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

Sebastian Gondzik, Dieter Bläser, Christoph Wölper, and Stephan Schulz[a]*

Dedicated to Prof. Dr. Dr. h.c. mult. Herbert W. Roesky on the occasion of his 75th birthday.

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Since the initial synthesis of decamethyldizincocene $Cp^*_2Zn_2$,[1] the first stable molecular compound containing a direct Zn-Zn bond with the Zn atoms in the formal oxidation state +1,[2] by *Carmona et al.* in 2004, an increasing number of Zn(I) complexes have been structurally characterized.[3] Most of these complexes, which are typically kinetically stabilized by sterically bulky, very often chelating organic ligands, have been synthesized by Wurtz-analogous coupling reaction of the corresponding halide-substituted complexes RZnX except for $Cp^*_2Zn_2$, which was initially prepared by reaction of Et_2Zn and Cp^*_2Zn. 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 alternate synthetic pathways. Very recently, we demonstrated that $Cp^*_2Zn_2$ is a promising starting reagent for protonation reactions. While the reaction with $[H(OEt_2)][Al(OC(CF_3)_3)_4]_2$ yielded $[Zn_2(dmap)_6][Al(OC(CF_3)_3)_4]_2$ 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 $Mesnacnac_2Zn_2$.[6] In addition, reactions with sterically demanding alcohols[7] and bis(iminodi(phenyl)phosphorano)methanes[8] also 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 $Dipp\text{-}BIAN_2Zn_2$ 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]

We herein report on the reaction of dizincocene with the potassium salt of tris(3,5-dimethyl)pyrazolylhydroborate, $Tp^{Me_2}K$, which proceeded with elimination of Cp*K and subsequent formation of $(Tp^{Me_2})Zn\text{-}Zn(Tp^{Me_2})_2$ **1**. In addition, zincocene Cp^*_2Zn was found to

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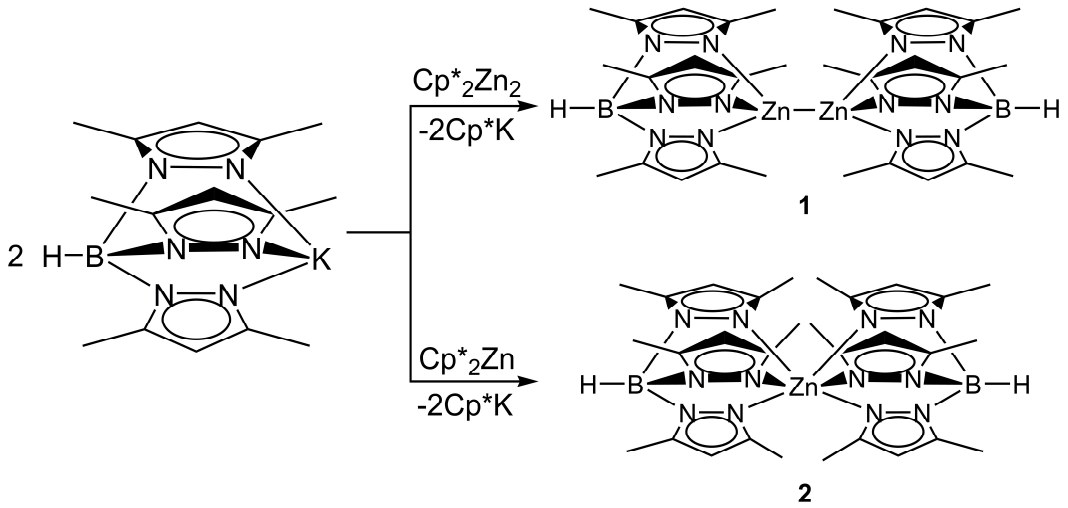
react analogously with two equivalents KTp^{Me_2} with formation of $(Tp^{Me_2})_2Zn$ **2**. **2** was prepared and structurally characterized for the first time by *Parkin et al*.[10]



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

1 was obtained by reaction of $Cp^*_2Zn_2$ with two equivalents of $Tp^{Me_2}K$ in THF at –30 °C in almost quantitative yield (>90%), which is significantly higher compared to yields reported for Zn(I) complexes obtained from reduction reactions. The formation of elemental zinc (*disproportionation reaction*) was not observed. Zincocene Cp^*_2Zn reacts analogously with formation of $(Tp^{Me_2})_2Zn$ **2**. **1** and **2** are soluble in organic solvents such as toluene and THF, respectively. ^1H, ^{13}C and ^{11}B NMR spectra of both complexes show resonances due to the tris(pyrazolyl)hydroborato ligands. H-B resonances were not observed in the ^1H NMR spectra as is typical for these complexes,[10a] but the IR spectra of **1** and **2** show strong vibrational bands at 2506 (**1**) and 2512 (**2**), respectively. **1** is extremely thermally robust ($T_{decomp.}$ 395 °C) compared to other Zn(I) complexes, most likely resulting from the steric shielding due to the pyrazolylhydroborate ligand and the high coordination number of the Zn atoms, which are tetrahedrally coordinated. A solution of **1** in organic solvents is stable for days, in contrast to $Cp^*_2Zn_2$, that decomposes within a very few hours.

