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Novel Synthetic Pathway for New Zn−Zn-Bonded Compounds from Dizincocene

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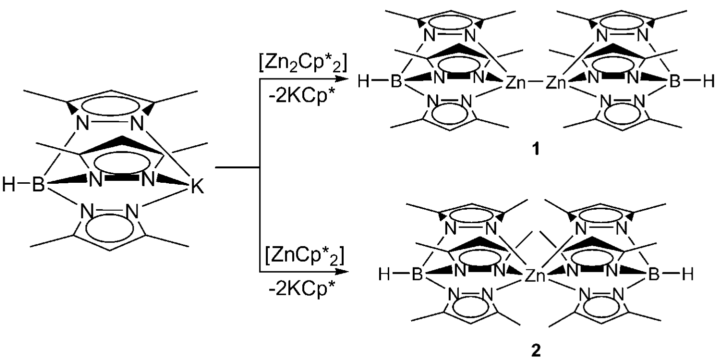
Dedicated to Professor Herbert W. Roesky on the occasion of his 75th birthday

Since 2004 when Carmona et al. first synthesized the decamethyldizincocene, $[Zn_2Cp^*_2]$[1]—the first stable molecular compound containing a direct Zn−Zn bond with the Zn atoms in the formal oxidation state +1[2]—an increasing number of Zn^I complexes have been structurally characterized.[3] Most of these complexes, which are typically kinetically stabilized by bulky and very often chelating organic ligands, have been synthesized by Wurtz-analogous coupling reactions of the corresponding halide-substituted complexes, RZnX, except for $[Zn_2Cp^*_2]$, which was initially prepared by the reaction of $[ZnEt_2]$ and $[ZnCp^*_2]$. Unfortunately, coupling reactions very often tend to proceed with formation of the corresponding Zn^{II} complexes and elemental zinc.[4] We therefore became interested in the development of alternative synthetic pathways. Very recently, we demonstrated that $[Zn_2Cp^*_2]$ is a promising starting reagent for protonation reactions. While the reaction with $[H(OEt_2)_2][Al\{OC(CF_3)_3\}_4]$ yielded $[Zn_2(dmap)_6][Al\{OC(CF_3)_3\}_4]_2$ (dmap = 4-dimethylaminopyridine) containing the first base-stabilized $[Zn_2]^{2+}$ dication,[5] the reaction with N−H acidic $\{[(2,4,6\text{-}Me_3C_6H_2)N(Me)C]_2CH\}H$ (MesnacnacH) proceeded with elimination of Cp*H and subsequent formation of the Zn^I complex $[Zn_2(Mesnacnac)_2]$.[6] In addition, reactions with sterically demanding alcohols[7] and bis[iminodi(phenyl)phosphorano]methanes[8] occurred with preservation of the Zn−Zn bond and formation of the corresponding (base-stabilized) Zn^I alkoxides and Zn^I bis[iminodi(phenyl)phosphorano]methanides, respectively. These protonation reactions can be performed at low temperature, hence also allowing the synthesis of thermally less stable Zn^I complexes. In contrast, the reaction of $[Zn_2(\text{Dipp-BIAN})_2]$ (Dipp-BIAN = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) with C−H acidic phenylacetylene occurred with H_2 elimination and formation of a binuclear, acetylene-bridged Zn^{II} complex (redox reaction) rather than with protonation of the Dipp-BIAN substituent.[9]

Herein, we report on the reaction of dizincocene with the potassium salt of tris(3,5-dimethylpyrazolyl)hydridoborate, $K(Tp^{Me_2})$, which proceeded with the elimination of KCp* and subsequent formation of $[Zn_2(Tp^{Me_2})_2]$ (**1**). In addition, $[ZnCp^*_2]$ was found to react analogously with $K(Tp^{Me_2})$ (2 equiv) to form $[Zn(Tp^{Me_2})_2]$ (**2**) (see Scheme 1). Compound **2** was prepared and structurally characterized for the first time by Parkin et al.[10a]



Scheme 1. Synthesis of pyrazolylhydridoborato zinc complexes **1** and **2**.

