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Synthesis and X-ray crystal structures of homoleptic Zinc complexes containing monoanionic β -ketoiminato and bis(thiophosphinoyl)methanediide ligands

Stephan Schulz,^{a,*} Raphaela Schäper,^a Dieter Bläser^a and Christoph Wölper^a

Dedicated to Prof. R. Hoppe on the Occasion of his 90th Birthday

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Homoleptic zinc complexes of the type L_2Zn containing monoanionic β -ketoiminato and bis(thiophosphinoyl)methanide substituents were synthesized in almost quantitative yield by reaction of $HC(CMe)_2(O)(N(H)CH_2CH_2NMe_2)$ and $H_2C(PPh_2=S)_2$ with zincocene Cp^*_2Zn at ambient temperature. The reactions proceeded with elimination of Cp^*H . $[HC(CMe)_2(O)(NCH_2CH_2NMe_2)]_2Zn$ **1** and $[HC(PPh_2=S)_2]_2Zn$ **2** were characterized by

NMR (1H , ^{13}C , ^{31}P) and IR spectroscopy as well as elemental analysis and single crystal X-ray diffraction. **1** and **2** were also obtained in reactions of dizincocene, $Cp^*_2Zn_2$, with two equivalents of the ligands. The reactions proceeded with disproportionation of initially formed monovalent dizinc complexes.

* Prof. S. Schulz

Fax: (+49) 201-183 3830

E-Mail: stephan.schulz@uni-due.de

[a] Inorganic Chemistry

University of Duisburg-Essen

Universitätsstr. 5-7, S07 S03 C30, D-45117 Essen

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Introduction

Monoanionic β -diketonates **I** and β -diketiminates **II** are suitable O,O' - and N,N' -chelating organic ligands, which have been intensely used in coordination chemistry of main group and transition metals in recent years.^[1] Heteroleptic zinc complexes of the type $LZnX$ ($X = \text{alkyl}, OR, NR_2$), in particular those containing β -diketiminato ligands, have been found to be very promising *living single-site catalysts* for the ring-opening polymerization of lactide and copolymerization of epoxides and carbon dioxide.^[2] Moreover, the suitability of β -diketiminato ligands to stabilize low-valent Zn-Zn bonded compounds was proven with the synthesis of $LZn-ZnL$ ($L = \{[(2,6-i-Pr_2-C_6H_3)N(Me)C]_2CH\}$ ^[3] and $\{[2,6-(2,4,6-Me_3-C_6H_2)N(Me)C]_2CH\}$ ^[4]).

In respect to the large number of structurally characterized homo- and heteroleptic zinc complexes containing β -diketonates and β -diketiminates, those containing the corresponding N,O -chelating β -ketoiminato ligand **III** have been structurally characterized in much lower number. To date, only three heteroleptic and 11 homoleptic complexes of the type $LZnX$ ^[5] and L_2Zn ^[5,6] have been structurally characterized. Homoleptic β -ketoiminato zinc complexes of the type L_2Zn were reported to show promising properties as *single source* precursor for the deposition of ZnO films by CVD processes.^[6b,6c] In addition, the corresponding monoanionic bis(thiophosphinoyl)methanides **IV** have also been studied to a far lesser extent, which is rather surprising

since the dianionic bis(thiophosphinoyl)methanediides **V** ligands have been investigated in detail due to their capability to form $M=C$ double bonds (metal carbenes).^[7] Only very recently, the synthesis of the homoleptic cobalt complex $[HC(PPh_2=S)_2]_2Co$ was reported.^[8] In addition, homoleptic complexes of the type L_2M such as $[L_2Ag][NO_3]$ ^[9] and $[L_2Cu][PF_6]$ ^[10] containing the neutral bis(thiophosphinoyl)methane ligand $[H_2C(PPh_2=S)_2]$ were also structurally characterized.

Scheme 1. Mono- and dianionic β -diketonates **I**, β -diketiminates **II**, β -ketoiminates **III**, bis(thiophosphinoyl)methanides **IV** and bis(thiophosphinoyl)methanediides **V**.