The solid-state structures of **1** (Fig. 1) and **2** (Fig. 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 °C. **1** crystallizes in the monoclinic space group $P2_1/n$ together with three CH_2Cl_2 and one THF molecules, **2** in the trigonal space group $R\bar{3}c$. With Zn atoms on special positions, two independent molecules together with highly disordered THF molecules result from the asymmetric unit [12].

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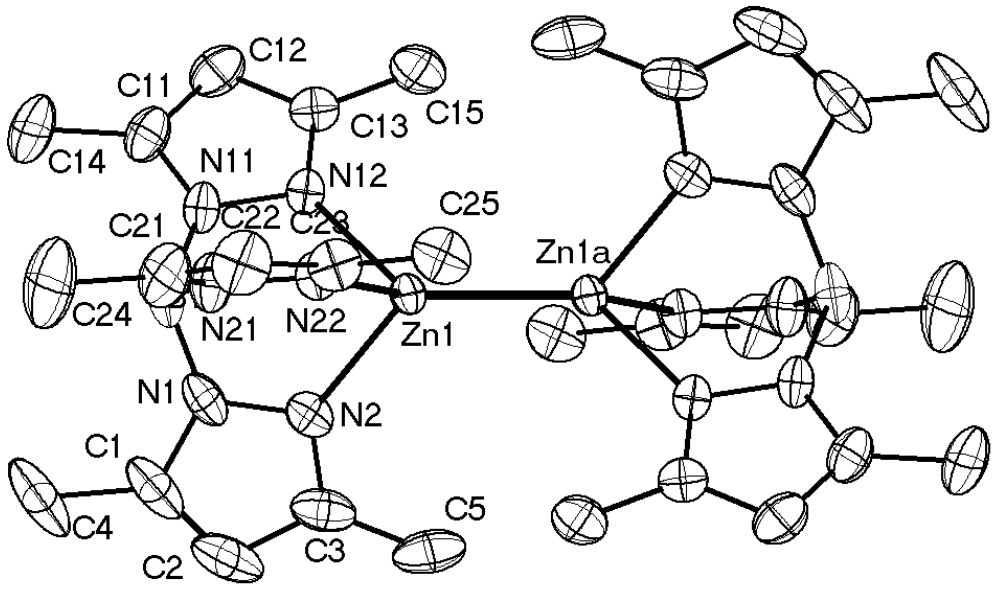

Figure 1. Solid state structure of **1**; Zn1a and non-labeled atoms symmetry-equivalent via inversion (-x+1,-y,-z+1), ellipsoids correspond to 50% probability levels; H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)-Zn(1)#1 2.3560(9), Zn(1)-N(2) 2.099(4), Zn(1)-N(22) 2.103(3), Zn(1)-N(12) 2.104(3), N(2)-Zn(1)-N(22) 88.02(14), N(2)-Zn(1)-N(12) 87.98(14), N(22)-Zn(1)-N(12) 86.71(13), N(2)-Zn(1)-Zn(1)1a 126.27(11), N(22)-Zn(1)-Zn(1)1a 126.12(10), N(12)-Zn(1)-Zn(1)1a 128.49(10).