Compound **1** was obtained in an almost quantitative yield (>90%) by the reaction of $[Zn_2Cp^*_2]$ with $K(Tp^{Me_2})$ (2 equiv) in THF at −30 °C. The yield of 90% is significantly higher than yields reported for Zn^I complexes obtained from reduction reactions. The formation of elemental zinc (a disproportionation reaction) was not observed. $[ZnCp^*_2]$ reacts analogously with the formation of **2**. Compounds **1** and **2** are soluble in toluene and THF, respectively. ^1H, ^{13}C, and ^{11}B NMR spectra of both complexes show resonances

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representing the tris(3,5-dimethylpyrazolyl)hydridoborato ligands. H–B resonances, typical for these complexes,[10a] were not observed in the ^{1}H NMR spectra, but the IR spectra of **1** and **2** show strong vibrational bands at 2506 and 2512 cm^{-1}, respectively. Compound **1** is extremely thermally robust ($T_{\mathrm{decomp.}} = 395\,^{\circ}\mathrm{C}$) compared with other Zn$^{\mathrm{I}}$ complexes, most likely resulting from the steric shielding exerted by the tris(3,5-dimethylpyrazolyl)hydridoborato ligands and the high coordination number of the Zn atoms, which are tetrahedrally coordinated. Compound **1** is stable for days in organic solvents, in contrast to [$Zn_2Cp^*_2$], which decomposes within a few hours.

The solid-state structures of **1** (Figure 1) and **2** (Figure 2) were determined by single-crystal X-ray diffraction.[11] Suitable crystals were obtained from solutions in THF/CH_2Cl_2 (**1**) and THF (**2**) after slow crystallization at $+4\,^{\circ}\mathrm{C}$. Compound **1** crystallizes in the monoclinic space group $P2_1/n$ together with three CH_2Cl_2 and one THF molecules; compound **2** in the trigonal space group $R\bar{3}c$. The asymmetric unit gives two independent molecules together with highly disordered THF molecules, with Zn atoms in special positions.[12]

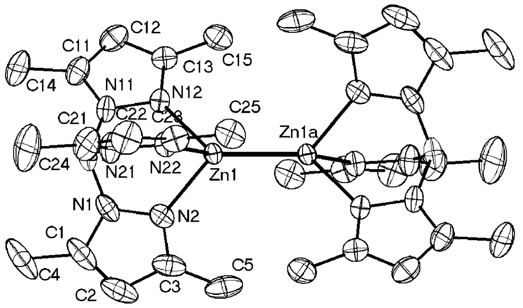

Figure 1. Solid-state structure of **1**; Zn(1a) and nonlabeled atoms are symmetry equivalent by inversion ($-x+1,-y,-z+1$), ellipsoids correspond to 50 % probability levels; H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–Zn1a 2.3560(9), Zn1–N2 2.099(4), Zn1–N22 2.103(3), Zn1–N12 2.104(3); N2-Zn1-N22 88.02(14), N2-Zn1-N12 87.98(14), N22-Zn1-N12 86.71(13), N2-Zn1-Zn1a 126.27(11), N22-Zn1-Zn1a 126.12(10), N12-Zn1-Zn1a 128.49(10).

