Dizincocene as a Building Block for Novel Zn−Zn-Bonded Compounds?

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*Summary: The reaction of decamethyldizincocene ($Cp^*_2Zn_2$, **1**) with MesnacnacH proceeds with protonation of the Cp* substituent and subsequent formation of the zinc−zinc-bonded complex $(Mesnacnac)_2Zn_2$ (**3**).*

The epoch-making synthesis of decamethyldizincocene ($Cp^*_2Zn_2$, **1**),[1] the first stable molecular compound containing a central Zn−Zn bond with the Zn atoms formally in the +1 oxidation state, has been the starting point of intensely growing research activity on low-valent organozinc complexes.[2] Since the report by Carmona et al. in 2004, six new Zn−Zn-bonded complexes of the type R_2Zn_2 containing sterically encumbered organic substituents (R = $EtMe_4Cp$,[3] $[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(Me)C]_2CH$ (Dippnacnac),[4] $2,6\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3)C_6H_3$,[5] $[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(Me)C]_2$,[6] $Me_2Si[N\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3)]_2$,[7] 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene[8]) have been structurally characterized. Moreover, the first molecular compounds containing Cd−Cd[5b,9] and Mg−Mg[10] bonds have been described. Except for **1**, which was initially prepared by reaction of Cp^*_2Zn and Et_2Zn, the new metal−metal-bonded complexes R_2M_2 were synthesized by a procedure analogous to the Wurtz coupling reaction of the corresponding halide-substituted compounds RMX (X = Cl, Br, I).

Remarkably, even though the nature of the Zn−Zn bond, in particular that of the Cp-substituted derivatives, has been theoretically investigated in detail,[11] only very limited information on the chemical reactivity of such compounds is available. Reactions of **1** with H_2O, *t*-BuOH, and NCXyl as reported by Carmona et al.[1] only proceeded with disproportionation and subsequent formation of elemental zinc and the corresponding Zn(II) complexes, whereas reactions with R_2Zn (R = Me, Mes) yielded the corresponding half-sandwich complexes Cp*ZnR. Moreover, the reaction with iodine occurred with oxidation and subsequent formation of Cp^*_2Zn and ZnI_2,[3] whereas no reaction was observed with H_2, CO, and CO_2. Reactions with Lewis bases such as NMe_3, pyridine, PMe_3, and others were unsuccessful until we only very recently reported on the reaction of **1** with the strong Lewis base 4-(dimethylamino)pyridine (dmap), yielding $Cp^*Zn{-}Zn(dmap)_2Cp^*$ (**2**), the first Lewis acid−base adduct of dizincocene.[12] Unexpectedly, the two dmap molecules were found to bind in a geminal binding mode to only one Zn atom. At the same time, Jones et al. reported on reactions of several Lewis bases with a low-valent organomagnesium(I) complex, yielding the corresponding vicinal bis adducts.[13]

Herein, we report on the reaction of **1** with $[((2,4,6\text{-}Me_3C_6H_2)N(Me)C)_2CH]H$ (MesnacnacH) containing an acidic N−H group.

Results and Discussion

Solutions of $Cp^*_2Zn_2$ (**1**) and MesnacnacH in *n*-pentane were combined at 0 °C, and the resulting solution was stirred for 12 h. $Mesnacnac_2Zn_2$ (**3**) precipitated as a colorless crystalline solid, which was isolated by filtration. Careful evaporation of the solvent of the remaining mother liquor under vacuum yielded a waxy solid, which was dispersed in 4 mL of cold pentane (0 °C) and then filtered. Resonances due to the formation of Cp*H were clearly observable in the filtrate, whereas the remaining white solid showed resonances of additional complex **3**.

3 is soluble in organic solvents such as hexane, toluene, and Et_2O. The ^1H NMR spectrum of **3** shows resonances due to the organic groups of the Mesnacnac substituent. No indication for

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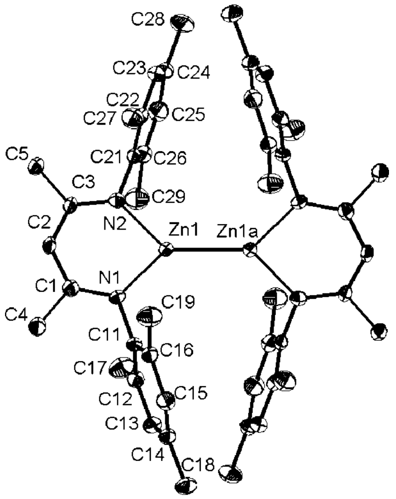


