

# Solid-state and Solution Studies on a $\beta$ -Diketiminato Zinc Hydride Complex

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*Dedicated to Professor Hubert Schmidbaur on the occasion of his 75<sup>th</sup> birthday*

[MesnacnacZn( $\mu$ -H)]<sub>2</sub> (**1**) was synthesized by reaction of MesnacnacZnI with either an equimolar amount of KNH(*i*Pr)BH<sub>3</sub> or an excess of NaH and characterized by multinuclear NMR and IR spectroscopy as well as X-ray diffraction. Two polymorphs of **1** were found and their structures determined on single crystals.

*Key words:* Zinc,  $\beta$ -Diketiminato, X-Ray Structure, Polymorphs

## Introduction

Zinc hydride complexes are suitable reducing reagents in organic chemistry [1]. However, the rather low thermal stability of ZnH<sub>2</sub> [2] prompted the interest in more stable organozinc hydrides RZnH. These can either be stabilized by coordination of a Lewis base such as pyridine, as was demonstrated for RZnH(pyridine) (R = Et, Ph) [3], or by sterically demanding groups such as scorpionato (Tp<sup>*p*-Tol,Me</sup>) [4],  $\beta$ -diketiminato (Mes'nacnac = [HC{C(Me)N(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>}]<sub>2</sub>) [5], and terphenyl substituents (Ar' = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>3</sub>-2,6-*i*-Pr<sub>2</sub>)<sub>2</sub>) [6]. These complexes were either synthesized by reaction of Et<sub>3</sub>SiH with the corresponding zinc fluoride complexes (Tp<sup>*p*-Tol,Me</sup>ZnH and [Mes'Zn( $\mu$ -H)]<sub>2</sub>) or by halide/hydride exchange reaction using NaH ([Ar'Zn( $\mu$ -H)]<sub>2</sub>). Very recently, Harder and coworkers synthesized DippnacnacZnH (Dippnacnac = [HC{C(Me)N(2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>}]<sub>2</sub>), which represents the first structurally characterized monomeric  $\beta$ -diketiminato zinc hydride complex, by reaction of DippnacnacZnCl with KN(*i*-Pr)HBH<sub>3</sub> [7]. We became recently interested in  $\beta$ -diketiminato zinc halide complexes of the type MesnacnacZnX (Mesnacnac = [HC{C(Me)N(Mes)}<sub>2</sub>], Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; X = Cl, I) [8], which we believed to be suitable starting reagents for the synthesis of the corresponding low-valent complexes Zn<sub>2</sub>R<sub>2</sub> as well as the zinc hy-

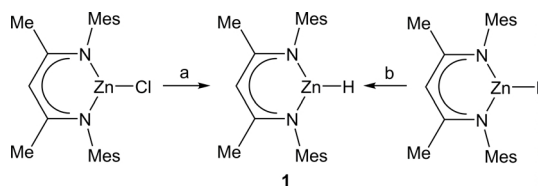
dride RZnH. Unfortunately, reactions with several reducing agents only resulted in the formation of ZnR<sub>2</sub> [9], whereas reduction of the comparable Dipp-substituted complex DippnacnacZnI (Dipp = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) yielded Dippnacnac<sub>2</sub>Zn<sub>2</sub> [10].

Herein, we report on the reactions of MesnacnacZnX with several hydride-transfer reagents. It was found that MesnacnacZnH can be most conveniently synthesized by reaction of MesnacnacZnI with KN(*i*-Pr)HBH<sub>3</sub>.

## Results and Discussion

MesnacnacZnX (X = Cl, I) was reacted with several traditional hydride-transfer reagents such as LiAlH<sub>4</sub>, NaH, KH and LiBEt<sub>3</sub>H. However, only the reaction of MesnacnacZnCl with an excess of NaH yielded **1** in rather low yield (30 %) after 3 d. In contrast, the reaction of MesnacnacZnI with KN(*i*-Pr)HBH<sub>3</sub>, which was very recently demonstrated by the Harder group to be a convenient hydride-transfer reagent, gave **1** after only 2 h in 75 % isolated yield after workup (Scheme 1).

Compound **1** was characterized by NMR and IR spectroscopy as well as elemental analysis. The IR spectrum shows typical absorption bands of the Mesnacnac substituent. <sup>1</sup>H and <sup>13</sup>C NMR spectra show the expected resonances due to the Mesnacnac substituent. In addition, a sharp resonance of the Zn-H group was observed in the <sup>1</sup>H NMR spectrum at 4.57 ppm in



a) NaH; b) KN(*i*-Pr)HBH<sub>3</sub>; Mes = 2,46-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>.