The tris(3,5-dimethylpyrazolyl)hydridoborato ligands of **1** and **2** bind in an η^3-coordination mode to the Zn atoms. As a consequence, the Zn atoms in **1** adopt tetrahedral coordination spheres, whereas the Zn atom in **2** is almost perfectly octahedrally coordinated by six N atoms. The Zn–N bond lengths in **2** (2.179(2) and 2.184(2) Å) are comparable to those reported previously for this complex,[10] whereas those in **1** are significantly shorter (average value = 2.102(4) Å). This finding clearly points to decreased steric interactions between the two substituents in **1** compared with those in **2**, due to the presence of the [Zn_2] unit. The tris(3,5-dimethylpyrazolyl)hydridoborato ligands in **1** adopt an almost perfect staggered orientation with respect to each other (torsions 58.15(17) and 61.16(18)°), which further decreases steric interactions. The bonding parameters (B–N, C–C, and C–N bond lengths) of the ligands in **1** and **2** are comparable and in the typical range for tris(3,5-dimethylpyrazolyl)hydridoborato zinc complexes of the types [$Zn(Tp^{Me_2})_2$][10] and [$Zn(Tp^{Me_2})X$].[14] The Zn–Zn bond length in **1** of 2.3560(9) Å is elongated relative to that observed for [$Zn_2Cp^*_2$] (2.305(3) Å),[1] but comparable to those reported for the homoleptic Zn$^{\mathrm{I}}$ complexes [$Zn_2\{CH_2(Ph_2P{=}NPh)_2\}_2$] (2.3490(1) Å)[8] and [$Zn_2$(Dippnacnac)$_2$] (Dippnacnac = $\{(2,6\text{-}i\mathrm{Pr}_2C_6H_3)N(Me)C\}_2CH$; 2.3586(7) Å) containing N,N′-chelating ligands.[3b] In contrast, the Zn–Zn bond in [Zn_2(Mesnacnac$_2$)] (2.3813(8) Å) is slightly elongated.[6]

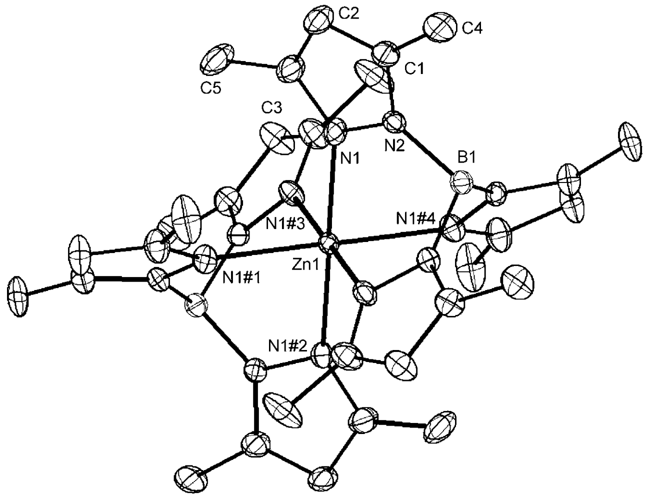

Figure 2. Solid-state structure of **2**; nonlabeled atoms symmetry equivalent by 32, ellipsoids correspond to 50 % probability levels; H atoms are omitted for clarity; only one of two independent molecules is presented. Selected bond lengths [Å] and angles [°]: Zn1–N1 2.179(2); N1#1-Zn1-N1 94.59(11), N1#2-Zn1-N1 179.74(12), N1#3-Zn1-N1 94.23(11), N1#4-Zn1-N1 85.59(8).[13]

In summary, the Cp* ligands in [$Zn_2Cp^*_2$] can easily be replaced by tris(3,5-dimethylpyrazolyl)hydridoborato ligands by the reaction with the corresponding potassium salt under mild reaction conditions. This new reaction type may give access to a larger number of Zn$^{\mathrm{I}}$ complexes in the near future, including complexes that cannot be obtained from Wurtz-analogous reductions reactions. We are currently investigating reactions with K salts of different types of organic substituents as well as their corresponding Li salts, which would greatly increase the applicability of the reaction type for the synthesis of novel Zn–Zn-bonded complexes.

