Non-Innocence of β -Diketiminato Ligands

S. Gondzik, D. Bläser, C. Wölper, S. Schulz*

Chemistry Department, University of Duisburg-Essen, Universitätsstr. 5-7, 45117 Essen, Germany

E-mail: stephan.schulz@uni-due.de; Phone: Int + 201-1834635; Fax: Int + 201-1833830

Abstract

The homoleptic thio- β -ketiminate zinc complex [MesNC(Me)CH{C(Me)NMes}S]₂Zn (**1**) was obtained from reactions of elemental sulfur with the β -diketiminato zinc complexes [CH{C(Me)NMes}₂]₂ZnMe, [CH{C(Me)NMes}₂]₂Zn₂ and [[CH{C(Me)NMes}₂]₂Zn-TePh]₂. **1** and the byproducts were characterized by multinuclear NMR (¹H, ¹³C, ¹²⁵Te) and IR spectroscopy, elemental analyses as well as by single crystal X-ray diffraction.

Keywords: Zinc, β -diketiminato, sulfur

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1. Introduction

Monoanionic β -diketiminato ligands, often also referred to as "nacnac" ligands, have been established over the last decades as powerful spectator ligands for the stabilization of main group and transition metal complexes as well as lanthanide complexes.^[1-3] According to the easy tunability of the steric and electronic properties of these ligands as well as their variable binding motifs,^[4] which range from pure σ to a combination of σ and π donation, they have evolved into one of the most ubiquitous systems in coordination chemistry. The kinetic stabilization of low-coordinated metal complexes such as low-valent M–M dimers of zinc,^[5] magnesium,^[6] manganese^[7] and tin, respectively,^[8] in which the metal atoms adopt the formal oxidation state +I, by use of sterically very demanding β -diketiminato ligands has been of particular interest.^[9-13] Moreover, β -diketiminato metal complexes are promising catalyst in different catalytic reactions such as ring opening polymerization (ROP) of cyclic ethers and others^[14-17] as well as in the copper catalyzed C–H amination and etherification,^[18,19] or magnesium and calcium catalyzed de-hydrocoupling of amino-boranes.^[20]

The β -diketiminato ligands are typically very stable and usually act as innocent spectator ligands. However, β -diketiminato ligands are also known to take part in different reactions. An early report by Jordan et al. showed that the β -diketiminato ligand can be attacked by ethylene with subsequent C–C bond formation^[21] and the redox-noninnocent behavior of β -diketiminato ligands was recently demonstrated.^[22-24] In addition, the oxidative degradation of the β -diketiminato ligand was demonstrated in reaction of β -diketiminato metal complexes with molecular oxygen,^[25-28] whereas Dyson et al. demonstrated that chelating β -diketiminato ligands can be transformed to a β -diimine ligand in reactions of Ru(II) arene complexes with hydrogen, ethylene and acetylene, respectively.^[29] Very recently, Fulton et al. reported on reactions of β -diketiminato lead complexes with phenylisocyanate, which unexpectedly occurred at the γ -carbon atom of the ligand backbone.^[30]

Due to our long term interest in the reactivity of β -diketiminato zinc complexes, in which the zinc atoms either adopt the usual formal oxidation state +II^[31-37] or the unusual oxidation state +I,^[38-40] respectively, we investigated reactions of several β -diketiminato zinc complexes with elemental sulfur. These reactions unexpectedly occurred with sulfurization of the γ -carbon atom of the β -diketiminato backbone and formation of [MesNC(Me)CH(S)C(Me)NMe]₂Zn (**1**).

2. Results and Discussion

Reactions of $[\text{Mesnacnac}]_2\text{Zn}_2$ (Method A) with elemental sulfur occurred with formation of $[\text{MesnacnacS}]_2\text{Zn}$ (**1**). In addition, analogous reactions of MesnacnacZnMe (Method B) and $[\text{MesnacnacZnTePh}]_2$ (Method C) with elemental sulfur proceeded with elimination of Me_2Zn and Ph_2Te_2 , respectively, and subsequent formation of **1** (scheme 1). **1** was characterized by multinuclear NMR (^1H , ^{13}C) and IR spectroscopy as well as by elemental analysis. In addition, the solid state structure of **1** was determined by single crystal X-ray diffraction.

Scheme 1. Synthesis of $[\text{MesNC}(\text{Me})\text{CH}(\text{S})\text{C}(\text{Me})\text{NMes}]_2\text{Zn}$ (**1**).

The ^1H and ^{13}C NMR spectra of **1** show the expected resonances due to the thio- β -ketiminate ligand. The resonances of the Me groups of the ligand are slightly shifted compared to those of the starting complexes. As expected, the most prominent difference in the spectra is the signal for the γ -C-H and the γ -C atoms in the backbone of the ligand. The γ -C-H is significantly shifted to higher field (4.61 ppm), whereas the γ -C is shifted to lower field (108.3 ppm) compared to the starting reagents $[\text{Mesnacnac}]_2\text{Zn}_2$ (^1H , 4.85 ppm; ^{13}C 95.5 ppm), MesnacnacZnMe (^1H , 4.97 ppm; ^{13}C 94.2 ppm) and $[\text{MesnacnacZnTePh}]_2$ (^1H , 4.93 ppm; ^{13}C 95.95 ppm), respectively. Moreover, the former singlet resonances of the four protons of the aryl groups of the starting complexes appears as two singlets - each with the integration of two protons - in **1**. The byproducts were characterized by ^1H -NMR (ZnMe_2 ,

Te₂Ph₂), ¹²⁵Te-NMR (Te₂Ph₂), single crystal X-ray diffraction (Te₂Ph₂) and EDX (ZnS). The ¹²⁵Te-NMR spectra showed two signals at 415 ppm for Te₂Ph₂ and -1915 ppm, which most likely indicate the formation of a [Te_{n-x}Zn_x]²⁺ dication.^[41] The most likely reaction mechanism is exemplary shown for Method B.

Scheme 2. Reaction mechanism of [MesnacnacS]₂Zn (**1**).

The new compound [MesNC(Me)CH(S)C(Me)NMe]₂Zn (**1**) is most likely formed via nucleophilic attack of the γ-carbon atom of the β-diketiminato ligands to the S₈ ring followed by S-S cleavage and subsequent elimination of S₇, coordination of the negatively charged sulfide to the Zn atom and finally the formation of the homoleptic complex upon elimination of ZnMe₂ (ligand exchange).^[25] Comparable reaction mechanism has been reported for reactions of β-diketiminato complexes with alkenes, molecular oxygen and other substrates.^[21-30] In addition, comparable reactions were reported for imidazole-2-ylidenes (NHC) as well as imidazolium salts, which are known to react with elemental sulfur (S₈) in a nucleophilic attack followed by S-S cleavage and subsequent formation of a C=S double bond.^[42,43]

Crystals of **1** suitable for a single crystal X-ray diffraction study were obtained from a solution in fluorobenzene after storage at +4 °C for 24 h.

Figure 1. Molecular structure of $[\text{MesNC}(\text{Me})\text{CH}(\text{S})\text{C}(\text{Me})\text{NMes}]_2\text{Zn}$ **1** (displacement parameters are drawn at 50 % probability level, solvent molecules and H atoms omitted for clarity) showing the atom-numbering scheme; selected bond lengths (Å) and angles (°): Zn-S1 2.273(7), Zn-S2 2.279(8), Zn-N1 2.089(2), Zn-N3 2.104(2), N1-C1 1.285(3), N3-C6 1.278(3), N2-C3 1.268(3), N4-C8 1.269(3), S1-Zn-S2 137.932(3), N1-Zn-N3 122.161(8), S1-Zn-N1 87.608(6), S1-Zn-N3 113.405(6), S2-Zn-N1 112.653(6), S2-Zn-N3 87.340(6).

1 crystallizes in the triclinic space group $P\bar{1}$ with one molecule and four disordered solvent molecules in the asymmetric unit. The central unit in this compound is a zinc atom, which is coordinated by two sulfur and two nitrogen atoms of the ligand. The zinc atom in the five membered C_2SNZn rings is slightly out of plane (deviation from the least-squares plane of the ligand 0.632(3) and 0.619(3) Å, r.m.s. deviation of the ligand atoms from the plane 0.0505

and 0.0715 Å). The average Zn-S (2.276 Å) bond lengths are in the range of known Zn-S complexes,^[44-49] but slightly shorter than the Zn-S bond length in ZnS. The C1-N1, C6-N3, C3-N2 and C8-N4 bond lengths (average of 1.275 Å) are in the range of C-N double bonds. This change of the bonding situation in **1** compared to Mesnacnac₂Zn₂ results in the loss of the π -system of the ligand. The Zn-N bond lengths (average of 2.096 Å) indicates dative bonds and confirmed the loss of the π -system. The endocyclic S2-Zn-N1 bond angle (112.653°) is slightly smaller compared to the endocyclic S1-Zn-N3 bond angle (113.405°). The bond angles S1-Zn-N1 (87.608°) and S2-Zn-N3 (87.340°) are significant smaller and the bond angles S1-Zn-S2, N1-Zn-N3, S1-Zn-N3 and S2-Zn-N1, which have a range from 112.653° to 137.932°, are significant larger compared to the ideal tetrahedron angle of 109.5°. Due to the bulkiness of the mesityl groups at the nitrogen atoms and the building of the five membered rings the tetrahedral coordination sphere at zinc atom is distorted.

To summarize, the studies presented herein clearly demonstrate that β -diketiminato ligands in various zinc complexes can serve as reactive groups due to the high nucleophilic character of the γ -carbon center, clearly revealing that this ligand is far away from being considered as non-innocent spectator ligand.

3. Experimental Section

3.1. General Considerations

All manipulations were performed in a glovebox under N₂-atmosphere or by standard Schlenk techniques. Mesnacnac₂Zn₂,^[38] MesnacnacZnMe^[33.] and [MesnacnacZnTePh]₂^[39] were prepared according to literature methods. ¹H NMR, ¹³C{¹H}, and ¹²⁷Te{¹H} NMR spectra were recorded with a Bruker DMX 300 spectrometer and are referenced to internal C₆D₅H (¹H NMR: δ = 7.16 ppm; ¹³C NMR: δ = 128.0 ppm) and TMS (¹²⁷Te{¹H}).^[50] 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 Duisburg-Essen.

3.2. Synthesis of [MesnacnacS]₂Zn (**1**)

Method A: Mesnacnac₂Zn₂ (0.08 g, 0.1 mmol) was dissolved in 10 mL of toluene at ambient temperature. A solution of freshly sublimed S₈ (0.012 g, 0.05 mmol) in 10 mL of toluene was added and the resulting solution was stirred for 12h, yielding a orange participate that was

isolated by filtration. The filtrate was concentrated to 5 mL and the solution was stored at +4 °C. Colorless crystals were obtained after 24h and isolated by filtration.

[MesnacnacS]₂Zn (**1**): Yield 0.05 g (62.8 %); M.p. 196 °C. Anal. Calc. for C₄₆H₅₈N₄S₂Zn (795.78 g/mol): C 69.4, H 7.29, N 7.04, S 8.05; Found: C 69.1, H 7.25, N 7.01, S 8.09. ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ = 1.71 (s, 6 H, CCH₃), 2.07 (s, 6 H, *p*-CH₃), 2.15 (s, 12 H, *o*-CH₃), 4.61 (s, 1 H, CH), 6.72 (s, 2 H, Ar-H), 6.79 (s, 2 H, Ar-H). ¹³C-NMR (75 MHz, [C₆D₆], 25 °C): δ = 18.5 (*o*-Me_{Ar}), 20.3 (*p*-Me_{Ar}), 20.8 (N=C-CH₃), 20.9 (N=C-CH₃), 108.3 (S-C), 115.3 (*p*-Ar), 115.6 (*p*-Ar), 128.9 (*m*-Ar), 129.4 (*m*-Ar), 132.0 (*o*-Ar), 137.8 (*o*-Ar), 141.0 (SC-C=N), 161.0 (ZnN=C), 168.7 (*ipso*-Ar), 169.9 (*ipso*-Ar). IR: ν = 2963, 2914, 2857, 1636, 1551, 1477, 1437, 1404, 1359, 1260, 1214, 1174, 1147, 1095, 1013, 970, 853, 804, 790, 563, 553, 528, 496, 468 cm⁻¹.

Method B: MesnacnacZnMe (0.04 g, 0.1 mmol) and S₈ (0.012 g, 0.05 mmol) were dissolved in 0.5 mL of C₆D₆ in a NMR tube and mixed at ambient temperature for 12h. The formation of **1** was proven by ¹H NMR spectroscopy.

Method C: [MesnacnacZnTePh]₂ (0.17 g, 0.15 mmol) was dissolved in 10 mL fluorobenzene at ambient temperature. A solution of S₈ (0.02 g, 0.08 mmol) in toluene was added. The solution was stirred for 12h and thereafter stored at +4 °C for 24h, yielding colorless and red crystals, which were separated under a microscope.

Yield: 0.065 g (54.1 %). ¹H-NMR (300 MHz, [C₆D₆], 25 °C): δ = 1.71 (s, 6 H, CCH₃), 2.07 (s, 6 H, *p*-CH₃), 2.15 (s, 12 H, *o*-CH₃), 4.61 (s, 1 H, CH), 6.72 (s, 2 H, Ar-H), 6.79 (s, 2 H, Ar-H), 6.84 (m, 8 H, Ph-H), 7.70 (m, 2 H, Ph-H). ¹²⁵Te-NMR (95 MHz, [C₆D₆], 25 °C): δ = 415 (Te₂Ph₂), -1915 ([Te_{n-x}Zn_x]²⁺).

3.3. X-ray Structure Solution and Refinement.

A crystal of **1** was mounted on a nylon loop in inert oil. Crystallographic data of **1** are summarized in Table 1. Figures 1 shows the solid state structures of **1** including selected bond lengths and angles. Data were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (mono-chromated MoK α radiation, λ = 0.71073 Å) at 180(1) K. The structure was solved by Direct Methods (SHELXS-97)^[51] and refined anisotropically by full-matrix least-squares on *F*² (SHELXL-97).^[52] Absorption corrections was performed semi-empirically from equivalent reflections on basis of multi-scans (Buker AXS APEX2,). Non-hydrogen atoms were refined anisotropically where possible and hydrogen atoms were refined using a

riding model or rigid methyl groups. Where needed the phenyl rings of the disordered solvent molecules were constrained to a regular hexagon (AFIX 66) or distance restraints (DFIX) were applied. C-F bond lengths were restrained to be equal (SADI).

Crystallographic data of **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1040407 (**1**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [Fax: (internal) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments. This work was financially supported by the University of Duisburg-Essen.

Table 1: Crystallographic Data and Measurements for 1.

	1
Empirical formula	C ₄₆ H ₅₈ S ₂ N ₄ Zn
<i>M</i>	795
Crystal size [mm]	0.26 × 0.22 × 0.18
<i>T</i> [K]	180(1)
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> [Å]	14.135(3)
<i>b</i> [Å]	14.990(3)
<i>c</i> [Å]	15.980(3)
α [°]	68.815(5)
β [°]	85.067(5)
γ [°]	75.136(5)
<i>V</i> [Å ³]	3051.3(10)
<i>Z</i>	2
<i>D</i> _{calc} [g · cm ⁻³]	1.233
μ (MoK α [Å])	0.71073
Transmissions	0.75/0.66
<i>F</i> (000)	1198
Index ranges	-19 ≤ <i>h</i> ≤ 19
	-20 ≤ <i>k</i> ≤ 20
	-21 ≤ <i>l</i> ≤ 21
$\theta_{\max}$ [°]	28.56
Reflections collected	58485
Independent reflections	15609
<i>R</i> _{int}	0.0280
Refined parameters	687
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0499
<i>wR</i> ₂ [all data]	0.1484
GooF	1.071
$\Delta\rho_{\text{final}}$ (max/min) [e · Å ⁻³]	0.603/-0.683

^a $RI = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ (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 = $\{\Sigma[w(|F_o^2| - |F_c^2|)^2]/(N_{\text{observns}} - N_{\text{params}})\}^{1/2}$

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DOI: 10.1016/j.jorganchem.2015.02.028

URN: urn:nbn:de:hbz:464-20201125-110115-9

This is the **Authors Accepted Manuscript** of an article published in:

Journal of Organometallic Chemistry, 783 (2015), 92-95.

The final version may be found at: <https://doi.org/10.1016/j.jorganchem.2015.02.028>

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