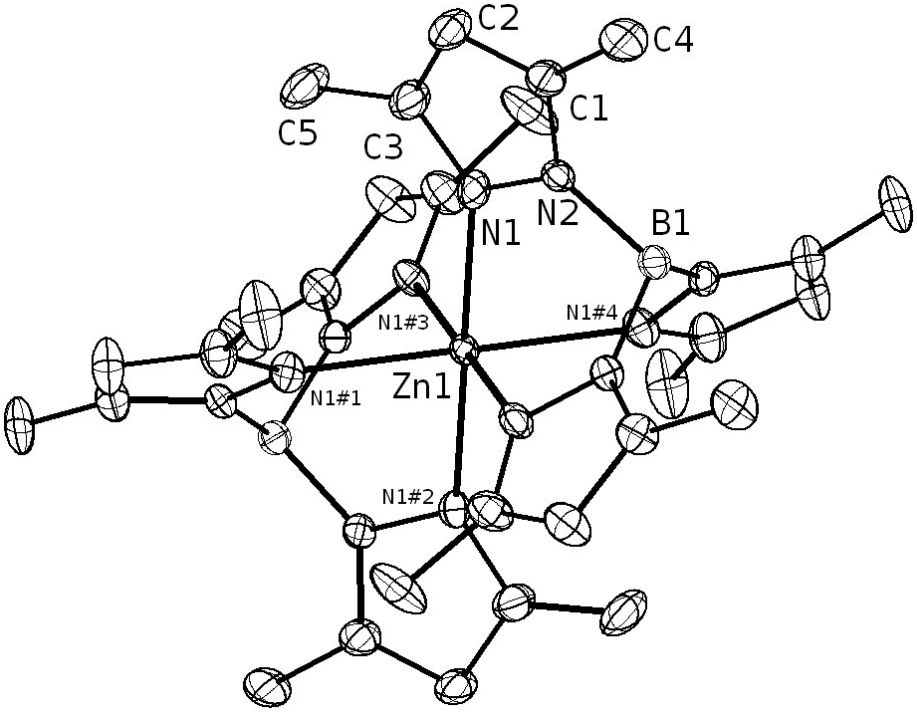

Figure 2. Solid state structure of **2**; non-labeled atoms symmetry-equivalent via 32, ellipsoids correspond to 50% probability levels; H atoms are omitted for clarity; only one of two independent molecules is presented. Selected bond lengths (Å) and angles (°): Zn(1)-N(1)

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2.179(2), N(1)1a-Zn(1)-N(1) 94.59(11), N(1)#2-Zn(1)-N(1) 179.74(12), N(1)#3-Zn(1)-N(1) 94.23(11), N(1)#4-Zn(1)-N(1) 85.59(8)[13].

The tris(pyrazolyl)hydroborato ligands in **1** and **2** bind in a η^3-coordination mode to the Zn atoms. As a consequence, the Zn atoms in **1** adopt tetrahedral coordination spheres, whereas that in **2** is almost perfect octahedrally coordinated by six N atoms. The Zn-N bond lengths in **2** (2.179(2), 2.184(2) Å) are comparable to those reported previously for this complex,[10] whereas those in **1** are significantly shorter (av. value 2.102(4) Å). This finding clearly points to decreased sterical interactions between the two substituents in **1** compared to **2** due to the presence of the Zn_2 unit. Both tris(pyrazolyl)hydroborato ligands in **1** adopt an almost perfect staggered orientation (torsions 58.15(17)°, 61.16(18)°) to each other in order to further decrease sterical interactions. The bonding parameters (B-N, C-C, C-N bond lengths) of the tris(pyrazolyl)hydroborates in **1** and **2** are comparable and in the typical range as was observed for tris(pyrazolyl)hydroborate zinc complexes of the types $(Tp^{Me_2})_2Zn$ [10] and $(Tp^{Me_2})_2ZnX$.[14] The Zn-Zn bond length in **1** of 2.3560(9) Å is elongated compared to that observed for $Cp^*_2Zn_2$ (2.305(3) Å),[1] but comparable to those reported for the homoleptic Zn(I)complexes $[CH_2(Ph_2P{=}NPh)_2]_2Zn_2$ (2.3490(1) Å)[8] and $Dippnacnac_2Zn_2$ (2.3586(7) Å) containing N,N' chelating-ligands.[3b] In contrast, the Zn-Zn bond in $Mesnacnac_2Zn_2$ (2.3813(8) Å) is slightly elongated.[6]

Conclusion. The Cp* ligands in $Cp^*_2Zn_2$ can easily be replaced by tris(pyrazolyl)hydroborato ligands by reaction with the corresponding potassium salt under mild reaction conditions. This new reaction type may give access to a larger number of Zn(I) complexes in the near future including complexes, which cannot be obtained from Wurtz-analogous reductions reactions. We are currently investigating reactions with potassium salts of different types of organic substituents as well as with 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

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. Cp^*_2Zn [15] and $Cp^*_2Zn_2$ [1b] were prepared according to literature methods, tris(3,5-dimethyl)pyrazolylhydroborate $Tp^{Me_2}K$ was commercially available from Acros. A Bruker Avance 500 spectrometer was used for NMR spectroscopy. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to internal THF-d_8 (^1H: $\delta = 3.58$; ^{13}C: $\delta = 67.4$). 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.

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Zn_2[3,5-Me-pz]$_2$ (1). 0.32 g (1.00 mmol) of $Tp^{Me_2}K$ and 0.20 g (0.50 mmol) of $Cp^*_2Zn_2$ were suspended in 50 mL of THF 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.