Experimental Section

General: All manipulations were performed in a glovebox under an Ar atmosphere or with standard Schlenk techniques. Solvents were dried by standard procedures and degassed prior to use. [$ZnCp^*_2$][15] and [$Zn_2Cp^*_2$][1b] were prepared according to literature methods, K(Tp^{Me_2}) was commercially available from Acros. A Bruker Avance 500 spectrometer was used for NMR spectroscopy. ^{1}H and $^{13}C\{^1H\}$ NMR spectra were referenced to internal [D_8]THF (^{1}H: $\delta = 3.58$ ppm; ^{13}C: $\delta = 67.4$ ppm). IR spectra were recorded on an Alpha-T FT-IR spectrometer with a single reflection attenuated total reflectance (ATR) sampling module. Melting points were measured in sealed capillaries and were not corrected.

Compound 1: K(Tp^{Me_2}) (0.32 g, 1.00 mmol) and $[Zn_2Cp^*{}_2]$ (0.20 g, 0.50 mmol) were suspended in THF (50 mL) at −30 °C and stirred for 6 h. The white precipitate was filtered and the solution concentrated in vacuum. CH_2Cl_2 was added and the resulting solution was stored at +4 °C for 24 h, yielding **1** as colorless crystals (0.33 g, 93.6 %), M.p. 395 °C; ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): $\delta = 2.35$ (s, 9 H; CH_3), 2.37 (s, 9 H; CH_3), 5.66 ppm (s, 3 H; CH); ^{13}C NMR (300 MHz, [D$_8$]THF, 25 °C): $\delta = 12.4$ (CH_3), 13.9 (CH_3), 105.1 (CH), 144.1(*C*CH_3), 148.9 ppm (*C*CH_3); ^{11}B NMR (300 MHz, [D$_8$]THF, 25 °C): $\delta = -9.6$ ppm (BH); IR: $\tilde{\nu} = 2962$, 2923, 2506 (B-H), 1543, 1446, 1417, 1385, 1350, 1258, 1194, 1181, 1057, 1013, 850, 784, 694, 642, 460, 391 cm^{-1}.

Compound 2: K(Tp^{Me_2}) (0.64 g, 2.00 mmol) and $[ZnCp^*{}_2]$ (0.32 g, 1.00 mmol) were suspended in *n*-pentane (50 mL) and stirred for 12 h at room temperature. The white precipitate was filtered and the solvent was removed in vacuum, yielding a white yellowish solid. The solid was dissolved in THF and stored at +4 °C. Colorless crystals of **2** formed after 24 h (0.25 g, 89.3 %). ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): $\delta = 1.34$ (s, 9 H; CH_3), 2.41 (s, 9 H; CH_3), 5.58 ppm (s, 3 H; CH); ^{13}C NMR (300 MHz, [D$_8$]THF, 25 °C): $\delta = 12.0$ (CH_3), 12.8 (CH_3), 105.3 (CH), 143.6 (*C*CH_3), 149.2 ppm (*C*CH_3); ^{11}B NMR (300 MHz, [D$_8$]THF, 25 °C): $\delta = -9.5$ ppm (BH); IR: $\tilde{\nu} = 2962$, 2924, 2512 (B-H), 1538, 1443, 1414, 1380, 1364, 1351, 1259, 1201, 1186, 1061, 1038, 841, 800, 766, 695, 644, 460, 392 cm^{-1}.

