First Reaction of Dizincocene with Preservation of the Zn-Zn-Bond

Daniella Schuchmann, Ulrich Westphal, Stephan Schulz,* Ulrich Flörke, Dieter Bläser, and Roland Boese

((Dedicated to Prof. Dr. E. Niecke on the occasion of his 70. birthday))

Since the epoch-making synthesis of decamethyldizincocene Cp^*_2Zn_2 **1**,^[1] the first complex containing a Zn-Zn bond, by Carmona et al. in 2004, a very few compounds of the type R_2Zn_2 stabilized by sterically demanding organic substituents ($\text{R} = \text{EtMe}_4\text{Cp}$,^[2] [2,6-(2,6-*i*-Pr₂C₆H₃)-C₆H₃],^[3] [{(2,6-*i*-Pr₂C₆H₃)N(Me)C₂CH₃}],^[4] [(2,6-*i*-Pr₂C₆H₃)N(Me)C],^[5] {Me₂Si[N-(2,6-*i*-Pr₂C₆H₃)]₂},^[6] 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian)^[7] have been synthesized and structurally characterized. Even though the nature of the Zn-Zn bond, in particular of Cp-substituted complexes such as **1**, has been theoretically investigated in detail by several groups,^[8] only limited information on the reactivity of such complexes is given. Carmona et al. reported on reactions of **1** with H₂O, *t*-BuOH, NCXyl^[11] and other Lewis bases (NMe₃, pyridine, PMe₃, ...),^[2] but either no reaction occurred or disproportionation reaction into elemental zinc and the corresponding Zn(II) compound was observed. Reactions of **1** with ZnR_2 ($\text{R} = \text{Me}$, Mes) yielded half-sandwich complexes Cp^*ZnR , whereas the reaction with iodine proceeded with oxidation and subsequent formation of Cp^*_2Zn and ZnI_2 . In contrast, no reaction was observed in reactions with H₂, CO, and CO₂, respectively. According to these observations, reactions with preservation of the Zn-Zn bond appeared to be problematical.

Recently, we became interested in organozinc complexes containing sterically less hindered N,N' chelating amidinate substituents,^[9] which might serve as starting reagents for the synthesis of the corresponding Zn-Zn bonded complexes. At the same time, we started to investigate the general reactivity of the Zn-Zn bond. These studies primary focused on reactions of Cp^*_2Zn_2 **1** due to the steric and electronic flexibility of the Cp* substituent.^[10] According to our long term interest in the Lewis acidity of metal organic compounds, we investigated adduct formation reactions of Cp^*_2Zn_2 **1**. The reaction with the strong Lewis base 4-dimethylaminopyridine (dmap),

which has been previously shown in our group to be very powerful for the synthesis of group 13 metal Lewis acid base adduct,^[11] resulted in the formation of the unexpected bisadduct **2**. In **2**, two dmap molecules bind in a geminal coordination mode under preservation of the Zn-Zn bond to one of the two Zn atoms.

A solution of **1** in toluene and *n*-pentane (1:4) reacts with two equivalents as well as with an excess of dmap at 0 °C with formation of **2**, which was isolated after crystallization at -30 °C as light yellow crystalline solid. In sharp contrast to previous reports, no disproportionation reaction was observed.^[2] The analogous reaction of Cp^*_2Zn with dmap yielded $\text{Cp}^*_2\text{Zn-dmap}$ **3**.

Scheme 1. Synthese der dmap-Addukte $\text{Cp}^*\text{Zn-Zn(dmap)}_2\text{Cp}^*$ **2** und $\text{Cp}^*_2\text{Zn-dmap}$ **3**

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The ¹H- and ¹³C-NMR spectra of **2** and **3** show resonances due to the Cp* groups and the Lewis base dmap. No indication for the formation of a zinc hydride complex was found in the ¹H NMR spectrum of **2** (no resonance between 4 - 5 ppm), and the IR spectrum also didn't show an absorption peak between 1650 and 1900 cm⁻¹, which is the typical regime of zinc hydrides.^[12] The ¹H NMR spectrum of single crystals of **2**, which were obtained from a solution in *n*-pentane/toluene, show additional resonances due to the presence of toluene. The Cp* substituents only show one resonance at 25 °C (δ 2.03 **2**, 2.08 ppm **3**), which points to fast exchange reactions between the non-equivalent Cp* substituents in **2** and indicates η⁵-bonded Cp* groups in solution. In contrast, the ¹H NMR spectrum of **2** recorded at very low temperature (-95 °C) shows two well separated resonances (δ 2.48, 2.73) of equal intensity due to the Cp* groups. The chemical shifts of both the Cp* and dmap resonances of **2** change with temperature, indicating a temperature-dependent

equilibrium reaction.^[13] The dissociation enthalpy of **2** in solution ($\Delta H_{\text{Diss}} = -40.4$ kJ/mol) was determined from these NMR spectra.^[14] In addition, the dissociation enthalpy of **3** ($\Delta H_{\text{Diss}} = -50.6$ kJ/mol) was determined, which demonstrates the higher Lewis acidity of Cp^*Zn compared to Cp^*Zn_2 .

