Me₃NHCl or a solution of HCl in Et₂O yielded (Mes)NacNacZnCl **2**, whereas (Mes)NacNacZnI **3** was obtained from the reaction of **1** with I₂. **1** - **3** were characterized by elemental analyses, mass and multinuclear (¹H, ¹³C{¹H}) NMR spectroscopy (¹H, ¹³C), **3**·THF also by single crystal X-ray analysis.

Keywords: Zinc, β -Diketimate, X-Ray Structure, DFT calculation

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** Dedicated to Prof. Dr. Edgar Niecke on the occasion of his 70th birthday

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Introduction

β -Diketiminato-ligands **I** are valuable substituents in coordination chemistry due to their high potential to act as spectator ligand (such as Cp) and their exceptional large steric demand, which moreover can easily be tuned by variation of the organic substituents bound to the imine centers.[1] As a consequence, a large number of metal complexes including unusual low-valent,[2] multiple-bonded,[3] and cationic p-block complexes[4] have been prepared by use of a large variety of β -diketiminates. Zinc complexes of the desired type, which are known for long times,[5] have seen a remarkable renaissance in the last decade, most likely due to the potential application of amide and alkoxide complexes of the type LZnX **II** ($\text{X} = \text{NR}_2, \text{OR}$; $\text{L} = \beta$ -diketiminato) to serve as *living single-site catalysts* for the ring-opening polymerization (ROMP) 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 with the synthesis of the Zn-Zn bonded complex LZn-ZnL **III** ($\text{L} = \{[2,6-(2,6-i\text{-Pr}_2\text{-C}_6\text{H}_3)\text{N}(\text{Me})\text{C}]\}_2\text{CH}\}$), which was obtained by reduction of the corresponding iodine complex $\text{LZn}(\mu\text{-I})_2\text{Li}(\text{OEt})_2$ with elemental potassium.[8] Compounds of this type have received growing interest since the landmark synthesis of decamethyldizincocen Cp^*_2Zn_2 by Carmona *et al.* in 2004.[9] The synthesis of as-described *single-site catalysts* and low-valent complexes typically requires alkyl- ($\text{X} = \text{Me}, \text{Et}$) or halide-substituted ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) complexes of the general type LZnX as starting materials. Several studies on DippNacNac substituted complexes of the desired type containing the sterically demanding Dipp substituent ($\text{Dipp} = 2,6-i\text{-Pr}_2\text{-C}_6\text{H}_3$) at the imine centers of the β -diketiminato group have been reported,[10] whereas complexes of the corresponding Mes-substituted β -diketiminato-ligand MesNacNac ($\text{Mes} = 2,4,6\text{-Me}_3\text{-C}_6\text{H}_2$) are unknown except for a dimeric zinc acetate complex **IV**. [11]

((Insert Scheme 1 here))

We became only recently interested in zinc complexes containing N,N'-chelating substituents and reported on the synthesis of several zinc amidinate complexes.[12] Herein, we report on the synthesis of β -diketiminato zinc complexes of the type LZnX (X = Me **1**, Cl **2**, Br **3**, I **4**) containing the sterically demanding MesNacNac ligand.

Experimental Section

General Procedure

All manipulations were performed in a glovebox under an Ar-atmosphere or with standard Schlenk techniques. Solvents were dried by use of a solvent purification system (MBRAUN) and degassed prior to use. MesNacNacH[13] and ZnI₂[14] were prepared according to literature methods, ZnMe₂ (1,2 M in toluene), Me₃NHCl, HCl (2N in Et₂O) and I₂ were obtained from Acros and used as received. A Bruker Avance 500 spectrometer was used for NMR spectroscopy. ¹H and ¹³C{¹H} NMR spectra were referenced to internal C₆D₅H (¹H: δ = 7.154; ¹³C: δ = 128.0). IR spectra were recorded on 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.

{[(2,4,6-Me₃-C₆H₂)N(Me)C]₂CH}ZnMe 1: 4.2 mL (5 mmol, 1.2M toluene) ZnMe₂ was added at ambient temperature to a solution of 1.99 g (5 mmol) MesNacNacH in toluene. After the gas evolution has stopped, the solution was stirred for additional 2 h. The solvent was removed in vacuum, yielding a yellow solid, which was re-crystallized from a solution in hexane at -30 °C. **1** was obtained as colorless crystalline solid within 24 h.