Single-crystal structure determination of 1 and 2: The crystals were mounted on nylon loops in inert oil. Data were collected on a Bruker D8 Kappa diffractometer with an APEX2 detector (monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) at 100 K. The structures were solved by direct methods using Bruker AXS APEX2 software[16] and refined by full-matrix least-squares on F^2. Semi-empirical absorption corrections were applied (SADABS). All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined by a riding model (SHELXL-97, Program for Crystal Structure Refinement).[17] The refinement of **1** was performed with solvent-free reflection data following Platon/Squeeze[18] run. A refinement of the untreated reflection data set produced ten signals with 1.5–2.1 e Å^3 corresponding to two highly disordered THF molecules with point symmetry $\bar{1}$. The ten most intense signals in the difference Fourier map were attributed to carbon atoms. This attempt resulted in $R1 = 0.1270$. The Squeeze refinement revealed voids with a total volume of 4436 Å^3 at the positions 0.026, 0.474, −0.026 and −0.076, 0.212, 0.212 and 0.125, 0.751, 0.375 corresponding to 1479 Å^3 each. Compound **2** contained disordered solvent: one molecule of THF and CH_2Cl_2 at the same site with SOF 0.5 each. The THF atoms (O(40), C(41–44)) were refined with fixed $U = 0.08$. The chlorine atoms of the CH_2Cl_2 (Cl(3,4)) were refined anisotropic while the carbon (C(31)) was refined isotropically.

CCDC-790372 (**1**) and 790371 (**2**) 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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Keywords: metal–metal interactions · N ligands · synthetic methods · X-ray diffraction · zinc

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[11] Crystal data for **1**: $C_{30}H_{28}N_{12}B_2Zn_2 \cdot 3\,CH_2Cl_2 \cdot C_4H_8O$, $M = 1052.01$, colorless crystal ($0.27 \times 0.22 \times 0.15$ mm); monoclinic; space group $P2_1/n$; $a = 7.9280(4)$, $b = 27.6966(13)$, $c = 11.5109(5)$ Å; $\beta = 103.231(2)°$, $V = 2460.5(2)$ Å^3; $Z = 2$; $\mu = 1.34$ mm^{-1}; $\rho_{calcd} = 1.420$ g cm^{-3}; 22749 reflections ($2\theta_{max} = 49.6°$), 4250 unique ($R_{int} = 0.0272$); 276 parameters; largest max/min in the final difference Fourier synthesis 1.024/−1.391 e Å^{-3}; max/min transmission 0.75/0.56; $R_1 = 0.0586$ [$I > 2\sigma(I)$], wR_2 (all data) = 0.1485. Crystal data for **2**: $C_{30}H_{44}B_2N_{12}Zn \cdot THF$, $M = 659.76$, colorless crystal ($0.28 \times 0.23 \times 0.16$ mm); trigonal; space group $R\bar{3}c$; $a = 17.1545(8)$, $b = 17.1545(8)$, $c = 52.772(3)$ Å; $\alpha = \beta = 90$, $\gamma = 120°$, $V = 13449.1(11)$ Å^3; $Z = 12$; $\mu = 1.63$ mm^{-1}; $\rho_{calcd} = 1.324$ g cm^{-3}; 45486 reflections ($2\theta_{max} = 56.6°$), 3673 unique ($R_{int} = 0.0286$); 137 parameters; largest max/min in the final difference Fourier synthesis 0.616/−0.459 e Å^{-3}; max/min transmission 0.75/0.59; $R_1 = 0.0640$ [$I > 2\sigma(I)$], wR_2 (all data) = 0.1399.

[12] The Zn atoms are located on special positions (Zn(1) on 32, Zn(2) on $\bar{3}$). The asymmetric unit contains one sixth of each molecule (as labeled in Figure 2 for Zn(1)) and apparently two highly disordered

molecules of THF with SOF ≈0.5 (treated with Squeeze). Consequently, the ratio Zn complex/THF is ≈1:3.

[13] Bond angles for the second independent molecule: N21-Zn2-N21#5 180.0, N21C-Zn2-N21#6 94.20(8), N21-Zn2-N21#7 85.80(8) Symmetry operations for equivalents: #1 $x-y+1/3,-y+2/3,-z+1/6$; #2 $-x+4/3$, $-x+y+2/3,-z+1/6$; #3 $y+1/3,x-1/3,-z+1/6$; #4 $-y+1,x-y,z$; #5 $-x,-y,-z$; #6 $y,-x+y,-z$; #7 $-y,x-y,z$.

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