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Low-Valent Lewis Acids

The Reaction of Dizincocene with Preservation of the Zn–Zn Bond**

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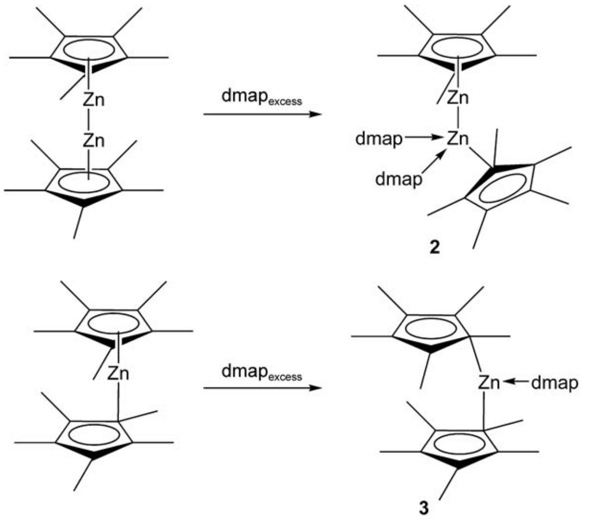
Dedicated to Professor Edgar Niecke on the occasion of his 70th birthday

Since the epoch-making synthesis of $[Cp^*_2Zn_2]$ (**1**; Cp* = Me_5C_5),[1] the first complex containing a Zn–Zn bond, by Carmona et al. in 2004, four compounds of the type R_2Zn_2 have been synthesized and structurally characterized that are stabilized by sterically demanding organic substituents: R = $EtMe_4C_5$,[2] [2,6-(2,6-$i$$Pr_2C_6H_3)_2C_6H_3$],[3] [{(2,6-$i$$Pr_2C_6H_3$)NC(Me)}$_2$CH],[4] [(2,6-$i$$Pr_2C_6H_3$)NC(Me)]$_2$,[5] Me_2Si[N(2,6-$i$$Pr_2C_6H_3$)]$_2$,[6] and 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian).[7] Although the nature of the Zn–Zn bond, and in particular in cyclopentadienyl-substituted complexes, has been theoretically investigated by several groups,[8] only limited information on the reactivity of such complexes is given. Carmona et al. reported reactions of **1** with H_2O, *t*BuOH, NCXyl (Xyl = 2,6-$Me_2C_6H_3$),[1] and other Lewis bases, such as NMe_3, pyridine, and PMe_3,[2] but either no reaction occurred, or disproportionation into elemental zinc and the corresponding zinc(II) compound was observed. Reactions with ZnR_2 (R = Me, 2,4,6-$Me_3C_6H_2$ (Mes)) yielded half-sandwich complexes [Cp*ZnR], whereas reaction with iodine led to oxidation and subsequent formation of $[Cp^*_2Zn]$ and ZnI_2. In contrast, no reaction was observed with H_2, CO, and CO_2. From 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 corresponding complexes with a Zn–Zn bond. We also began investigations into the general reactivity of the Zn–Zn bond. These studies focused primarily on reactions of $[Cp^*_2Zn_2]$ (**1**) because of the steric and electronic flexibility of the Cp* substituent.[10] As part of our interest in the Lewis acidity of Group 13 compounds, we investigated the Lewis acidity of **1**. We have shown that the strong Lewis base 4-dimethylaminopyridine (dmap) is very powerful tool for the synthesis of Group 13 metal Lewis acid–base adducts.[11] Reaction of **1** with dmap resulted in the formation of the unexpected adduct **2**, in which two dmap molecules bind in a geminal coordination mode to one of the two zinc atoms with preservation of the Zn–Zn bond.

A toluene/*n*-pentane (1:4) solution of **1** reacted with two equivalents and with an excess of dmap at 0 °C to give compound **2**, which was isolated after crystallization at −30 °C as a pale yellow crystalline solid. In contrast to previous reports with other Lewis bases, no disproportionation reaction was observed.[2] The analogous reaction of $[Cp^*_2Zn]$ with dmap yielded $[Cp^*_2Zn(dmap)]$ (**3**; Scheme 1)



Scheme 1. Synthesis of the dmap adducts **2** and **3**.