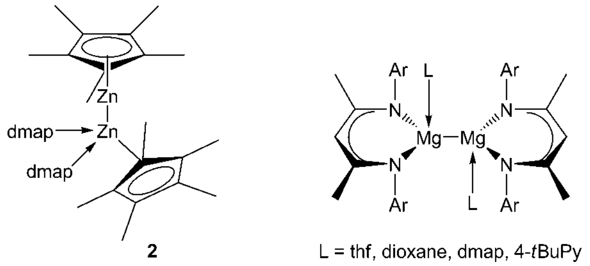
Figure 1. Solid-state structure of **3**. Thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1−Zn1a = 2.3813(8), Zn1−N1 = 2.005(2), Zn1−N2 = 2.000(3), N1−C1 = 1.336(4), N1−C11 = 1.446(4), N2−C3 = 1.331(4), N2−C21 = 1.458(4), C1−C2 = 1.396(4), C2−C3 = 1.416(4); N1−Zn1−N2 = 93.8(2), N1−Zn1−Zn1a = 133.0(1), N2−Zn1−Zn1a = 133.3(1).

the formation of a zinc hydride species was found in the ^{1}H NMR of **3**, and the IR spectra also showed no absorption peak due to a Zn−H group in the typical range from 1600 to 1900 cm^{-1}.[14] Moreover, no disproportionation reaction with formation of elemental zinc and (Mesnacnac)$_2$Zn was observed.[15]

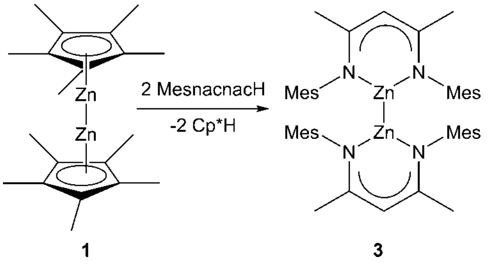
Single crystals of **3** suitable for an X-ray structure determination were obtained from a solution in *n*-pentane/toluene at −30 °C (Figure 1). The central structural motif of **3** is the Zn−Zn bond (2.3813(8) Å), which is, surprisingly, slightly elongated compared to that observed for the sterically more hindered complex Dippnacnac$_2$Zn$_2$ (**6**; 2.3586(7) Å)[4] containing the larger Dipp substituents. The torsion angle (N1−Zn1−Zn1′−N1′ = 42.8°) observed for **3** is significantly smaller compared to that of **6** (86.6°). The Zn−Zn bond length previously observed for R$_2$Zn$_2$ complexes ranges from 2.29 to 2.35 Å, whereas comparable Zn−Zn bond lengths were observed for the doubly reduced diimine derivative (R = [(2,6-*i*-Pr$_2$C$_6$H$_3$)N(Me)C]$_2$; 2.3994(6) Å)[6] and the very recently reported Lewis acid−base adduct Cp*Zn−Zn(dmap)$_2$Cp* (**2**; 2.4184(4) Å).[12] The C$_3$N$_2$Zn rings in **3** are almost planar with the Zn atoms slightly out of the plane, as was previously observed in Dippnacnac-ZnN(SiMe$_3$)$_2$[16] and **6**.[4]

DFT calculations were performed to improve the understanding of the formation and the bonding situation of **3**. The reaction of **1** with MesnacnacH is exothermic (−48 kcal/mol), and the calculated structure of **3** is very similar to the calculated structure of Dippnacnac$_2$Zn$_2$ (**6**).[4] The Zn atoms in **3** carry a partial charge of 0.86 (0.85 for **6**), and the Zn−Zn bond has mainly s character (s 94.5%, p 4.25%, d 1.29%), as was observed for **6**. The computed Zn−Zn bond distance of 2.378 Å agrees almost perfectly with the experimental value observed for **3** (2.3813(8) Å) as well as the calculated value for **6** (2.392 Å).

Scheme 1. Lewis Acid−Base Adducts of Low-Valent Organozinc and Organomagnesium Complexes



Scheme 2. Synthesis of Complex 3



The use of Cp*$_2$Zn$_2$ (**1**) as the starting reagent for the synthesis of novel low-valent organozinc complexes may open a general access to this interesting class of compounds, including complexes which cannot be obtained from procedures analogous to the Wurtz coupling reactions. For instance, several attempts to synthesize **3** by reduction reactions of MesnacnacZnX (X = Cl, I)[17] with different reducing agents (Na, K, K−graphite, Na−napthalenide) only resulted in the formation of Zn(II) complex (Mesnacnac)$_2$Zn (**5**) in high yield.[15] Reactions of **1** with different substituents containing acidic H atoms are currently under investigation.

Experimental Section

General Comments. All manipulations were performed under an Ar atmosphere. Solvents were dried over Na/K and degassed prior to use. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Avance 500 spectrometer and are referenced to internal C$_6$D$_5$H (^{1}H, δ 7.154; ^{13}C, δ 128.0). The IR spectrum of **3** was recorded on a ALPHA-T FT-IR spectrometer equipped with a single-reflection ATR sampling module. The melting point of **3** was measured in a sealed capillary and was not corrected. Elemental analyses were performed at the *Elementaranalyse Labor* of the University of Essen.

Preparation of (Mesnacnac)$_2$Zn$_2$ (3). A 0.32 g portion of MesnacnacH (1.0 mmol) dissolved in 5 mL of *n*-pentane was added at 0 °C to a solution of 0.20 g of Cp*$_2$Zn$_2$ (0.5 mmol) in 10 mL of *n*-pentane and the mixture stirred for 2 h at −4 °C. **3** precipitated as a colorless crystalline solid, which was isolated by filtration. Yield: 0.12 g (0.38 mmol, 40%). Melting point: 240 °C. Anal. Found (calcd) for C$_{46}$H$_{58}$N$_4$Zn$_2$ (797.73 g/mol): H, 7.21 (7.33); C, 69.07 (69.26); N, 6.94 (7.02). ^{1}H NMR (500 MHz, C$_6$D$_6$, 25 °C): δ 1.55 (s, 6 H, C*Me*), 1.84 (s, 12 H, α *o-H*), 2.29 (s, 6H, α *p-H*), 4.86 (s, 1 H, C*H*), 6.89 (s, 4H, *m-H*). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 25 °C): δ 19.2 (α *o-C*), 21.1 (α *p-C*), 22.6 (C*C*H$_3$), 95.5 (*C*H), 129.0 (*m-C*), 131.3 (*o-C*), 132.8 (*p-C*), 146.7 (*C*N), 164.7 (*C*CH$_3$). IR: ν 2905, 1532, 1450, 1386, 1259, 1200, 1146, 1013, 852, 800, 741, 567, 497, 388 cm^{-1}.

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Single-Crystal X-ray Analysis. Data were collected on a Bruker AXS SMART APEX CCD diffractometer, (Mo Kα radiation, λ = 0.710 73 Å; T = 173(2) K). The structure was solved by direct methods (SHELXS-97)[18] and refined by full-matrix least squares on F^2. A semiempirical absorption correction was applied. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined by a riding model (SHELXL-97, Program for Crystal Structure Refinement).[19]

Data for **3**: $C_{46}H_{58}N_4Zn_2$, M = 797.73, colorless crystal (0.15 × 0.11 × 0.04 mm), monoclinic, space group $P2/n$, a = 13.4527(10) Å, b = 8.3904(7) Å, c = 19.4814(14) Å, β = 103.768(6), V = 2135.8(3) Å^3, Z = 2, μ = 1.158 mm^{-1}, ρ_{calcd} = 1.240 g cm^{-3}, 16 314 reflections ($2\theta_{\max}$ = 50°), 3753 unique reflections (R_{int} = 0.0809), 243 parameters; largest maximum/minimum in the final difference Fourier synthesis 0.269/−0.336 e Å^{-3}, maximum/minimum transmission 0.9552/0.8455; R1 = 0.0428 ($I > 2\sigma(I)$), wR2 (all data) = 0.0782.

Computational Calculations. DFT calculations were carried out with the Gaussian03 suite of programs (M. J. Frisch, et al., Gaussian 03, Revision D.02; Gaussian Inc., Pittsburgh, PA, 2003; the complete reference is given in the Supporting Information). The molecular structure of **3** was obtained by performing a complete energy optimization of all geometric parameters at the b3lyp/svp level; SVP is the split-valence basis set with the additional polarization functions of Ahlrichs et al. Atomic charges of **3**, which were calculated from NBO population analyses, are given in the Supporting Information.

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Supporting Information Available: Tables, text, figures, and a CIF file giving X-ray crystallographic data, absolute energies and NBO analyses of **3**, and the full citation for Gaussian 03. This material is available free of charge via the Internet at http://pubs.acs.org.

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