Abb. 1. Molecular structure of **2**. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–Zn2 2.418(1), Zn1–C1 2.425(2), Zn1–C2 2.395(2), Zn1–C3 2.328(2), Zn1–C4 2.300(2), Zn1–C5 2.360(2), Zn2–C11 2.174(2), Zn2–N1 2.115(2), Zn2–N3 2.125(2); $\text{Cp}^*_{\text{centr.}}$ –Zn1–Zn2 159.6, Zn1–Zn2–C11 115.4(1), N1–Zn2–N3 95.3(1), N1–Zn2–Zn1 105.0(1), N3–Zn2–Zn1 110.1(1), N1–Zn2–C11 113.9(1), N3–Zn2–C11 115.0(1).

Single crystals of **2** and **3** were obtained from solutions in *n*-pentane/toluene (**2**) and *n*-pentane (**3**), respectively, upon storage at -30 °C.^[15] The central Zn atom in **3** is coordinated by a single dmap molecule and two η^2 -bonded Cp^* groups (Zn1–C10 2.090(5), Zn1–C12 2.483(5); Zn1–C20 2.169(5), Zn1–C22 2.300(5) Å). In contrast, the reaction of sterically less hindered ZnMe_2 with dmap yielded the bisadduct $(\text{dmap})_2\text{ZnMe}_2$.^[16] The two dmap molecules in **2** coordinate in a geminal binding mode to one Zn atom (Zn2), whereas the second zinc center (Zn1) is coordinated only by one η^5 -bonded Cp^* substituent ($\text{Cp}^*_{\text{centr.}}$ –Zn1 2.033 Å; compare to 2.04 Å in **1**).^[17] The Zn1– C_{Cp^*} bond lengths (2.300(2) – 2.425(2) Å) show a stronger variation compared to those observed in **1** (2.27 – 2.30 Å) since the Zn1 atom does not adopt the central position over the Cp^* substituent.^[1a] The coordination sphere of Zn2 is completed by a σ -bonded Cp^* ligand (Zn2–C11 2.174(2) Å), whereas the distances to the next closest C_{Cp^*} atoms (Zn2–C15 2.696(3), Zn2–C12 2.773(3) Å) are significantly elongated. The Zn–N bond distances in **2** (Zn2–N1 2.115(2), Zn2–N3 2.125(2) Å) are significantly elongated compared to that in **3** (Zn1–N1 2.024(3) Å), but shorter than those observed for $\text{Me}_2\text{Zn}(\text{dmap})_2$ (Zn1–N1/2 2.177(2) Å) containing a fourfold-coordinated Zn atom.^[16] The central Zn1–Zn2 bond length (2.418(1) Å) is significantly elongated by more than 11 pm compared to that in **1** (2.305(3) Å), most likely due to the higher coordination number of Zn2. This bond length is the longest Zn–Zn bond observed, to date. Zn_2R_2 complexes typically show Zn–Zn distances ranging from 2.29 to 2.35 Å.^[1–7] Comparable Zn–Zn bond lengths were only ob-

served in H-bridged organozinc complexes of the general type $[\text{RZnH}]_2$ ($\text{R} = [2,6-(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{-C}_6\text{H}_3]$ 2.408(1) Å,^[3] $[(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}(\text{Me})\text{C}(\text{CH}_3)_2]$ 2.451(1) Å^[18]). While the $\text{Cp}^*_{\text{centr.}}$ –Zn–Zn– $\text{Cp}^*_{\text{centr.}}$ unit in **1** is almost linearly oriented (177.4(1)°), **2** deviates significantly from the linear arrangement due to the coordination of two dmap molecules (Zn1–Zn2–C11 115.4(1)°; Zn2–Zn1– $\text{Cp}^*_{\text{centr.}}$ 159.6°). The dmap molecules adopt an almost orthogonal orientation. In particular the N1–Zn2–N3 bond angle (95.3(1)°) is significantly smaller than the N–Zn2–Zn1 (105.0(1), 110.1(1)°) and N–Zn2–C11–bond angles (113.9(1), 115.0(1)°).

Abb. 1. Molecular structure of **3**. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–C10 2.090(5), Zn1–C12 2.483(5), Zn1–C20 2.169(5), Zn1–C22 2.300(5), Zn1–N1 2.024(3); N1–Zn1–C10 115.6(2), N1–Zn1–C20 115.8(2).