The ^1H- and ^{13}C NMR spectra of **2** and **3** show signals corresponding to the Cp* groups and to dmap. No indication of zinc hydride complex formation was found in the ^1H NMR spectrum of **2** (no signal between $\delta = 4$–5 ppm), and the IR spectrum had no absorption peak between 1650 and 1900 cm^{-1}, which is the typical range for zinc hydride complexes.[12] The ^1H NMR spectrum of single crystals of **2**, which were obtained from a *n*-pentane/toluene solution, has additional signals owing to the presence of toluene. The Cp* substituents result in only one resonance at 25 °C (**2**: $\delta = 2.03$, **3**: 2.08 ppm), which points to fast exchange reactions between the non-equivalent Cp* substituents in **2** and indicates η^5-bonded Cp* groups in solution. In contrast, the ^1H NMR

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spectrum of **2** recorded at −95 °C has two broad and well-separated signals ($\delta = 2.48$, 2.73 ppm) of equal intensity that are 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 ($\Delta H_{\text{Diss}} = -40.4\ \text{kJ mol}^{-1}$) was determined from these NMR spectra.[14] The dissociation enthalpy of **3** ($\Delta H_{\text{Diss}} = -50.6\ \text{kJ mol}^{-1}$) was also determined, and demonstrates the higher Lewis acidity of [Cp$^*_2$Zn] compared to [Cp$^*_2$Zn$_2$].

Single crystals of **2** and **3** (Figure 1) were obtained from solutions in *n*-pentane/toluene (**2**) and *n*-pentane (**3**) upon storage at −30 °C.[15] The central zinc 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 the sterically less-hindered compound ZnMe$_2$ with dmap gave the bisadduct [(dmap)$_2$ZnMe$_2$].[16] The two dmap molecules in **2** coordinate in a geminal fashion to one zinc atom (Zn2), whereas the second zinc center (Zn1) is coordinated only by one η^5-bonded Cp* substituent (Cp$^*_{\text{centr}}$−Zn1 2.033 Å; compare with 2.04 Å in **1**).[17] The Zn1−C$_{\text{Cp*}}$ bond lengths (2.300(2)–2.395(2) Å) vary more strongly than those observed in **1** (2.27–2.30 Å), as the atom Zn1 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); the distances to the next closest C$_{\text{Cp*}}$ atoms (Zn2−C15 2.696(3), Zn2−C12 2.773(3) Å) are significantly elongated. The Zn−N bonds in **2** (Zn2−N1 2.115(2), Zn2−N3 2.125(2) Å) are significantly longer than that in **3** (Zn1−N1 2.024(3) Å), but shorter than those observed for [Me$_2$Zn(dmap)$_2$] (Zn1−N1/2 2.177(2) Å), which contains a four-coordinate zinc atom.[16] The central Zn1−Zn2 bond in **2** (2.418(1) Å) is significantly longer than that in **1** (2.305(3) Å); this difference of over 0.11 Å is most likely due to the higher coordination number of Zn2. This bond length is the longest Zn−Zn bond observed to date; Zn$_2$R$_2$ complexes typically have Zn−Zn bond lengths ranging from 2.29 to 2.35 Å.[1–7] Comparable Zn−Zn bond lengths were observed only in H-bridged organozinc complexes of the general type [{RZnH}$_2$] (R = [2,6-(2,6-*i*Pr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$] 2.408(1) Å,[3] [{(2,6-*i*Pr$_2$C$_6$H$_3$)NC(Me)}$_2$CH] 2.451(1) Å[18]). Whereas **1** has an almost linear structure (177.4(1)°), **2** deviates significantly from linearity owing to the coordination of two dmap molecules. The deviation for the η^5-bound Cp* ligand (Zn2-Zn1-Cp$^*_{\text{centr}}$ 159.6°) is as expected les pronounced that that of the σ-bound Cp* ligand (Zn1-Zn2-C11 115.4(1)°). 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)°).