We became recently interested in the synthesis of homo- and heteroleptic zinc complexes containing X,X' -chelating ligands and reported on the synthesis and structures of several amidinates,^[11] amidates,^[12] carboxylates^[13] and thiocarboxylates,^[14] respectively. These were typically obtained from insertion reactions of the corresponding heterocumulene (carbodiimide, isocyanate, CO_2) into the Zn-C bond of Me_2Zn or Cp^*_2Zn or by insertion into the Zn-H bond of a zinc-hydride complex. Moreover, heteroleptic β -diketiminato complexes of the type $LZnX$ ($X = H, Me, I$) were obtained from alkane elimination and salt elimination reactions.^[15] Herein we expand our studies on homoleptic zinc complexes L_2Zn containing monoanionic β -ketoiminato

and bis(thiophosphinoyl)methanediide ligands, which were prepared by reactions of zincocene Cp^*_2Zn with the corresponding neutral ligands LH. $[\text{HC}(\text{CMe})_2(\text{O})(\text{NCH}_2\text{CH}_2\text{NMe}_2)]_2\text{Zn}$ (**1**) and $[\text{HC}(\text{PPh}_2=\text{S})_2]_2\text{Zn}$ (**2**) were obtained in almost quantitative yield and characterized by multinuclear NMR (^1H , ^{13}C , ^{31}P) and IR spectroscopy, elemental analyses and single crystal X-ray diffraction.

Results and Discussion

A hexane solution of Cp^*_2Zn reacts with a twofold amount of either $\text{HC}(\text{CMe})_2(\text{O})(\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{NMe}_2)$ or $\text{H}_2\text{C}(\text{PPh}_2=\text{S})_2$ at ambient temperature within 2 h with elimination of two equivalents of Cp^*H and subsequent formation of the corresponding homoleptic complexes $[\text{HC}(\text{CMe})_2(\text{O})(\text{NCH}_2\text{CH}_2\text{NMe}_2)]_2\text{Zn}$ (**1**) and $[\text{HC}(\text{PPh}_2=\text{S})_2]_2\text{Zn}$ (**2**), respectively. Moreover, the reaction of Cp^*_2Zn with one equivalent of both ligands also yielded the homoleptic complexes **1** and **2**, which was unambiguously proven by *in situ*-NMR spectroscopy. **1** and **2** were also obtained in reactions of dizincocene, Cp^*_2Zn_2 , with two equivalents of the ligands. Cp^*H elimination occurred at $-30\text{ }^\circ\text{C}$, but the resulting monovalent dizinc complexes immediately disproportionate to **1** and **2**, respectively, and elemental zinc.

Scheme 2. Synthesis of $[\text{HC}(\text{CMe})_2(\text{O})(\text{NCH}_2\text{CH}_2\text{NMe}_2)]_2\text{Zn}$ (**1**) and $[\text{HC}(\text{PPh}_2=\text{S})_2]_2\text{Zn}$ (**2**).

Single crystals of **1** were obtained from a solution in hexane upon storage at $4\text{ }^\circ\text{C}$. **1** crystallizes in the orthorhombic space group $Pbca$ with eight molecules in the unit cell.^[16] The central Zn atom of **1** is coordinated by two β -ketoiminato ligands, which serve as meridional tridentate donor ligands. The total coordination number of Zn is 4+2, resulting in an octahedral arrangement. The two tertiary amine side-arm functions are rather weakly coordinated to the zinc atom (geometric data see figure caption) and adopt the axial positions of the octahedron. The ketone functions adopt a *cisoid* orientation related to each other and are opposite to the long Zn–N bonds. The bond angles at the Zn range from $72.46(4)^\circ$ to $107.25(4)^\circ$ and $156.94(5)^\circ$ to $169.13(4)^\circ$, respectively, showing a slight distortion of the octahedron. The mean Zn–O and Zn–N bond lengths found in a CSD database search ($2.047\text{ \AA}$ and $2.093\text{ \AA}$) agree well with those of the short Zn–O and Zn–N bonds observed for **1**. The longest Zn–N bond length in **1** approximately equals the longest one found in the CSD ($2.804\text{ \AA}$, refcode DEPZAA^[17]).