Yield 2.03 g (98 %). Mp: 117 °C. Elemental Analysis $C_{24}H_{32}N_2Zn$ (413.90 g/mol): found (calcd): H, 7.94 (7.79); C, 69.48 (69.65); N, 6.68 (6.77) %.

1H -NMR (300 MHz, $[D_8]THF$, 25 °C): δ -0.6 (s, 3H, $ZnCH_3$), 1.67 (s, 6H, $\beta-CH_3$), 2.15 (s, 12H, (*o*-Ar CH_3), 2.17 (s, 6H, *p*-Ar CH_3), 5.00 (s, 1H, $\gamma-CH$), 6.85 (s, 4H, *m*-Ar H). **^{13}C -NMR** (125 MHz, $[D_8]THF$, 25 °C): δ 18.2 (*o*-Ar CH_3), 20.0 ($\beta-CCH_3$), 20.7 (*p*-Ar CH_3), 94.2 ($\gamma-C$), 127.7 (*m*-Ar), 131.7 (*o*-Ar), 133.3 (*p*-Ar), 141.6 (*i*-Ar), 160.8 ($\beta-C$). **IR** (nujol): ν 2923, 2856, 1527, 1454, 1397, 1377, 1260, 1200, 1148, 1090, 1019, 860, 799, 751 cm^{-1} .

$\{[(2,4,6-Me_3-C_6H_2)N(Me)C]_2CH\}ZnCl$ 2: Method A: 0.48 g (5 mmol) Me_3NHCl was added to a solution of 2.07 g (5mmol) **1** in 40 ml Et_2O , immediately followed by a gas evolution. The suspension was stirred at ambient temperature for 12 h. **2** was isolated by filtration and re-crystallized from a solution in toluene and THF (1:6). Yield 1.92 g (89 %).

Method B: 2.5 mL HCl (5 mmol, 2N in Et_2O) was added dropwise at ambient temperature to 2.07 g (5 mmol) **1** dissolved in 40 ml Et_2O . After the gas evolution has stopped, the resulting suspension was stirred for additional 2 h. **2** was isolated by filtration as colorless solid. Yield 1.99 g (92 %).

Mp: > 240 °C. Elemental Analysis $C_{23}H_{29}ClN_2Zn$ (433.8 g/mol): found (calcd): H, 6.78 (6.73); C, 63.70 (63.61); N, 6.33 (6.45) %.

1H -NMR (300 MHz, $[D_8]THF$, 25 °C): δ 1.65 (s, 6H, $\beta-CH_3$), 2.20 (s, 12H, (*o*-Ar CH_3), 2.21 (s, 6H, *p*-Ar CH_3), 4.84 (s, 1H, $\gamma-CH$), 6.84 (s, 4H, *m*-Ar H). **^{13}C -NMR** (125 MHz, $[D_8]THF$, 25 °C): δ 18.5 (*o*-Ar CH_3), 20.3 ($\beta-CCH_3$), 20.9 (*p*-Ar CH_3), 94.5 ($\gamma-C$), 129.2 (*m*-Ar), 132.3 (*o*-Ar), 134.1 (*p*-Ar), 142.1 (*i*-Ar), 167.5 ($\beta-C$). **IR** (nujol): ν 2924, 2855, 1525, 1458, 1377, 1261, 1205, 1149, 1093, 1021, 860, 799 cm^{-1} .

{[(2,4,6-Me₃-C₆H₂)N(Me)C]₂CH}ZnI 3: A suspension of 1.27 g (5 mmol) I₂ in 10 mL Et₂O was added to a 2.07 g (5 mmol) **1** dissolved in 30 ml Et₂O at -78 °C. The resulting mixture was warmed to ambient temperature and stirred for additional 12 h. A colorless solid precipitates, which was isolated by filtration.

Yield: 2.58 g (98 %). Mp: > 240 °C. Elemental Analysis C₂₃H₂₉IN₂Zn (525.77 g/mol): found (calcd): H, 5.70 (5.56); C, 53.01 (52.54); N, 5.19 (5.33) %. Colorless crystals of **3**·THF were obtained within 24 h from a solution in THF at -30 °C.