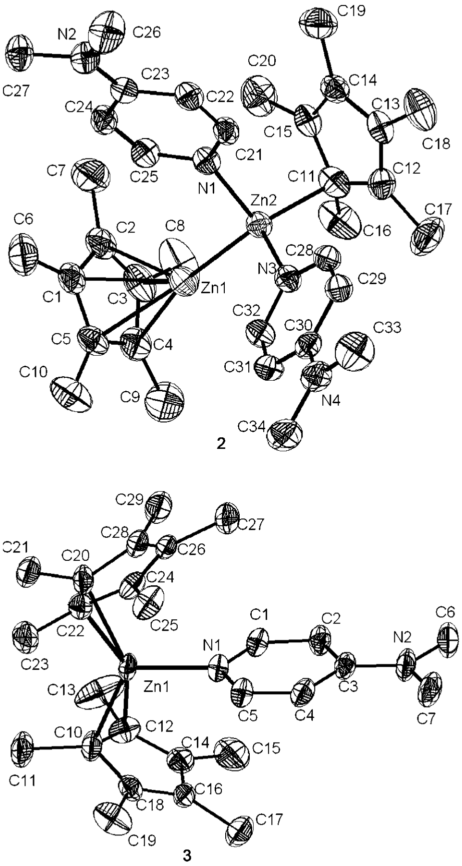

Figure 1. Molecular structures of **2** and **3**. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **2**: Zn1–Zn2 2.418(1), Zn1–C1 2.425(2), Zn1–C2 2.395(2), Zn1–C3 2.328(2), Zn1–C4 2.300(2), Zn1–C5 2.360(2), Zn2–C11 2.174(2), Zn2–N1 2.115(2), Zn2–N3 2.125(2); Cp$^*_{\text{centr}}$-Zn1-Zn2 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). **3**: 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).

To better understand the formation and the bonding situation in **2**, DFT calculations were performed.[19] The formation of [Cp$^*_2$Zn$_2$(dmap)] (**1′**) by coordination of one dmap molecule to **1** is exothermic (−4.6 kcal mol^{-1}), with an only marginal elongation of the Zn−Zn bond (**1**: 2.36 Å, **1′**: 2.37 Å). However, the zinc atoms in **1′** carry different partial charges. In **1′**, the dmap-coordinated zinc atom is more electropositive (0.99) than the second Zn atom (0.76), whereas in **1** both zinc centers are equally charged (0.89). The coordination of a second dmap molecule in a vicinal position is endothermic (+2.6 kcal mol^{-1}), whereas geminal coordination is strongly exothermic (−9.2 kcal mol^{-1}). Consequently, the formation of **2** with geminal coordination of the dmap molecules is strongly favored (−13.8 kcal mol^{-1}, −57.7 kJ mol^{-1}) over vicinal coordination (−2.0 kcal mol^{-1}). Upon coordination of two dmap molecules, the Zn−Zn bond in **2** significantly increases in length to 2.44 Å, which agrees very well with the experimental findings (2.418(1) Å). Both zinc atoms in **2** are differently charged, with Zn1 (0.60) carrying a significantly higher electronic charge than the dmap-coordinated Zn2 atom (1.15). The NBO analysis shows a decrease in 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** owing to population of the antibonding Zn−Zn LUMO, which agrees very well with previously published bonding analyses for **1**.[1b]

The unexpected formation of **2** is the first reaction of [Cp$^*_2$Zn$_2$] **1** that proceeds with preservation of the central Zn−Zn bond. The reaction to form **2** is strongly exothermic, which makes the synthesis of adducts with other strong Lewis bases likely, and will allow a detailed understanding of the reactivity of **1** and the chemical stability of the Zn–Zn bond to be investigated.

Experimental Section

All manipulations were performed under an argon 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 were internally referenced to C_6D_5H (^{1}H: $\delta = 7.154$ ppm, ^{13}C: $\delta = 128.0$ ppm). IR spectra were recorded on an ALPHA-T FT-IR spectrometer. Melting points were measured in sealed capillaries and were not corrected.

2: dmap (0.24 g, 2.0 mmol) dissolved in toluene (5 mL) was added at 0°C to a solution of [$Cp^*_2Zn_2$] (0.20 g, 0.5 mmol) in *n*-pentane (5 mL) and stirred for 2 h at −25°C. The resulting suspension was dissolved in additional 5 mL of toluene and stored at −30°C. Pale yellow crystals of **2**·toluene were obtained after 7 days. Yield of isolated crystals 0.08 g (0.12 mmol, 25%). M.p.: 105°C. ^{1}H NMR (500 MHz, C_6D_6, 25°C): $\delta = 2.03$ (s, 30H, C_5Me_5), 2.09 (s, 1.5H, toluene), 2.20 (s, 12H, NMe_2), 6.09 (dd, $^3J_{HH} = 6.3$, $^3J_{HH} = 1.6$ Hz, 4H, C(3)H), 6.89–7.20 (m, 2.5H, toluene), 8.46 ppm (dd, $^3J_{HH} = 6.3$, $^3J_{HH} = 1.6$ Hz, 2H, C(2)H). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25°C): $\delta = 10.4$ ($C_5\mathit{Me}_5$), 38.3 (NMe_2), 106.8 (C(3)), 109.0 (C_5Me_5), 150.5 (C(2)), 154.3 ppm (C(4)). IR (Nujol): $\tilde{\nu} = 2853$, 1611, 1461, 1377, 1224, 1013, 802 cm^{-1}.