Figure 1. Molecular structure of **1**. H atoms are omitted for clarity. Thermal ellipsoids at 50% probability levels. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Zn(1)–O(2) $2.0171(10)$, Zn(1)–N(3) $2.0404(12)$, Zn(1)–N(1) $2.0446(12)$, Zn(1)–O(1) $2.0519(10)$, Zn(1)–N(2) $2.4042(12)$, Zn(1)–N(4) $2.8075(12)$, O(2)–Zn(1)–N(3) $93.99(4)$, O(2)–Zn(1)–N(1) $107.25(4)$, N(3)–Zn(1)–N(1) $156.94(5)$, O(2)–Zn(1)–O(1) $96.10(4)$, N(3)–Zn(1)–O(1) $95.98(4)$, N(1)–Zn(1)–O(1) $90.70(4)$, O(2)–Zn(1)–N(2) $88.93(4)$, N(3)–Zn(1)–N(2) $93.27(4)$, N(1)–Zn(1)–N(2) $78.59(5)$, O(1)–Zn(1)–N(2) $169.13(4)$, O(2)–Zn(1)–N(4) $166.29(4)$, N(3)–Zn(1)–N(4) $72.46(4)$, N(1)–Zn(1)–N(4) $86.46(4)$, O(1)–Zn(1)–N(4) $83.55(4)$, N(2)–Zn(1)–N(4) $93.83(4)$.

The packing of **1** is dominated by chains parallel to b which are formed by $\text{C–H}\cdots\text{O}$ and $\text{C–H}\cdots\pi$ interactions. Since no further directed interactions between these chains can be found their arrangement is likely governed by close packing.

Figure 2. Packing of **1**. Chains parallel to b . #1 $-x+1/2, y-1/2, z$.

$\text{C17–H17C}\cdots\text{O1\#1}$ $d(\text{H}\cdots\text{A})$ $2.62\text{ \AA}$ $\angle(\text{DH}\cdots\text{A})$ 142.1° , $\text{C18–H18A}\cdots(\text{O2/C8})\#1$ $d(\text{H}\cdots\text{centroid})$ $2.72\text{ \AA}$ $\angle(\text{DH}\cdots\text{centroid})$ 163.6° $\angle(\text{H}\cdots\text{centroid}\cdots\text{plane of } \pi \text{ system})$ 90.0° .

Single crystals of **2** were obtained from a solution in hexane upon storage at $4\text{ }^\circ\text{C}$. **2** crystallizes in the monoclinic space group $C2/c$ with four molecules in the unit cell.^[16] Zn1 is located on a two-fold axis. The Zn atoms are tetrahedrally coordinated by two monoanionic bis(thiophosphinoyl)methanide groups, which adopt a $\text{S,S}'$ -chelating coordination mode as was previously observed for the corresponding Li-^[18] and Co-complexes $[\text{HC}(\text{PPh}_2=\text{S})_2]_2\text{Co}$.^[8] In contrast, the formation of metal-carbon bonds were observed for the corresponding Ge(II) and Sn(II) complexes of the type $\text{CIM}[\text{CH}(\text{PPh}_2=\text{S})_2]_2$ ($\text{M} = \text{Ge}, \text{Sn}$).^[18] Moreover, a comparable structural motif was observed for complexes such as $[\text{MgC}(\text{PPh}_2=\text{S})_2(\text{THF})]_2$ containing dianionic bis(thiophosphinoyl)methanediide ligands, which typically serve as SCS pincer ligands upon