¹H-NMR (300 MHz, [D₈]THF, 25 °C): δ 1.67 (s, 6H, β-CH₃), 2.18 (s, 12H, (o-Ar CH₃), 2.22 (s, 6H, p-Ar CH₃), 4.90 (s, 1H, γ-CH), 6.83 (s, 4H, m-Ar H). ¹³C-NMR (125 MHz, [D₈]THF, 25 °C): δ 18.3 (o-Ar CH₃), 19.9 (β-CCH₃), 22.3 (p-Ar CH₃), 93.8 (γ-C), 128.7 (m-Ar), 131.6 (o-Ar), 133.4 (p-Ar), 144.4 (i-Ar), 167.5 (β-C). IR (nujol): ν 2923, 2852, 1527, 1454, 1398, 1377, 1261, 1200, 1148, 1090, 1018, 860, 799, 751, 727 cm⁻¹.

X-ray Structure Solution and Refinement of 3. Crystallographic data of **3** are given in Table 1.

Figure 1 shows the ORTEP diagram of the solid state structure of **3**. Single crystals of **3** suitable for a single crystal X-ray diffraction study were obtained from a solution in THF at -30 °C.

{[(2,4,6-Me₃-C₆H₂)N(Me)C]₂CH}ZnI(THF) (C₂₇H₃₇IN₂OZn), colorless crystals, 0.49 x 0.40 x 0.39 mm, monoclinic, space group *P*2₁, *a* = 8.054(3), *b* = 16.252(7), *c* = 10.721(5) Å, β = 102.150(7)°, *V* = 1371.8(10) Å³, *Z* = 2, λ (MoKα) = 0.71073 Å, μ = 2.040 mm⁻¹, ρ_{ber.} = 1.447 g cm⁻³, *T* = 153(2) K, F(000) = 608. Data were collected on a Bruker-AXS SMART APEX CCD (12020 reflections (2θ_{max} = 50°) collected (6371 independent, *R*_{int} = 0.0204). The structure was solved by Direct Methods (SHELXS-97)[15] and refined by full-matrix least-squares on F² (SHELXL-97).[16] All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (*R*₁ = 0.0216 (*I* > 2σ(*I*)), *wR*₂ = 0.0550, 297 parameters, largest diff.peak and hole -

0.461 eÅ⁻³ and 0.845 eÅ⁻³. Multi-scan absorption correction was applied (min./max. transmission 0.5033/0.4346). Crystallographic data for the structure (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-689832 (**3**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code_(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 ZnMe₂ and MesNacNacH react at ambient temperature with smooth gas evolution and subsequent formation of {[(2,4,6-Me₃-C₆H₂)N(Me)C]₂CH}ZnMe **1** in almost quantitative yield. **1** was obtained after workup and re-crystallization from a solution in hexane at -30 °C as colorless crystalline solid. ¹H and ¹³C NMR spectra of **1** show the expected resonances due to MesNacNac ligand. In addition, a resonance at -0.6 ppm in the ¹H NMR spectrum clearly proves the presence of a Zn-Me group.

DFT calculations were performed in order to investigate the bonding situation and charge distribution within **1**.^[17] The C-N (1.334 Å) and C-C bond lengths (1.413 Å) of the central six-membered ZnN₂C₃ ring are comparable to those reported for {[(2,6-*i*-Pr₂-C₆H₃)N(Me)C]₂CH}ZnMe containing the sterically more hindered DippNacNac ligand (C-N 1.329(3), 1.334(3); C-C 1.401(3), 1.399(3) Å).^[10d] They clearly reveal the π-bonding contribution within the β-diketiminato moiety. The Zn-N bonds show high ionic bonding contributions and the highest atomic charge was found for the carbon atom of the Zn-Me group (-1.32). According to these calculations, it should be possible to use the carbanionic Me group bound to the Zn atom in **1** for further reactions.

Reactions with HCl and Me₃NHCl in Et₂O, respectively, occurred with protonation of the Me group and subsequent elimination of methane, yielding the Cl-substituted complex $\{[(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2)\text{N}(\text{Me})\text{C}]_2\text{CH}\}\text{ZnCl}$ **2** in good yields. In addition, the reaction of equimolar amounts of **1** and I₂ proceeds with formation of $\{[(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2)\text{N}(\text{Me})\text{C}]_2\text{CH}\}\text{ZnI}$ **3**. The latter reaction avoids the formation of a LiI adduct as was previously reported for the reaction of DippNacNacLi and ZnI₂.^[10e]

((Insert Scheme 2 here))

¹H NMR spectra of **2** and **3** are almost identical. Small shifts of the resonances due to the γ-CH of the MesNacNac ligand (5.00 **1**, 4.84 **2**, 4.90 **3**) were observed. The largest *upfield* shift was observed for **2** containing the most electronegative Cl substituent, whereas the largest downfield shift was observed for **1** with the most electropositive Me group. Even though the reactions were performed in Et₂O, no adduct formation was observed, indicating the Lewis acidity of the Zn center to be rather low. Unfortunately, single crystals of **1** and **2** suitable for X-ray structure determination could not be obtained despite numerous attempts in different organic solvents. In contrast, re-crystallization of **3** in THF at -30 °C yielded the corresponding thf adduct as colorless crystals of X-ray quality.