Scheme 1. Synthesis of MesnacnacZnH **1**.

C<sub>6</sub>D<sub>6</sub>, which corresponds very well to those reported for [Ar'Zn( $\mu$ -H)]<sub>2</sub> (4.84 ppm), [Mes'nacnacZn( $\mu$ -H)]<sub>2</sub> (4.59 ppm) and DippnacnacZnH (4.39 ppm), respectively. Interestingly, the Zn-H resonance significantly shifts to higher field in [D<sub>8</sub>]THF (3.39 ppm). This finding indicates a stronger hydridic (electron-rich) Zn-H group, which most likely results from the donation of electron density by coordination of a thf solvent molecule to the Zn center. Moreover, temperature-dependent NMR studies in [D<sub>8</sub>]toluene show a large shift of the Zn-H resonance. Even though no additional resonance for the Zn-H group appeared, the formation of a monomer/dimer equilibrium in [D<sub>8</sub>]toluene solution, as was previously reported for DippnacnacZnH [7], seems reasonable. In contrast, a temperature-dependent study of **1** dissolved in [D<sub>8</sub>]THF only showed a very small shift of the Zn-H resonance, indicating a monomeric (thf-stabilized) structure in this solvent. Pulsed gradient spin echo (PGSE) diffusion measurements of a solution of **1** at 25 °C in different solvents yield hydrodynamic radii of 4.96(25) Å ([D<sub>8</sub>]toluene) and 5.26(26) Å ([D<sub>8</sub>]THF), which correspond well with those reported for monomeric DippnacnacZnH (5.2(1) Å) [7] and MesnacnacZnMe (4.65(23) Å in [D<sub>8</sub>]toluene), which are suggested to be monomeric in solution. These results clearly indicate that **1** is rather monomeric in solution.

The molecular structure of **1** in the solid state was investigated by single crystal X-ray diffraction. Two independent studies revealed the formation of two polymorphic forms of **1**. Complex **1** either crystallizes in the triclinic space group  $P\bar{1}$  with one molecule in the unit cell (**1a**, Fig. 1) or in the monoclinic space group  $P2_1/n$  with two molecules in the unit cell (**1b**, Fig. 2). Complex **1b** is isostructural to the recently reported low-valent complex Mesnacnac<sub>2</sub>Zn<sub>2</sub> [11]. The bridging hydrogen atoms were located in the electron difference map. Complex **1a** shows a crystallographic inversion center whereas **1b** displays a crystallographically imposed C<sub>2</sub> axis. The C<sub>3</sub>N<sub>2</sub>Zn rings in both **1a** and **1b** are almost planar with the

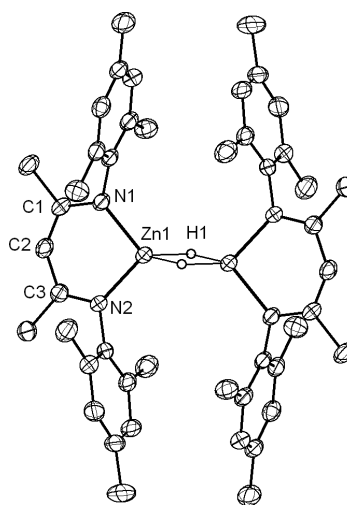


Fig. 1. Molecular structure of the  $P\bar{1}$  polymorph of **1** in the crystal (**1a**). The molecule has a crystallographically imposed center of inversion.

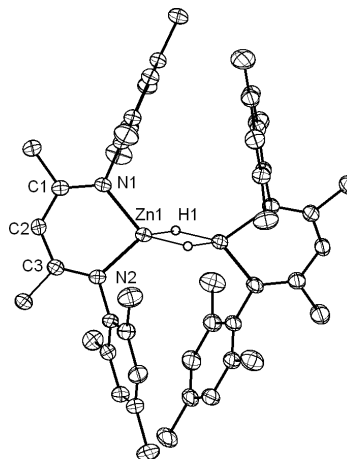


Fig. 2. Molecular structure of the  $P2_1/n$  polymorph of **1** in the crystal (**1b**). The molecule has a crystallographically imposed C<sub>2</sub> axis.