formation of a metal-carbon double bond.^[19] Both six-membered $\text{ZnS}_2\text{P}_2\text{C}$ rings adopt *boat-type* conformations as was observed for bis(thiophosphinoyl)methanides complexes. The Zn-S bond lengths (2.3485(4), – 2.3485(5) Å) are within the typical range observed for Zn-S bonds. The P-C bond lengths in **2** (1.7169(16), 1.7166(16) Å) are significantly shorter than those in $\text{CH}_2(\text{PPh}_2=\text{S})_2$ (1.829 Å), whereas the P-S bond lengths in **2** (2.0319(6), 2.0422(6) Å) are elongated compared to those of $\text{CH}_2(\text{PPh}_2=\text{S})_2$ (1.944 Å).^[20] Comparable P-C and P-S bond lengths were reported for the Li salt $[\text{HC}(\text{PPh}_2=\text{S})_2]\text{Li}(\text{Et}_2\text{O})\text{THF}$ (P-S: 1.993(2), 1.993(2) Å; P-C: 1.712(4), 1.711(4) Å) and for three group 13 metal complexes of the type $[\text{MCl}[\text{C}(\text{PPh}_2=\text{S})_2]]_2$ (M = Al, Ga, In) containing dianionic bis(thiophosphinoyl)methanediide ligands,^[18] indicating a π -delocalization within the SPCPS backbone in **2**. The P(2)-C(13)-P(1) bond angle in **2** (124.45(9)°) is also comparable to that in $[\text{HC}(\text{PPh}_2=\text{S})_2]\text{Li}(\text{Et}_2\text{O})\text{THF}$ (126.8(3)°) but larger than that of $\text{H}_2\text{C}(\text{PPh}_2=\text{S})_2$ (118.4(2)°). In contrast, the endocyclic S(1)-Zn(1)-S(2) bond angle in **2** (116.089(15)°) is significantly larger than the S(2)-Li(1)-S(1) bond angle in $[\text{HC}(\text{PPh}_2=\text{S})_2]\text{Li}(\text{Et}_2\text{O})\text{THF}$ (108.1(4)°).

Figure 3. Molecular structure of **2**. H atoms are omitted for clarity. Asymmetric unit are presented in dark bonds. Thermal ellipsoids at 50% probability levels. Selected bond lengths [Å] and angles [°], #1 $-x+2, y, -z+1/2$: Zn(1)-S(1) 2.3485(4), Zn(1)-S(2) 2.3485(5), S(1)-P(1) 2.0319(6), S(2)-P(2) 2.0422(6), P(1)-C(13) 1.7169(16), P(2)-C(13) 1.7166(16), S(1)-Zn(1)-S(1)#1 98.62(2), S(1)-Zn(1)-S(2)#1 104.643(16), S(1)-Zn(1)-S(2) 116.089(15), S(2)-Zn(1)-S(2)#1 115.84(3), P(1)-S(1)-Zn(1) 100.79(2), P(2)-S(2)-Zn(1) 102.93(2), C(13)-P(1)-S(1) 118.89(6), C(13)-P(2)-S(2) 117.46(6), P(2)-C(13)-P(1) 124.45(9).

2 is isostructural to the analogue bis(selenophosphinoyl)-methanide complex $[\text{HC}(\text{PPh}_2=\text{Se})_2]_2\text{Zn}$,^[21] for which a different asymmetric unit was chosen. The mean elongation $\varepsilon = 0.0089$ ^[22] shows minimum deviation of the unit cells. Despite the general agreement of the structural parameters, the Zn-S bond lengths are about 0.11 Å shorter than the corresponding Zn-Se bonds as was expected, whereas the bond angles at S and Se match very well.

Conclusions

Zincocene Cp^*_2Zn was found to readily react with H-acidic β -ketoiminate and bis(thiophosphinoyl)methane with elimination of Cp^*H and subsequent formation of homoleptic complexes **1** and **2** containing monoanionic β -ketoiminate and bis(thiophosphinoyl)methanide ligands. The potential capability of **1** and **2** to serve as *single source*

precursor for the formation of ZnO and ZnS by MOCVD process is currently under investigation.

Experimental Section

All manipulations were performed under an Ar atmosphere. Cp^*_2Zn ,^[23] $\text{HC}(\text{CMe}_2\text{O})(\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{NMe}_2)$ ^[24] and $\text{H}_2\text{C}(\text{PPh}_2=\text{S})_2$ ^[25] were prepared according to literature methods. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{31}P NMR spectra were recorded on a Bruker DMX 300 spectrometer and are referenced to internal CHCl_3 (^1H : $\delta = 7.260$; ^{13}C : $\delta = 77.0$) and external 85 % H_3PO_4 (^{31}P : $\delta = 0$). IR spectra were recorded on an ALPHA-T FT-IR spectrometer equipped 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.