3: A solution of [Cp^*_2Zn] (0.67 g, 2.0 mmol) and dmap (0.48 g, 4.0 mmol) in *n*-hexane (15 mL) were heated under reflux for 1 h and then stored at −30°C. Colorless crystals of **3** were obtained after 36 h. Yield of isolated crystals 0.49 g (1.1 mmol, 55%). M.p.: 205°C. ^{1}H NMR (500 MHz, C_6D_6, 25°C): $\delta = 1.99$ (s, 6H, NMe_2), 2.08 (s, 30H, C_5Me_5), 5.68 (dd, $^3J_{HH} = 6.9$, $^3J_{HH} = 1.6$ Hz, 2H, C(3)H), 7.22 ppm (dd, $^3J_{HH} = 6.9$, $^3J_{HH} = 1.6$ Hz, 2H, C(2)H). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25°C): $\delta = 12.3$ ($C_5\mathit{Me}_5$), 38.3 (NMe_2), 105.3 (C(3)), 114.1 (C_5Me_5), 147.5 (C(2)), 154.5 ppm (C(4)). IR (Nujol): $\tilde{\nu} = 2923$, 1623, 1546, 1440, 1390, 1261, 1228, 1075, 1021, 801, 604 cm^{-1}.

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[15] Bruker AXS SMART APEX CCD diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å; $T = 203(2)$ (**2**), 153(2) K (**3**)). Structures were solved by direct methods (SHELXS-97, G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467) and refined by full-matrix least-squares on F^2. Semi-empirical absorption corrections were applied. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97, Program for Crystal Structure Refinement, G. M. Sheldrick, University of Göttingen, **1997**). **2**: $C_{34}H_{50}N_4Zn_2\cdot 0.25\,C_7H_8$, $M_r = 666.54$, pale yellow crystal ($0.28 \times 0.22 \times 0.13$ mm), triclinic, $P\bar{1}$; $a = 10.8055(6)$, $b = 11.1214(6)$, $c = 17.1985(9)$ Å, $\alpha = 71.822(2)$, $\beta = 89.356(3)$, $\gamma = 75.260(3)°$, $V = 1893.78(18)$ Å^3; $Z = 2$, $\mu = 1.293$ mm^{-1}, $\rho_{calcd} = 1.169$ g cm^{-3}; 73213 reflections ($2\theta_{max} = 58°$), 11020 unique ($R_{int} = 0.0640$), 395 parameters, largest max./min. in the final difference Fourier synthesis 1.054 e Å^{-3}/−0.285 e Å^{-3}, max./min. transmission 0.8816/0.7820; $R_1 = 0.0463$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.1367. Disordered toluene molecule (C61–C64) with inversion center, SOF 0.5. **3**: $C_{27}H_{40}N_2Zn$, $M_r = 457.98$, colorless crystal ($0.48 \times 0.44 \times 0.13$ mm), triclinic, $P\bar{1}$; $a = 9.848(5)$, $b = 10.104(6)$, $c = 14.489$ (8) Å, $\alpha = 98.791(11)$, $\beta = 98.449(11)$, $\gamma = 111.355(11)°$, $V = 1294.4(12)$ Å^3; $Z = 2$, $\mu = 0.963$ mm^{-1}, $\rho_{calcd} = 1.175$ g cm^{-3}; 10044 reflections ($2\theta_{max} = 54°$), 5669 unique ($R_{int} = 0.0826$), 283 parameters, largest max./min. in the final difference Fourier synthesis 0.989 e Å^{-3}/−0.560 e Å^{-3}, max./min. transmission 0.8850/0.6549; $R_1 = 0.0695$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.1627. CCDC-694349 (**2**) and CCDC-694247 (**3**) 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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[19] DFT calculations were carried out with the Gaussian03 suite of programs (Gaussian 03 (Revision D.02): M. J. Frisch et al., Gaussian Inc., Pittsburgh, PA, **2003**; see the Supporting Information). The molecular structures were obtained by performing a complete energy optimization of all geometric parameters at the B3LYP/SVP level; SVP is the split-valence basis set with additional polarization functions of Ahlrichs et al. Atomic charges, which were calculated from NBO population analyses for **2**, are given in the Supporting Information.