Zn atoms slightly out of the plane, as was previously observed in [Mes'nacnacZn( $\mu$ -H)]<sub>2</sub> [5], DippnacnacZnH [7], DippnacnacZnN(SiMe<sub>3</sub>)<sub>2</sub> [13], and DippnacnacZn( $\mu$ -H)<sub>2</sub>BH<sub>2</sub> [14]. In **1a**, the almost planar C(CN)<sub>2</sub>Zn six-membered rings adopt a co-planar orientation, whereas in **1b** the rings are twisted by 42.6° as was observed for [Mes'nacnacZn( $\mu$ -H)]<sub>2</sub> [5]. As a consequence, the Zn–N bond lengths (**1a**: 1.971(2), 1.975(2) Å; **1b**: 2.0046(16), 2.0056(17) Å) differ, whereas the C–N (**1a**: 1.331(4) Å; **1b**: 1.333(3), 1.332(3) Å) and C–C (**1a**: 1.397(4), 1.406(4) Å; **1b**: 1.409(3), 1.401(3) Å) bond lengths are almost identical. In addition, the Zn–Zn distances (**1a**: 2.4705(7) Å; **1b**: 2.4239(5) Å) differ by almost 0.05 Å. Interatomic Zn–Zn distances in dimeric zinc hydrides [RZn( $\mu$ -H)]<sub>2</sub> were found to range from 2.4084(3) Å ([Ar'Zn( $\mu$ -H)]<sub>2</sub>) [6] to 2.4513(9) Å ([Mes'nacnacZn( $\mu$ -H)]<sub>2</sub>), which is elongated compared to that in the corre-

sponding Zn–Zn bonded complexes Mesnacnac<sub>2</sub>Zn<sub>2</sub> (2.3813(8) Å) [11] and Dippnacnac<sub>2</sub>Zn<sub>2</sub> (2.3586(7) Å) [12]. In contrast, the unusual sodium hydride-bridged complex Ar'Zn( $\mu$ -H)( $\mu$ -Na)ZnAr' shows a significantly shorter Zn–Zn bond length (2.352(2) Å), which is essentially the same as observed for the Zn–Zn bonded complex Ar'Zn–ZnAr' (2.3591(9) Å) [6]. The Zn–H bond lengths in **1a** (1.699(33)/1.798(24) Å) and **1b** (1.79(2) Å) are comparable to those reported for dimeric [Mes'nacnacZn( $\mu$ -H)]<sub>2</sub> (1.766 Å) [5] and ([Ar'Zn( $\mu$ -H)]<sub>2</sub> (1.67(2)/1.79(3) Å) [6], whereas the Zn–H bond of monomeric DippnacnacZnH is significantly shorter (1.46(2) Å) [7].

## Experimental Section

Manipulations were performed in a glove box under an atmosphere of argon or with standard Schlenk techniques. Dry solvents were obtained from a solvent purification system (MBraun) and were degassed prior to use. KN(*i*Pr)HBH<sub>3</sub> [5, 15] and MesnacnacZnI [8] were prepared according to literature methods. A Bruker Avance 500 spectrometer was used for NMR spectroscopy. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were referenced to internal C<sub>6</sub>D<sub>5</sub>H (<sup>1</sup>H:  $\delta$  = 7.154; <sup>13</sup>C:  $\delta$  = 128.0) and [D<sub>8</sub>]THF (<sup>1</sup>H:  $\delta$  = 1.73 and 3.58; <sup>13</sup>C:  $\delta$  = 25.2 and 67.4). IR spectra were recorded on an Alpha-T FT-IR spectrometer with a single reflection ATR sampling module. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were performed at the Elementaranalyse Labor of the University of Essen.

### [MesnacnacZnH]<sub>2</sub> (**1**)

**Method A:** A suspension of 2.16 g (5.0 mmol) MesnacnacZnCl and 0.29 g NaH (12 mmol) in 50 mL of THF was stirred at ambient temperature for 3 d. Thereafter, THF was removed *in vacuo*, and the remaining solid was suspended in toluene and filtered. The resulting clear solution was concentrated to 5 mL and stored at –30 °C. Colorless crystals of **1** were formed within 48 h, yield 0.83 g (43 %).

**Method B:** 2.40 g (2.2 mmol) of KNH(*i*Pr)BH<sub>3</sub> was dissolved in 30 mL of THF and added to a solution of 1.05 g (2.0 mmol) of MesnacnacZnI in 30 mL of THF. The solution was stirred at ambient temperature for 2 h. Thereafter, THF was removed *in vacuo*, and the remaining solid was suspended in toluene and filtered. The resulting clear solution was concentrated to 5 mL and stored at –30 °C. Colorless crystals of **1** were formed within 48 h, yield 0.58 g (75 %). M. p. 220 °C. – IR:  $\nu$  = 1525, 1453, 1398, 1258, 1085, 1012, 856, 794 cm<sup>-1</sup>. – <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 1.56 (s, 6 H, C(CH<sub>3</sub>)), 2.07 (s, 12 H, *o*-CH<sub>3</sub>), 2.21 (s, 6 H, *p*-CH<sub>3</sub>), 4.57 (s, 1 H, ZnH), 4.92 (s, 1 H, CH), 6.78 (s, 4 H, Ar-H). – <sup>1</sup>H NMR (300 MHz, [D<sub>8</sub>]THF, 298 K):

Table 1. Crystal structure data of the polymorphs **1a** and **1b**.