$[\text{HC}(\text{CMe}_2\text{O})(\text{NCH}_2\text{CH}_2\text{NMe}_2)]_2\text{Zn}$ (1**).** 0.17 g $\text{HC}(\text{CMe}_2\text{O})(\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{NMe}_2)$ (1 mmol) was added to a solution of 0.17 g Cp^*_2Zn (0.5 mmol) in 15 ml of hexane and stirred for 2 h at ambient temperature. Colorless crystals of **1** were formed after concentration within 12 h and storage at 4 °C.

1: Yield: 0.18 g (91 %). Melting point: 56 °C. Anal. Found (calcd) for $\text{C}_{18}\text{H}_{34}\text{N}_4\text{O}_2\text{Zn}$ (403.86 g/mol): H 8.57 (8.48), C 53.21 (53.53), N 13.74 (13.87)%. ^1H NMR (300 MHz, CDCl_3 , 25 °C): $\delta = 1.89$ (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 2.17 (s, 6H, $\text{N}(\text{CH}_3)_2$), 2.37 (m, 1H, CH_2), 2.48 (m, 1H, CH_2), 3.29 (m, 1H, CH_2), 3.39 (m, 1H, CH_2), 4.74 (s, 1H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 22.1$ (C_βMe), 28.8 (C_δMe), 45.3 ($\text{NCH}_2\text{CH}_2\text{NMe}_2$), 47.4 ($\text{NCH}_2\text{CH}_2\text{NMe}_2$), 58.9 ($\text{NCH}_2\text{CH}_2\text{NMe}_2$), 96.6 (C_γ), 171.5 (C_βN), 182.8 (C_αO). IR: ν 2914, 2853, 2814, 2766, 2140, 2121, 1657, 1577, 1508, 1477, 1412, 1347, 1293, 1247, 1202, 1092, 1060, 1004, 987, 935, 887, 789, 746, 733, 722, 672, 642, 616, 580, 545, 496, 472, 435.

$[\text{HC}(\text{PPh}_2=\text{S})_2]_2\text{Zn}$ (2**).** A solution of 0.45 g $\text{H}_2\text{C}(\text{PPh}_2=\text{S})_2$ (1 mmol) in CH_2Cl_2 was added to a solution of 0.17 g Cp^*_2Zn (0.5 mmol) in hexane and stirred for 2 h at ambient temperature. Colorless crystals of **2** were formed after concentration within 12 h and storage at ambient temperature.

2: Yield: 0.46 g (95 %). Melting point: > 210 °C. Anal. Found (calcd) for $\text{C}_{50}\text{H}_{42}\text{P}_4\text{S}_4\text{Zn}$ (960.41 g/mol): H 4.56 (4.41), C 62.17 (62.53), S 12.41 (13.35)%. ^1H NMR (300 MHz, CDCl_3 , 25 °C): $\delta = 3.98$ (t; $^2J_{\text{P-H}} = 13.4$ Hz, 1H, HCP_2), 7.19 – 7.31 (m, 12H, C_6H_5), 7.77 – 7.85 (m, 8H, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 16.9$ (t, PCP, $^1J_{\text{P-C}} = 92.6$ Hz), 127.8 (t, m-Ph, $^3J_{\text{P-C}} = 6.4$ Hz), 130.4 (s, p-Ph), 131.7 (t, o-Ph, $^2J_{\text{P-C}} = 5.8$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (120 MHz, CDCl_3 , 25 °C): $\delta = 36.7$. IR: ν 3053, 3001, 2962, 2884, 1478, 1433, 1306, 1261, 1164, 1099, 1027, 999, 799, 772, 736, 685, 619, 570, 557, 534, 502, 485, 476, 410.

Supporting Information X-ray crystallographic data of **1** and **2** are given in the electronic supplement. The crystallographic data (without structure factors) were also deposited as „supplementary publication no. CCDC-869017 (**1**) and CCDC-869016 (**2**) at the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre: CCDC, 12 Union Road, Cambridge, CB21EZ (Fax: (+44)1223/336033; E-mail: deposit@ccdc.cam.ac.uk).

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Synthesis and X-ray crystal structures of homoleptic Zinc complexes containing monoanionic β -ketoiminate and bis(thiophosphinoyl)methanediide ligands

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