

Solid-state and Solution Studies on a β -Diketiminato Zinc Hydride Complex

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

[MesnacnacZn(μ -H)]₂ (**1**) was synthesized by reaction of MesnacnacZnI with either an equimolar amount of KNH(*i*Pr)BH₃ 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, β -Diketiminato, X-Ray Structure, Polymorphs

Introduction

Zinc hydride complexes are suitable reducing reagents in organic chemistry [1]. However, the rather low thermal stability of ZnH₂ [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^{*p*-Tol,Me}) [4], β -diketiminato (Mes'nacnac = [HC{C(Me)N(2,6-Me₂C₆H₃)₂}] [5], and terphenyl substituents (Ar' = C₆H₃-2,6-(C₆H₃-2,6-*i*-Pr₂)₂) [6]. These complexes were either synthesized by reaction of Et₃SiH with the corresponding zinc fluoride complexes (Tp^{*p*-Tol,Me}ZnH and [Mes'Zn(μ -H)]₂) or by halide/hydride exchange reaction using NaH ([Ar'Zn(μ -H)]₂). Very recently, Harder and coworkers synthesized DippnacnacZnH (Dippnacnac = [HC{C(Me)N(2,6-*i*-Pr₂C₆H₃)₂}] [7], which represents the first structurally characterized monomeric β -diketiminato zinc hydride complex, by reaction of DippnacnacZnCl with KN(*i*-Pr)HBH₃ [7]. We became recently interested in β -diketiminato zinc halide complexes of the type MesnacnacZnX (Mesnacnac = [HC{C(Me)N(Mes)₂}] [8], Mes = 2,4,6-Me₃C₆H₂; X = Cl, I) [8], which we believed to be suitable starting reagents for the synthesis of the corresponding low-valent complexes Zn₂R₂ as well as the zinc hy-

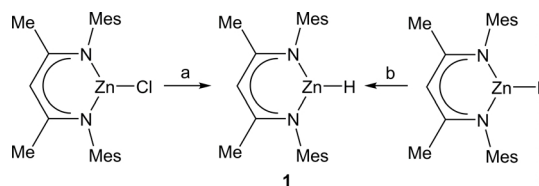
dride RZnH. Unfortunately, reactions with several reducing agents only resulted in the formation of ZnR₂ [9], whereas reduction of the comparable Dipp-substituted complex DippnacnacZnI (Dipp = 2,6-*i*-Pr₂C₆H₃) yielded Dippnacnac₂Zn₂ [10].

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)HBH₃.

Results and Discussion

MesnacnacZnX (X = Cl, I) was reacted with several traditional hydride-transfer reagents such as LiAlH₄, NaH, KH and LiBEt₃H. 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)HBH₃, 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. ¹H and ¹³C 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 ¹H NMR spectrum at 4.57 ppm in



a) NaH; b) KN(*i*-Pr)HBH₃; Mes = 2,46-Me₃C₆H₂.

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

C₆D₆, which corresponds very well to those reported for [Ar'Zn(μ -H)]₂ (4.84 ppm), [Mes'nacnacZn(μ -H)]₂ (4.59 ppm) and DippnacnacZnH (4.39 ppm), respectively. Interestingly, the Zn-H resonance significantly shifts to higher field in [D₈]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 [D₈]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 [D₈]toluene solution, as was previously reported for DippnacnacZnH [7], seems reasonable. In contrast, a temperature-dependent study of **1** dissolved in [D₈]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 ([D₈]toluene) and 5.26(26) Å ([D₈]THF), which correspond well with those reported for monomeric DippnacnacZnH (5.2(1) Å) [7] and MesnacnacZnMe (4.65(23) Å in [D₈]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*/*n* with two molecules in the unit cell (**1b**, Fig. 2). Complex **1b** is isostructural to the recently reported low-valent complex Mesnacnac₂Zn₂ [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 C₂ axis. The C₃N₂Zn rings in both **1a** and **1b** are almost planar with the

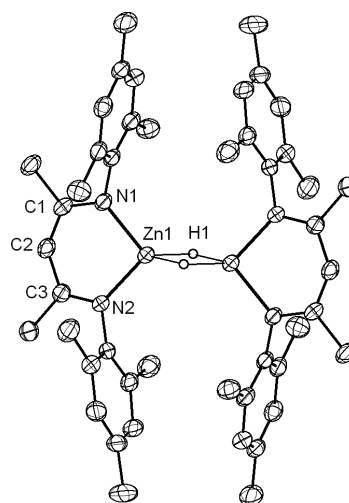


Fig. 1. Molecular structure of the *P* $\bar{1}$ polymorph of **1** in the crystal (**1a**). The molecule has a crystallographically imposed center of inversion.