((Insert Figure 1 here))

3·THF crystallizes in the monoclinic space group *P2(1)*. Central structural motif is the six-membered C(CN)₂Zn ring, with the β-diketiminate moiety serving as chelating two-electron donor. The four-coordinate Zn atom has moved out of the plane, resulting in a *boat-type* conformation. Comparable findings have been previously observed for DippNacNacZn*t*Bu(THF) and DippNacNacZnPh complexes.^[10d] The N-C (N(1)-C(19) 1.322(3), N(2)-C(21) 1.331(3) Å) and C-C bond lengths (C(19)-C(20) 1.401(3); C(20)-C(21) 1.406(3) Å) within the six-membered

ring are almost equal and the β -diketiminato core is almost planar (sum of bond angles of 360.0° (N1, C19, C20, C21 and 359.6° (N2)), indicating a delocalized π -electron system. The fourfold-coordinated Zn atom in **3·THF** adopts a distorted tetrahedral coordination sphere, with the exocyclic N(1)-Zn(1)-N(2) bond angle (99.3(1)°) being significantly smaller than the exocyclic N-Zn-I bond angles (N(1)-Zn(1)-I(1) 128.1(1), N(2)-Zn(1)-I(1) 117.7(1)). The Zn-N bond lengths (Zn(1)-N(1) 1.968(2); Zn(1)-N(2) 1.952(2) Å) are slightly shorter compared to those observed for amidinate complexes[12] but within the typical range reported for β -diketiminato zinc complexes of the desired type.[6,7,10] The Zn-I bond length of 2.513(1) Å is typical for four-coordinate Zn-I complexes,[18] whereas the bridging Zn-I bonds observed for DippNacNacZn(μ -I)₂Li(OEt)₂ (2.614(1), 2.665(1) Å)[10e] are significantly elongated.

Conclusion. {[(2,4,6-Me₃-C₆H₂)N(Me)C]₂CH}ZnMe **1**, which can be prepared in almost quantitative yield, is a convenient starting reagent for the synthesis of β -diketiminato zinc halide complexes of the general type {[(2,4,6-Me₃-C₆H₂)N(Me)C]₂CH}ZnX (X = Cl **2**, I **3**). The potential of these complexes for the synthesis of low-valent and cationic zinc complexes is currently under investigation.

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Supplement. Final molecular structure, list of the final atomic coordinates and energy, selected bond lengths, and NBO atomic charges of **1** (DFT calculations).

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[18] Cambridge Structural Database (CSD) v5.29 (November 2007, Update 1 Jan. 08). Zn-I bond lengths typically range from 2.50 and 2.60 Å.

Scheme 1

Scheme 2

Figure 1

Figure Caption

Scheme 1. Zinc complexes containing N,N'-chelating β -diketiminato-ligands.

Scheme 2. Synthesis of β -diketimate zinc complexes **1** - **3**.

Figure 1. Molecular structure and atom numbering scheme of **3**·THF; thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn(1)-N(1) 1.968(2), Zn(1)-N(2) 1.952(2), Zn(1)-I(1) 2.513(1), Zn(1)-O(1) 2.107(2), N(1)-C(1) 1.442(3), N(1)-C(19) 1.322(3), N(2)-C(10) 1.441(3), N(2)-C(21) 1.331(3), C(19)-C(20) 1.401(3), C(20)-C(21) 1.406(3), N(1)-Zn(1)-N(2) 99.3(1), C(19)-N(1)-Zn(1) 118.5(2), N(1)-C(19)-C(20) 124.9(2), C(19)-C(20)-C(21) 129.0(2), C(20)-C(21)-N(2) 124.5(2), C(21)-N(2)-Zn(1) 118.4(2), I(1)-Zn(1)-O(1) 104.8(1), Zn(1)-N(1)-C(1) 121.6(2), C(19)-N(1)-C(1) 120.0(2), Zn(1)-N(2)-C(10) 123.7(2), C(21)-N(2)-C(10) 117.5(2).

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