In order to better understand the formation and the bonding situation of **2**, DFT calculations were performed.^[19] The formation of $\text{Cp}^*\text{Zn}_2(\text{dmap})$ **1'** by coordination of one dmap molecule to Cp^*Zn_2 **1** proceeds exothermic (–4.6 kcal/mol) with an only marginal elongation of the Zn–Zn bond length (2.36 **1**; 2.37 **1'** Å). However, the Zn atoms in **1'** carry different partial charges. The dmap-coordinated Zn atom is more electropositive (0.99) than the second Zn atom (0.76), whereas in **1** both Zn centers are equally charged (0.89). The coordination of a second dmap molecule in a vicinal position is endothermic (+2.6 kcal/mol), while the geminal coordination proceeds strongly exothermic (–9.2 kcal/mol). Consequently, the formation of **2** with geminal coordination mode of the dmap molecules is strongly favored (–13.8 kcal/mol, –57.7 kJ/mol) compared to the vicinal binding mode (–2.0 kcal/mol). Upon coordination of two dmap molecules, the Zn–Zn bond length of **2** significantly increases to 2.44 Å, which agrees very well with the experimental findings (2.418(1) Å). Both Zn atoms in **2** are differently charged with Zn1 (0.60) carrying a significantly higher electronic charge compared to the dmap-coordinated Zn2 atom (1.15) due to the influence of two electron withdrawing N centers. The NBO analysis shows a decrease of the bond order from 0.93 (96.7% s, 2.1% p, 1.2% d) in **1** to 0.85 (92.9% s, 7.0% p, 0.1% d) in **2** due to the population of the antibonding Zn–Zn orbital (LUMO), which agrees very well with previously published bonding analyses of **1**.^[1b]

The Lewis acid-base reaction of Cp^*Zn_2 **1** with an excess of dmap proceeded with preservation of the central Zn–Zn bond. Surprisingly, the bisadduct **2**, in which the dmap molecules adopt an

unusual geminal binding mode, was formed. The reaction is strongly exothermic, which makes the formation of adducts with other strong Lewis bases, which are currently investigated, in the near future supposable.

Experimental

All manipulations were performed under an Ar atmosphere. Solvents were dried over Na/K and degassed prior to use. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker Avance 500 spectrometer and are referenced to internal $\text{C}_6\text{D}_5\text{H}$ (^1H : $\delta = 7.154$; ^{13}C : $\delta = 128.0$). IR spectra were recorded on a ALPHA-T FT-IR spectrometer. Melting points were measured in sealed capillaries and were not corrected.

2: 0.24 g dmap (2.0 mmol) dissolved in 5 mL of toluene was added at 0 °C to a solution of 0.20 g Cp^*Zn_2 (0.5 mmol) in 5 mL of *n*-pentane and stirred for 2 h at -25 °C. The resulting suspension was dissolved in additional 5 mL of toluene and stored at -30 °C. Light yellow crystals of **2-toluene** were obtained after 7 days.

Yield (isolated crystals) 0.08 g (0.12 mmol, 25%). Melting point: 105 °C. ^1H -NMR (500 MHz, C_6D_6 , 25 °C): $\delta = 2.03$ (s, 30 H, C_5Me_5), 2.09 (s, 1.5H, Toluol), 2.20 (s, 12 H, NMe_2), 6.09 (dd, $^3J_{\text{HH}} = 6.3$ Hz, $^3J_{\text{HH}} = 1.6$ Hz, 4 H, C(3)-H), 6.89-7.20 (m, 2.5H, toluene), 8.46 (dd, $^3J_{\text{HH}} = 6.3$ Hz, $^3J_{\text{HH}} = 1.6$ Hz, 2 H, C(2)-H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, C_6D_6 , 25 °C): $\delta = 10.4$ (C_5Me_5), 38.3 (NMe_2), 106.8 (C(3)), 109.0 (C_5Me_5), 150.5 (C(2)), 154.3 (C(4)). IR (Nujol): $\nu = 2853$, 1611, 1461, 1377, 1224, 1013, 802 cm^{-1} .

3: A solution of 0.67 g Cp^*Zn (2.0 mmol) and 0.48 g dmap (4.0 mmol) in 15 mL of *n*-hexane were heated under reflux for 1 h and then stored at -30 °C. Colorless crystals of **2-toluene** were obtained after 36 h.

Yield (isolated crystals) 0.49 g (1.1 mmol, 55%). Melting point: 205 °C. ^1H -NMR (500 MHz, C_6D_6 , 25 °C): $\delta = 1.99$ (s, 6 H, NMe_2), 2.08 (s, 30 H, C_5Me_5), 5.68 (dd, $^3J_{\text{HH}} = 6.9$ Hz, $^3J_{\text{HH}} = 1.6$ Hz, 2 H, C(3)-H), 7.22 (dd, $^3J_{\text{HH}} = 6.9$ Hz, $^3J_{\text{HH}} = 1.6$ Hz, 2 H, C(2)-H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, C_6D_6 , 25 °C): $\delta = 12.3$ (C_5Me_5), 38.3 (NMe_2), 105.3 (C(3)), 114.1 (C_5Me_5), 147.5 (C(2)), 154.5 (C(4)). IR (Nujol): $\nu = 2923$, 1623, 1546, 1440, 1390, 1261, 1228, 1075, 1021, 801, 604 cm^{-1} .

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Low valent Lewis Acid

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Cp*₂Zn₂ **1** reacts with an excess of the strong Lewis base 4-dimethylaminopyridine (dmap) with subsequent formation of the unexpected Lewis acid base adduct **2**, in which both dmap molecules coordinate in a geminal binding mode to only one Zn atom.

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