Yield 0.1 g (93.6 %); m.p. 395 °C (decomp.); IR: ν = 2962, 2923, 2506 (B-H), 1543, 1446, 1417, 1385, 1350, 1258, 1194, 1181, 1057, 1013, 850, 784, 694, 642, 460, 391 cm^{-1};^{1}H NMR (300 MHz, [D8]THF, 25°C): δ = 2.35 (s, 9H, C*Me*), 2.37 (s, 9H, C*Me*), 5.66 (s, 3H, C*H*); ^{13}C NMR (300 MHz, [D8]THF, 25°C): δ = 12.4 (CH_3), 13.9 (CH_3), 105.1 (C*C*(H)C), 144.1 (*C*C(H)C), 148.9 (CC(H)*C*); ^{11}B NMR (300 MHz, [D8]THF, 25°C): δ = -9.6 (*B*H).

Zn[3,5-Me-pz]$_2$ (2). 0.64 g (2.00 mmol) of $Tp^{Me_2}K$ and 0.32 g (1.00 mmol) of Cp^*_2Zn were suspended at room temperature in 50 mL of *n*-pentane and stirred for 12 h. The white precipitate was filtered and the solvent 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.

Yield 0.25 g (89.3 %); IR: ν = 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}; ^{1}H NMR (300 MHz, [D8]THF, 25°C): δ = 1.34 (s, 9H, C*Me*), 2.41 (s, 9H, C*Me*), 5.58 (s, 3H, C*H*); ^{13}C NMR (300 MHz, [D8]THF, 25°C): δ = 12.0 (CH_3), 12.8 (CH_3), 105.3 (C*C*(H)C), 143.6 (*C*C(H)C), 149.2 (CC(H)*C*); ^{11}B NMR (300 MHz, [D8]THF, 25°C): δ = -9.5 (*B*H).

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 APEX2-detector (monochromated MoK_α radiation, λ = 0.71073 Å) at 100 K. The structures were solved by Direct Methods using Bruker AXS APEX 2 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 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 produces ten peaks with 1.5–2.1 e/Å^3 corresponding to two highly disordered THF molecules with point symmetrie $\bar{1}$. The ten highest peaks in the difference Fourier map were attributed to carbon atoms. This attempt resulted in R1 = 0.1270. The SQUEEZE refinement revealed voids with 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. **2** contained disordered solvent: one molecule of THF and dichloromethane at the same site with SOF 0.5 each. The THF atoms [O(40), C(41-44)] were refined with fixed U = 0.08.

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The chlorine atoms of the dichloromethan [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.

Acknowledgements

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Layout 2:

Phrase: Making new from existing

Sebastian Gondzik, Dieter Bläser, Roland Boese, and Stephan Schulz*

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[11] **Crystal data for 1**: $C_{30}H_{28}N_{12}B_2Zn_2$*3[$CH_2Cl_2$]*$C_4H_8O$, M = 1052.01, colorless crystal (0.27 x 0.22 x 0.15 mm); monoclinic, space group $P2_1/n$; a = 7.9280(4), b = 27.6966(13), c = 11.5109(5) Å; β = 103.231(2)°, V = 2460.5(2) Å^3; Z = 2; μ = 1.34 mm^{-1}; $\rho_{ber.}$ = 1.420 g cm^{-3}; 22749 reflexes ($2\theta_{max}$ = 49.6°), 4250 unique (R_{int} = 0.0272); 276 parameters; largest max./min. in the final difference Fourier synthesis 1.024/-1.391 eÅ^{-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**: $C_{30}H_{44}B_2N_{12}Zn$*THF, M = 659.76, colorless crystal (0.28 x 0.23 x 0.16 mm); trigonal, space group $R\bar{3}c$; a = 17.1545(8), b = 17.1545(8), c = 52.772(3) Å; α = β = 90°, γ = 120°, V = 13449.1(11) Å^3; Z = 12; μ = 1.63 mm^{-1}; $\rho_{ber.}$ = 1.324 g cm^{-3}; 45486 reflexes ($2\theta_{max}$ = 56.6°), 3673 unique (R_{int} = 0.0286); 137 parameters; largest max./min. in the final difference Fourier

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synthesis 0.616/-0.459 eÅ^{-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 Fig. 2 for Zn(1)] and apparently two, highly disordered molecules of THF with SOF ~0.5 (treated with SQUEEZE). Consequently, the ratio Zn complex to THF is approx. 1:3.

[13] Bond angles for the second independent molecule: N(21)-Zn(2)-N(21)#5 180.0; N(21)-Zn(2)-N(21)#6 94.20(8), N(21)-Zn(2)-N(21)#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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