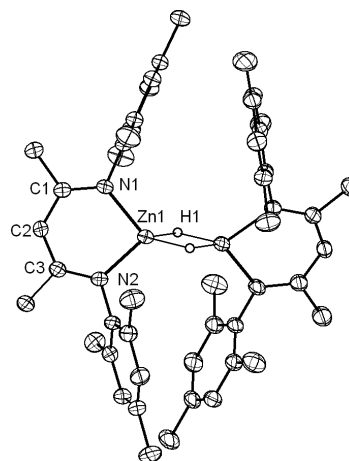


Fig. 2. Molecular structure of the *P2*/*n* polymorph of **1** in the crystal (**1b**). The molecule has a crystallographically imposed C₂ axis.

Zn atoms slightly out of the plane, as was previously observed in [Mes'nacnacZn(μ -H)]₂ [5], DippnacnacZnH [7], DippnacnacZnN(SiMe₃)₂ [13], and DippnacnacZn(μ -H)₂BH₂ [14]. In **1a**, the almost planar C(CN)₂Zn six-membered rings adopt a co-planar orientation, whereas in **1b** the rings are twisted by 42.6° as was observed for [Mes'nacnacZn(μ -H)]₂ [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(μ -H)]₂ were found to range from 2.4084(3) Å ([Ar'Zn(μ -H)]₂) [6] to 2.4513(9) Å ([Mes'nacnacZn(μ -H)]₂), which is elongated compared to that in the corre-

sponding Zn–Zn bonded complexes Mesnacnac₂Zn₂ (2.3813(8) Å) [11] and Dippnacnac₂Zn₂ (2.3586(7) Å) [12]. In contrast, the unusual sodium hydride-bridged complex Ar'Zn(μ -H)(μ -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(μ -H)]₂ (1.766 Å) [5] and ([Ar'Zn(μ -H)]₂ (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)HBH₃ [5, 15] and MesnacnacZnI [8] were prepared according to literature methods. 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) and [D₈]THF (¹H: δ = 1.73 and 3.58; ¹³C: δ = 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]₂ (**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)BH₃ 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: ν = 1525, 1453, 1398, 1258, 1085, 1012, 856, 794 cm^{–1}. – ¹H NMR (300 MHz, C₆D₆, 298 K): δ = 1.56 (s, 6 H, C(CH₃)), 2.07 (s, 12 H, *o*-CH₃), 2.21 (s, 6 H, *p*-CH₃), 4.57 (s, 1 H, ZnH), 4.92 (s, 1 H, CH), 6.78 (s, 4 H, Ar-H). – ¹H NMR (300 MHz, [D₈]THF, 298 K):

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

	1a	1b
Formula	C ₄₆ H ₆₀ N ₄ Zn ₂	C ₄₆ H ₆₀ N ₄ Zn ₂
<i>M_r</i>	799.72	799.72
Crystal size, mm ³	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 ₁ / <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)
α , deg	70.531(2)	90
β , deg	80.582(2)	103.632(5)
γ , deg	77.367(2)	90
<i>V</i> , Å ³	1054.05(7)	2139.4(2)
<i>Z</i>	1	2
<i>D</i> _{calcd} , g cm ^{–3}	1.26	1.24
μ (MoK α), cm ^{–1}	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> _{int}	0.0752	0.0475
Param. refined	240	246
<i>R</i> 1(<i>F</i>) / <i>wR</i> 2(<i>F</i> ²) ^a (all refl.)	0.0440 / 0.0950	0.0342 / 0.0867
GoF (<i>F</i> ²) ^b	1.041	1.034
$\Delta\rho_{\text{fin}}$ (max / min), e Å ^{–3}	0.327 / –0.367	0.596 / –0.685

^a *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 = $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; ^b GoF = $[\Sigma w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

δ = 1.64 (s, 6 H, C(CH₃)), 2.11 (s, 12 H, *o*-CH₃), 2.21 (s, 6 H, *p*-CH₃), 3.39 (s, 1 H, ZnH), 4.85 (s, 1 H, CH), 6.81 (s, 2 H, Ar-H). – ¹³C NMR (125 MHz, [D₈]THF, 298 K): δ = 18.89 (*o*-CH₃), 20.98 (β -CCH₃), 22.90 (*p*-CH₃), 94.88 (γ C), 129.62 (*m*-Ar), 132.03 (*o*-Ar), 133.73 (*p*-Ar), 146.78 (CN), 167.03 (CCH₃). – C₄₆H₆₀N₄Zn₂ (799.7): calcd. C 69.09, H 7.56, N 7.01; found C 68.91, H 7.60, N 6.90.

Temperature-dependent ¹H NMR spectra in [D₈]THF (500 MHz)

T = 213 K: δ = 1.61 (s, 6 H, C(CH₃)), 2.11 (s, 12 H, *o*-CH₃), 2.21 (s, 6 H, *p*-CH₃), 3.20 (s, 1 H, ZnH), 4.81 (s, 1 H, CH), 6.83 (s, 4 H, Ar-H).

T = 298 K: δ = 1.64 (s, 6 H, C(CH₃)), 2.11 (s, 12 H, *o*-CH₃), 2.19 (s, 6 H, *p*-CH₃), 3.37 (s, 1 H, ZnH), 4.86 (s, 1 H, CH), 6.82 (s, 4 H, Ar-H).

T = 333 K: δ = 1.66 (s, 6 H, C(CH₃)), 2.11 (s, 12 H, *o*-CH₃), 2.22 (s, 6 H, *p*-CH₃), 3.46 (s, 1 H, ZnH), 4.92 (s, 1 H, CH), 6.83 (s, 4 H, Ar-H).

Temperature-dependent ¹H NMR spectra in [D₈]toluene (500 MHz)

T = 213 K: δ = 1.39 (s, 6 H, C(CH₃)), 1.98 (s, 12 H, *o*-CH₃), 2.30 (s, 6 H, *p*-CH₃), 4.85 (s, 1 H, ZnH), 4.76 (s, 1 H, CH), 6.64 (s, 4 H, Ar-H).

$T = 233\text{ K}$: $\delta = 1.40$ (s, 6 H, C(CH₃)), 1.97 (s, 12 H, *o*-CH₃), 2.29 (s, 6 H, *p*-CH₃), 4.78 (s, 1 H, ZnH), 4.76 (s, 1 H, CH), 6.65 (s, 4 H, Ar-H).

$T = 253\text{ K}$: $\delta = 1.43$ (s, 6 H, C(CH₃)), 1.98 (s, 12 H, *o*-CH₃), 2.27 (s, 6 H, *p*-CH₃), 4.69 (s, 1 H, ZnH), 4.79 (s, 1 H, CH), 6.67 (s, 4 H, Ar-H).

$T = 273\text{ K}$: $\delta = 1.47$ (s, 6 H, C(CH₃)), 2.01 (s, 12 H, *o*-CH₃), 2.23 (s, 6 H, *p*-CH₃), 4.57 (s, 1 H, ZnH), 4.84 (s, 1 H, CH), 6.70 (s, 4 H, Ar-H).

$T = 298\text{ K}$: $\delta = 1.53$ (s, 6 H, C(CH₃)), 2.04 (s, 12 H, *o*-CH₃), 2.19 (s, 6 H, *p*-CH₃), 4.43 (s, 1 H, ZnH), 4.88 (s, 1 H, CH), 6.73 (s, 4 H, Ar-H).

$T = 313\text{ K}$: $\delta = 1.56$ (s, 6 H, C(CH₃)), 2.05 (s, 12 H, *o*-CH₃), 2.17 (s, 6 H, *p*-CH₃), 4.35 (s, 1 H, ZnH), 4.90 (s, 1 H, CH), 6.74 (s, 4 H, Ar-H).

$T = 333\text{ K}$: $\delta = 1.58$ (s, 6 H, C(CH₃)), 2.06 (s, 12 H, *o*-CH₃), 2.15 (s, 6 H, *p*-CH₃), 4.27 (s, 1 H, ZnH), 4.93 (s, 1 H, CH), 6.75 (s, 4 H, Ar-H).

$T = 353\text{ K}$: $\delta = 1.60$ (s, 6 H, C(CH₃)), 2.07 (s, 12 H, *o*-CH₃), 2.14 (s, 6 H, *p*-CH₃), 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 α radiation, $\lambda = 0.71073\text{ \AA}$). 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.

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