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

Stephan Schulz,^{a} Daniella Schuchmann,^a Ulrich Westphal,^a Michael Bolte^b*

^a Institute of Inorganic Chemistry, University of Duisburg-Essen, 45117 Essen, Germany; ^bInstitute of Inorganic Chemistry, University of Frankfurt, 60438 Frankfurt, Germany

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

* To whom correspondence should be addressed. Prof. Dr. Stephan Schulz, Institute of Inorganic Chemistry, University of Duisburg-Essen, 45117 Essen, Germany; Phone: +49 0201-1834635; Fax: +49 0201-1834635; e-mail: stephan.schulz@uni-due.de. ¹ Institute of Inorganic Chemistry, University of Frankfurt, 60438 Frankfurt, Germany.

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 $(\text{Mesnacnac})_2\text{Zn}_2$ **3**.

Introduction

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 an 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 ($\text{R} = \text{EtMe}_4\text{Cp}$,³ [$\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}(\text{Me})\text{C}\}_2\text{CH}$] (Dippnacnac),⁴ [2,6-(2,6-*i*-Pr₂C₆H₃)-C₆H₃],⁵ [(2,6-*i*-Pr₂C₆H₃)N(Me)C]₂,⁶ {Me₂Si[N-(2,6-*i*-Pr₂C₆H₃)]₂},⁷ and 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene⁸) have been structurally characterized. Moreover, the first molecular compounds containing Cd-Cd^{9,5b} and Mg-Mg¹⁰ 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 Wurtz-analogous coupling reaction of the corresponding halide-substituted compounds RMX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).

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 ($\text{R} = \text{Me}, \text{Mes}$) 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-dimethylaminopyridine (dmap), yielding $\text{Cp}^*\text{Zn-Zn}(\text{dmap})_2\text{Cp}^*$ **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* bisadducts.¹³

((Scheme 1 here))

Herein, we report on the reaction of **1** with $[\{(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}(\text{Me})\text{C}\}_2\text{CH}]\text{H}$ (MesnacnacH) containing an acidic N-H group.

Results and Discussion

Solutions of Cp^*Zn_2 **1** and MesnacnacH in *n*-pentane were combined at 0 °C and the resulting solution was stirred for 12 h. Mesnacnac $_2\text{Zn}_2$ **3** precipitated as colorless crystalline solid, which was isolated by filtration. Careful evaporation of the solvent of the remaining mother liquor in 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**.

((Scheme 2 here))

3 is soluble in organic solvents such as hexane, toluene and Et_2O , respectively. The ^1H NMR spectrum of **3** shows the resonances due to the organic groups of the Mesnacnac substituent. No indication for the formation of a zinc hydride species was found in the ^1H 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 $(\text{Mesnacnac})_2\text{Zn}$ was observed.¹⁵

((Figure 1 here))

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). 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 $\text{Dippnacnac}_2\text{Zn}_2$ **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_2Zn_2 complexes ranges from 2.29 – 2.35 Å, whereas comparable Zn-Zn bond lengths were observed for the doubly reduced diimine derivative ($\text{R} = [(2,6\text{-i-Pr}_2\text{C}_6\text{H}_3)\text{N}(\text{Me})\text{C}]_2$; 2.3994(6) Å)⁶ and the very recently reported Lewis acid-base adduct $\text{Cp}^*\text{Zn-Zn}(\text{dmap})_2\text{Cp}^*$ **2** (2.4184(4) Å).¹² The $\text{C}_3\text{N}_2\text{Zn}$ rings in **3** are almost planar with the Zn atoms slightly out of the plane as was previously observed in $\text{DippnacnacZnN}(\text{SiMe}_3)_2$ 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 Dippnacnac₂Zn₂ **6**.⁴ The Zn atoms in **3** carry a partial charge of 0.86 (0.85 **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).

The use of Cp*₂Zn₂ **1** as 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 can't be obtained from Wurtz-analogous coupling reactions. For instance, several attempts to synthesize **3** by reduction reaction of MesnacnacZnX (X = Cl, I)¹⁸ with different reducing agents (Na, K, K-graphite, Na-naphthalenide) only resulted in the formation of Zn(II) complex (Mesnacnac)₂Zn **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. ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker Avance 500 spectrometer and are referenced to internal C₆D₅H (¹H: δ = 7.154; ¹³C: 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)₂Zn₂ **3:** 0.32 g MesnacnacH (1.0 mmol) dissolved in 5 mL of *n*-pentane was added at 0 °C to a solution of 0.20 g Cp*₂Zn₂ (0.5 mmol) in 10 mL of *n*-pentane and stirred for 2 h at -4 °C. **3** precipitated as colorless crystalline solid, which was isolated by filtration. Yield 0.12 g (0.38 mmol, 40%). Melting point: 240 °C. Elemental Analysis C₄₆H₅₈N₄Zn₂ (797.73 g/mol): found (calcd): H, 7.21 (7.33); C, 69.07 (69.26); N, 6.94 (7.02) %. ¹H-NMR (500 MHz, C₆D₆, 25 °C): δ = 1.55 (s, 6 H, CMe), 1.84 (s, 12 H, α *o*-H), 2.29 (s, 6H, α *p*-H), 4.86 (s, 1 H, CH), 6.89 (s, 4H, *m*-H). ¹³C{¹H}-NMR (125 MHz, C₆D₆, 25 °C): δ = 19.2 (α *o*-C), 21.1 (α *p*-C), 22.6 (CCH₃), 95.5 (CH), 129.0 (*m*-C), 131.3

(*o*-C), 132.8 (*p*-C), 146.7 (CN), 164.7 (CCH₃). IR: ν = 2905, 1532, 1450, 1386, 1259, 1200, 1146, 1013, 852, 800, 741, 567, 497, 388 cm⁻¹.

Single crystal X-ray analysis. Data were collected on a Bruker AXS SMART APEX CCD diffractometer, (MoK α radiation, λ = 0.71073 Å; T = 173(2) K). The structure was solved by Direct Methods (SHELXS-97)¹⁹ and refined by full-matrix least-squares on F^2 . Semi-empirical absorption correction was applied. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model. (SHELXL-97, Program for Crystal Structure Refinement).²⁰

3: C₄₆H₅₈N₄Zn₂, M = 797.73, colorless crystal (0.15 x 0.11 x 0.04 mm); monoclinic, space group $P2_1/n$; a = 13.4527(10), b = 8.3904(7), c = 19.4814(14) Å; β = 103.768(6), V = 2135.8(3) Å³; Z = 2; μ = 1.158 mm⁻¹; $\rho_{\text{ber.}}$ = 1.240 g cm⁻³; 16314 reflexes ($2\theta_{\text{max}}$ = 50°), 3753 unique (R_{int} = 0.0809); 243 parameters; largest max./min. in the final difference Fourier synthesis 0.269 eÅ⁻³/–0.336 eÅ⁻³; max./min. transmission 0.9552/0.8455; R_1 = 0.0428 ($I > 2\sigma(I)$), wR_2 (all data) = 0.0782.

Computational calculation. 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, complete reference is given in the supplement). 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 additional polarization functions of Ahlrichs et al. Atomic charges of **3**, which were calculated from NBO population analyses, are given in the electronic supplement.

Acknowledgment. S. Schulz thanks the German Science Foundation (DFG) for financial support. D. Schuchmann is grateful to the Fonds der Chemischen Industrie for a doctoral fellowship.

Supporting Information Available: X-ray crystallographic data including a cif file, and tables of absolute energies and NBO analyses of **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Figure Captions

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 [°]: 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).

Scheme 1. Lewis acid-base adducts of low-valent organozinc and organomagnesium complexes

Scheme 2. Synthesis of complex **3**.

References

- (1) (a) Resa, I.; