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Synthesis and X-ray crystal structures of zinc dichloride complexes supported by a β -diimine ligand

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β -diimine zinc dichloride complexes $[\text{CH}_2\{\text{C}(\text{Me})\text{NAr}\}_2]\text{ZnCl}_2$ (Ar = Mes **1**, Dipp **2**) were obtained from the reactions of ZnCl_2 with the corresponding β -iminoamines $[\text{ArN}(\text{H})\text{C}(\text{Me})\text{CHC}(\text{Me})\text{NAr}]$. **1** and **2** were characterized by multinuclear NMR (^1H , ^{13}C) and IR

spectroscopy, elemental analyses as well as by single crystal X-ray diffraction. The energy differences between the enamine-imine tautomers of the β -iminoamines were quantified by quantum chemical calculations.

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Introduction

Monoanionic β -diketiminate 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, in which the metal centers adopt low formal oxidation states, by use of sterically very demanding β -diketiminate ligands has been of particular interest.^[5-9] Moreover, β -diketiminate metal complexes are promising catalyst in different catalytic reactions such as ring opening polymerization (ROP) of cyclic ethers and others.^[10-13]

While a large number of metal complexes containing monoanionic β -diketiminate ligands have been explored, complexes containing the neutral β -iminoamine (β -diketimine) ligands are rather rare, whereas α -diimines complexes, which have been established over the last decade as very powerful catalysts (Brookhart-type), are well known.^[14-17] β -diketimines can formally exist in the enamine and the imine form, but the enamine tautomer is typically energetically favoured (scheme 1). However, the β -diimine tautomer can be stabilized by use of sterically demanding substituents as was successfully demonstrated in the synthesis of the bulky diimine $\text{CH}_2[\text{C}(t\text{-Bu})\text{NDipp}]_2$ (Dipp = 2,6-*i*-Pr₂C₆H₃), which does not interconvert in

hydrocarbon solutions to the enamine form $[\text{DippN}(\text{H})\text{C}(t\text{-Bu})\text{CHC}(t\text{-Bu})\text{NDipp}]$.^[18]

Scheme 1. Enamine-imine tautomers of β -iminoamine.

Moreover, the β -diimine form can be stabilized in the coordination sphere of transition metals as was initially shown for the nickel complex $[\text{CH}_2\{\text{C}(\text{Me})\text{NDipp}\}_2]\text{NiBr}_2$, which was obtained from the reaction of NiBr_2 with the β -iminoamine $[\text{DippN}(\text{H})\text{C}(\text{Me})\text{CHC}(\text{Me})\text{NDipp}]$.^[19] Since then, a few neutral^[20-23] as well as cationic metal complexes^[24-26] of the desired type have been synthesized and structurally characterized (scheme 2).

Scheme 2. Structurally characterized neutral and cationic β -diimine transition metal complexes.

We herein report on the synthesis and solid state structures of first β -diimine zinc dichloride complexes $[\text{CH}_2\{\text{C}(\text{Me})\text{NAr}\}_2]\text{ZnCl}_2$ (Ar = Mes **1**, Dipp **2**).

Results and Discussion

Reactions of ZnCl_2 with equimolar amounts of the β -iminoamines $[\text{ArN}(\text{H})\text{C}(\text{Me})\text{CHC}(\text{Me})\text{NAr}]$ proceed with formation of the corresponding β -diimine complexes $[\text{CH}_2\{\text{C}(\text{Me})\text{NAr}\}_2]\text{ZnCl}_2$ (Ar = Mes **1**, Dipp **2**). **1** and **2** were characterized by multinuclear NMR (^1H , ^{13}C) and IR spectroscopy as well as by elemental analysis.^[27] In addition, the solid state structure of **1** and **2** were determined by single crystal X-ray diffraction.

Scheme 3. Synthesis of **1** and **2**.

Compared to the starting β -iminoamines, the ^1H NMR spectra of **1** and **2** show a resonances for the methylene group and the C-Me groups with a relative intensity of 2:6, while the resonances of the N-H protons (R = Mes 12.08; Dipp 12.07 ppm) have disappeared. In addition, the γ -CH backbone resonances in the ^1H NMR spectra of the β -diketimines (Mes 4.91; Dipp 4.94 ppm) are shifted significantly to higher field (**1**: 4.20, **2**: 4.34 ppm), indicating the formation of a methylene group (γ -CH₂). This was further proven by ^{13}C NMR spectroscopy, which also showed a significant highfield shift of the γ -C resonance (**1**: 44.9, **2**: 45.1 ppm) compared to the β -iminoamines (Mes 93.9; Dipp 93.3 ppm). Moreover, the dept-135 ^{13}C NMR spectra show a negative signal, verifying the formation of a γ -CH₂ group. The presence of the imine functionality was also proven by IR spectroscopy. IR spectra of **1** and **2** show strong absorption bands at 1659 (**1**) and 1656 cm^{-1} (**2**) due to the N=C group.

Crystals of **1** and **2** suitable for a single crystal X-ray diffraction study were obtained from solutions in CHCl_3 **1** and THF **2** after storage at ambient temperature for 24 h.

Figure 1. Molecular structure of **1** (displacement parameters are drawn at 50 % probability level, solvent molecules and H atoms omitted) showing the atom-numbering scheme; selected bond lengths (Å) and angles (°): Zn1-C11 2.2095(2), Zn1-C12 2.2528(2), Zn1-N1 2.0328(7), Zn1-N2 2.0351(7), C1-C2 1.5119(12), C2-C3 1.5101(11), N1-C1 1.2836(10), N2-C3 1.2851(10); N1-Zn1-N2 95.27(3), C11-Zn1-C12 (112.678(9), C1-C2-C3 121.90(7).

Table 1. Crystallographic Data and Measurements for **1** and **2**.

	1	2
Empirical formula	C ₂₅ H ₃₂ Cl ₈ N ₂ Zn	C ₂₉ H ₄₂ Cl ₂ N ₂ Zn
<i>M</i>	709.52	554.91
Crystal size [mm]	0.5 × 0.5 × 0.45	0.362 × 0.279 × 0.138
<i>T</i> [K]	100(1)	100(1)
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	13.3781(8)	13.3723(7)
<i>b</i> [Å]	13.2265(8)	16.1334(8)
<i>c</i> [Å]	18.1080(12)	14.9812(7)
α [°]	90	90
β [°]	101.614(3)	110.875(2)
γ [°]	90	90
<i>V</i> [Å ³]	3138.5(3)	3019.9(3)
<i>Z</i>	4	4
<i>D</i> _{calc} [g · cm ⁻³]	1.502	1.221
μ (MoK α [mm ⁻¹])	1.482	1.009
Transmissions	0.75/0.66	1.0/0.8721
<i>F</i> (000)	1448	1176
Index ranges	-21 ≤ <i>h</i> ≤ 20 -21 ≤ <i>k</i> ≤ 21 -28 ≤ <i>l</i> ≤ 29	-20 ≤ <i>h</i> ≤ 20 -24 ≤ <i>k</i> ≤ 24 -21 ≤ <i>l</i> ≤ 23
θ_{max} [°]	36.24	33.197
Reflections collected	70900	136502
Independent reflections	14035	11549
<i>R</i> _{int}	0.0210	0.0285
Refined parameters	333	317
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0241	0.0304
<i>wR</i> ₂ [all data]	0.0661	0.0827
Goof	1.031	1.022
$\Delta\rho_{\text{final}}$ (max/min) [e · Å ⁻³]	1.218/-0.801	0.938/-0.500

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ (for $I > 2\sigma(I)$). [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] Goodness of fit = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{\text{observs}} - N_{\text{params}})\}^{1/2}$

1 crystallizes in the monoclinic space group *P*2₁/*n* with one molecule in the asymmetric unit accompanied by two chloroform molecules. **2** crystallizes in space group *P*2₁/*c* without any solvent. The central six-membered, nonplanar C₃N₂Zn rings in **1** and **2** adopt boat-type conformations as was previously reported for this type of complexes, resulting from the protonation of the backbone carbon atom (γ -C). The fourfold-coordinated Zn1 atom, which adopts a distorted tetrahedral coordination sphere, and the C2 atom are slightly out of the plane (C2: 0.4062(12) Å, Zn: 0.5216(11) Å (**1**); C2: 0.4826(19) Å, Zn: 0.7400(15) Å (**2**)) defined by N1, N2, C1 and C3. The endocyclic N1-Zn1-N2 bond angles (**1**: 95.27(3)°, **2**: 93.13(3)°) are significantly smaller than the exocyclic C11-Zn1-C12 bond angle (**1**: 112.678(9)°, **2**: 118.128(17)°). The endocyclic C1-C2-C3

bond angles of 121.90(7)° in **1** and 119.76(10)° in **2** are significantly larger than the ideal tetrahedral value of a sp³-hybridized carbon atom. The N1 and N2 atoms are trigonal planar (Σ of the bond angles **1**: 359.7°, **2**: 359.84 (N1) and **1**: 359.9°, **2**: 358.96 (N2)), which is fully consistent with the description of sp²-hybridized (imine) N atoms. The Zn-Cl bond lengths in **1** differ by almost 5 pm (2.2095(2), 2.2528(2) Å) and in **2** by only 3 pm (2.1979(3), 2.2212(4) Å). The Zn-N bond lengths in **2** are slightly elongated compared to those in **1** (**1**: 2.0328(7), 2.0351(7) Å; **2**: 2.0515(8), 2.0515(8) Å), reflecting the larger steric demand of the Dipp substituents. The Zn-N bond lengths in **1** and **2** are elongated by almost 6 pm compared to the average Zn-N bond lengths reported in the Cambridge structure database for 23 structurally characterized neutral β -diketiminate-zinc complexes containing the analogous Mes-substituted ligand (58 Zn-N bonds, mean value 1.977(3), median value 1.971 Å).^[28-40] The C1-C2 (**1**: 1.5119(12) Å; **2**: 1.5163(16) Å) and C2-C3 (**1**: 1.5101(11) Å; **2**: 1.5151(15) Å) bond lengths as well as the N1-C1 (**1**: 1.2836(10) Å; **2**: 1.2802(14) Å) and N2-C3 (**1**: 1.2851(10) Å; **2**: 1.2816(13) Å) bond lengths agree perfectly with the description of C-C single bonds and C-N double bonds.

Figure 2. Molecular structure of **2** (displacement parameters are drawn at 50 % probability level, H atoms omitted) showing the atom-numbering scheme; selected bond lengths (Å) and angles (°): Zn(1)-N(2) 2.0515(8), Zn(1)-N(1) 2.0515(8), Zn(1)-Cl(2) 2.1979(3), Zn(1)-Cl(3) 2.2212(4), C(1)-C(2) 1.5163(16), C(2)-C(3) 1.5151(15), N(1)-C(1) 1.2802(14), N(2)-C(3) 1.2816(13), N(2)-Zn(1)-N(1) 93.13(3), Cl(2)-Zn(1)-Cl(3) 118.128(17), C(3)-C(2)-C(1) 119.76(10).

Since there is no experimental evidence that the β -aminoamines [ArN(H)C(Me)CHC(Me)NAr] form an equilibrium with the corresponding β -diimine tautomers in solution, we investigated the relative energies of both tautomers using quantum chemical calculations.^[41] Geometry optimization of both tautomeric forms clearly revealed that both molecules [ArN(H)C(Me)CHC(Me)NAr] strongly prefer the enamine form by 31.51 (Ar = Mes **1a**) and 33.68 kJ/mol (Ar = Dipp **2a**), respectively. Therefore, the formation of the β -diimine complexes **1** and **2** must be initiated by the coordination of the β -iminoamines to the electrophilic ZnCl₂, followed by proton shift to the nucleophilic γ -carbon of the ligand backbone.

Figure 3. Geometry-optimized structures of both tautomeric forms of [MesN(H)C(Me)CHC(Me)NMes] (enamine **1a**, imine **1b**).

Conclusions

The syntheses of β -diimine zinc dichloride complexes [CH₂{C(Me)NAr}₂]ZnCl₂ (Ar = Mes **1**, Dipp **2**) is described and the solid state structures of **1** and **2** are determined. According to quantum chemical calculations, the enamine tautomeric forms of the β -iminoamines [ArN(H)C(Me)CHC(Me)NAr] (Ar = Mes, Dipp) are preferred by 31.51 kJ/mol (Ar = Mes) and 33.68 kJ/mol (Ar = Dipp). Obviously, the formation of the β -diimine tautomers in **1** and **2** is initiated by coordination of the β -iminoamines to the electrophilic zinc dichloride.

Experimental Section

All manipulations were performed in a glovebox under N₂-atmosphere or by standard Schlenk techniques. L^{1/2}H (L¹ = [MesN(H)C(Me)CHC(Me)NMes], L² = [DippN(H)C(Me)CHC(Me)NDipp]) were prepared according to literature methods.^[42] ¹H and ¹³C{¹H} spectra were recorded using a Bruker AMX 300 spectrometer and are referenced to internal CD₂Cl₂ ($\delta^1\text{H}$ 5.32, $\delta^{13}\text{C}$ 53.8). 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.

General Preparation of [CH₂{C(Me)NAr}₂]ZnCl₂.

0 A solution of 2.0 mmol L^{1/2}H (L¹ = [MesN(H)C(Me)CHC(Me)NMes] 0.67 g; L² = [DippN(H)C(Me)CHC(Me)NDipp] 0.84 g) and 0.27 g ZnCl₂ (2.0 mmol) in 10 mL of CHCl₃ was stirred for 1 h at ambient temperature. The solution was stored for 24 h, yielding colorless crystals of **1**, whereas **2** crystallized in THF.
[CH₂{C(Me)NMes}₂]ZnCl₂ (1**).** Yield 0.88 g (93 %); m.p. 321 °C. Anal. Calc. for C₂₃H₃₀N₂ZnCl₂ (470.78 g/mol): C 58.68, H 6.42, N 5.95; Found: C 58.14, H 6.44, N 5.83%. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ = 2.11 (s, 6H, β -CCH₃), 2.21 (s, 12H, *o*-CH₃), 2.32 (s, 6H, *p*-CH₃), 4.20 (s, 2H, γ -CH₂), 6.98 (s, 4H, *m*-H). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂, 25 °C): δ = 18.6 (*o*-CH₃), 20.5 (β -CCH₃), 24.7 (*p*-CH₃), 44.9 (γ -C), 128.6 (*m*-C), 129.4 (*o*-C), 136.3 (*p*-C), 140.8 (*i*-C), 178.0 (β -CCH₃). ATR-IR: ν = 2997, 2986, 2954, 2914, 2870, 1659, 1631, 1476, 1428, 1385, 1207, 1188, 1139, 1034, 1014, 856, 825, 722, 606, 549, 436, 403.
[CH₂{C(Me)NDipp}₂]ZnCl₂ (2**).** Yield 0.99 g (89 %); m.p. 256 °C. Anal. Calc. for C₂₉H₄₂N₂ZnCl₂ (554.94 g/mol): C 62.77, H 7.63, N 5.05; Found: C 62.41, H 7.34, N 5.17%. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ = 1.16 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 1.32 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 2.12 (s, 6H, β -CCH₃), 3.03 (sept, ³J_{HH} = 6.8 Hz, 4H, CH(CH₃)₂), 4.34 (s, 2H, γ -CH₂), 7.28–

7.38 (6H, *m/p*-H). ¹³C NMR (75 MHz, CD₂Cl₂, 25 °C) δ = 24.0 (CH(CH₃)₂), 24.7 (β-CCH₃), 26.3 (CH(CH₃)₂), 28.5 (CH(CH₃)₂), 45.1 (γ-C), 124.5 (*m*-C), 127.5 (*p*-C), 139.9 (*o*-C), 140.4 (*i*-C), 178.8 (β-CCH₃). ATR-IR: ν = 3061, 2964, 2869, 1656, 1551, 1463, 1441, 1383, 1260, 1096, 1017, 797, 752, 391.

Single crystal X-ray diffraction. Crystals of **1** and **2** were mounted on nylon loops in inert oil. Crystallographic data of **1** and **2** are summarized in Table 1. Figures 1 and 2 show the solid state structures of **1** and **2** 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 structures were solved by Direct Methods (SHELXS-97)^[43] and refined anisotropically by full-matrix least-squares on *F*² (SHELXL-97).^[44] Absorption corrections was performed semi-empirically from equivalent reflections on basis of multi-scans (Buker AXS APEX2, **1**) and by face-indexing (**2**). All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model or rigid methyl groups. The crystallographic data of **1** and **2** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1035846 (**1**) and CCDC-1037909 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): ¹H NMR, ¹³C NMR and IR spectra of β-aminoimines and **1** and **2**, X-ray crystallographic data of **1** and **2** incl. cif files as well as results from computational calculations.

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Synthesis and X-ray crystal structures of zinc dichloride complexes supported by a β -diimine ligand

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