	<b>1a</b>	<b>1b</b>
Formula	C <sub>46</sub> H <sub>60</sub> N <sub>4</sub> Zn <sub>2</sub>	C <sub>46</sub> H <sub>60</sub> N <sub>4</sub> Zn <sub>2</sub>
<i>M<sub>r</sub></i>	799.72	799.72
Crystal size, mm <sup>3</sup>	0.10 × 0.10 × 0.10	0.22 × 0.13 × 0.04
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2/ <i>n</i>
<i>a</i> , Å	8.4720(3)	13.4581(9)
<i>b</i> , Å	10.0339(4)	8.3662(4)
<i>c</i> , Å	13.5438(5)	19.5522(13)
$\alpha$ , deg	70.531(2)	90
$\beta$ , deg	80.582(2)	103.632(5)
$\gamma$ , deg	77.367(2)	90
<i>V</i> , Å <sup>3</sup>	1054.05(7)	2139.4(2)
<i>Z</i>	1	2
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.26	1.24
$\mu$ (MoK $\alpha$ ), cm <sup>-1</sup>	1.2	1.2
<i>F</i> (000), e	424	848
<i>hkl</i> range	–9 ≤ <i>h</i> ≤ +10 –10 ≤ <i>k</i> ≤ +11 0 ≤ <i>l</i> ≤ +16	–13 ≤ <i>h</i> ≤ +17 –10 ≤ <i>k</i> ≤ +10 –25 ≤ <i>l</i> ≤ +25
Refl. measured / unique	31013 / 3688	26409 / 4704
<i>R</i> <sub>int</sub>	0.0752	0.0475
Param. refined	240	246
<i>R</i> 1( <i>F</i> ) / <i>wR</i> 2( <i>F</i> <sup>2</sup> ) <sup>a</sup> (all refl.)	0.0440 / 0.0950	0.0342 / 0.0867
GoF ( <i>F</i> <sup>2</sup> ) <sup>b</sup>	1.041	1.034
$\Delta\rho_{\text{fin}}$ (max / min), e Å <sup>-3</sup>	0.327 / –0.367	0.596 / –0.685

<sup>a</sup> *R*1 =  $\Sigma||F_o| - |F_c||/\Sigma|F_o|$  [for *I* ≥ 2σ(*I*)], *wR*2 =  $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ ; *R*1 =  $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ ; <sup>b</sup> GoF =  $[\Sigma w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$ .

$\delta$  = 1.64 (s, 6 H, C(CH<sub>3</sub>)), 2.11 (s, 12 H, *o*-CH<sub>3</sub>), 2.21 (s, 6 H, *p*-CH<sub>3</sub>), 3.39 (s, 1 H, ZnH), 4.85 (s, 1 H, CH), 6.81 (s, 2 H, Ar-H). – <sup>13</sup>C NMR (125 MHz, [D<sub>8</sub>]THF, 298 K):  $\delta$  = 18.89 (*o*-CH<sub>3</sub>), 20.98 ( $\beta$ -CCH<sub>3</sub>), 22.90 (*p*-CH<sub>3</sub>), 94.88 ( $\gamma$ C), 129.62 (*m*-Ar), 132.03 (*o*-Ar), 133.73 (*p*-Ar), 146.78 (CN), 167.03 (CCH<sub>3</sub>). – C<sub>46</sub>H<sub>60</sub>N<sub>4</sub>Zn<sub>2</sub> (799.7): calcd. C 69.09, H 7.56, N 7.01; found C 68.91, H 7.60, N 6.90.

### Temperature-dependent <sup>1</sup>H NMR spectra in [D<sub>8</sub>]THF (500 MHz)

*T* = 213 K:  $\delta$  = 1.61 (s, 6 H, C(CH<sub>3</sub>)), 2.11 (s, 12 H, *o*-CH<sub>3</sub>), 2.21 (s, 6 H, *p*-CH<sub>3</sub>), 3.20 (s, 1 H, ZnH), 4.81 (s, 1 H, CH), 6.83 (s, 4 H, Ar-H).

*T* = 298 K:  $\delta$  = 1.64 (s, 6 H, C(CH<sub>3</sub>)), 2.11 (s, 12 H, *o*-CH<sub>3</sub>), 2.19 (s, 6 H, *p*-CH<sub>3</sub>), 3.37 (s, 1 H, ZnH), 4.86 (s, 1 H, CH), 6.82 (s, 4 H, Ar-H).

*T* = 333 K:  $\delta$  = 1.66 (s, 6 H, C(CH<sub>3</sub>)), 2.11 (s, 12 H, *o*-CH<sub>3</sub>), 2.22 (s, 6 H, *p*-CH<sub>3</sub>), 3.46 (s, 1 H, ZnH), 4.92 (s, 1 H, CH), 6.83 (s, 4 H, Ar-H).

### Temperature-dependent <sup>1</sup>H NMR spectra in [D<sub>8</sub>]toluene (500 MHz)

*T* = 213 K:  $\delta$  = 1.39 (s, 6 H, C(CH<sub>3</sub>)), 1.98 (s, 12 H, *o*-CH<sub>3</sub>), 2.30 (s, 6 H, *p*-CH<sub>3</sub>), 4.85 (s, 1 H, ZnH), 4.76 (s, 1 H, CH), 6.64 (s, 4 H, Ar-H).

$T = 233$  K:  $\delta = 1.40$  (s, 6 H, C(CH<sub>3</sub>)), 1.97 (s, 12 H, *o*-CH<sub>3</sub>), 2.29 (s, 6 H, *p*-CH<sub>3</sub>), 4.78 (s, 1 H, ZnH), 4.76 (s, 1 H, CH), 6.65 (s, 4 H, Ar-H).

$T = 253$  K:  $\delta = 1.43$  (s, 6 H, C(CH<sub>3</sub>)), 1.98 (s, 12 H, *o*-CH<sub>3</sub>), 2.27 (s, 6 H, *p*-CH<sub>3</sub>), 4.69 (s, 1 H, ZnH), 4.79 (s, 1 H, CH), 6.67 (s, 4 H, Ar-H).

$T = 273$  K:  $\delta = 1.47$  (s, 6 H, C(CH<sub>3</sub>)), 2.01 (s, 12 H, *o*-CH<sub>3</sub>), 2.23 (s, 6 H, *p*-CH<sub>3</sub>), 4.57 (s, 1 H, ZnH), 4.84 (s, 1 H, CH), 6.70 (s, 4 H, Ar-H).

$T = 298$  K:  $\delta = 1.53$  (s, 6 H, C(CH<sub>3</sub>)), 2.04 (s, 12 H, *o*-CH<sub>3</sub>), 2.19 (s, 6 H, *p*-CH<sub>3</sub>), 4.43 (s, 1 H, ZnH), 4.88 (s, 1 H, CH), 6.73 (s, 4 H, Ar-H).

$T = 313$  K:  $\delta = 1.56$  (s, 6 H, C(CH<sub>3</sub>)), 2.05 (s, 12 H, *o*-CH<sub>3</sub>), 2.17 (s, 6 H, *p*-CH<sub>3</sub>), 4.35 (s, 1 H, ZnH), 4.90 (s, 1 H, CH), 6.74 (s, 4 H, Ar-H).

$T = 333$  K:  $\delta = 1.58$  (s, 6 H, C(CH<sub>3</sub>)), 2.06 (s, 12 H, *o*-CH<sub>3</sub>), 2.15 (s, 6 H, *p*-CH<sub>3</sub>), 4.27 (s, 1 H, ZnH), 4.93 (s, 1 H, CH), 6.75 (s, 4 H, Ar-H).

$T = 353$  K:  $\delta = 1.60$  (s, 6 H, C(CH<sub>3</sub>)), 2.07 (s, 12 H, *o*-CH<sub>3</sub>), 2.14 (s, 6 H, *p*-CH<sub>3</sub>), 4.21 (s, 1 H, ZnH), 4.94 (s, 1 H, CH), 6.75 (s, 4 H, Ar-H).

#### Crystal structure determination

Data were collected on a Bruker AXS SMART APEX CCD diffractometer for **1a** and on a Stoe IPDS-II diffrac-

tometer for **1b** (MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å). The structures were solved by Direct Methods (SHELXS-97 [16]) and refined by full-matrix least-squares on  $F^2$ . Semi-empirical absorption corrections were applied. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model except for Zn-H, which were found from the difference fourier maps and refined freely (SHELXL-97 [17]). Crystal data and parameters pertinent to the structure determination of **1a** and **1b** are summarized in Table 1.

CCDC 745610 (**1a**) and 745612 (**1b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from 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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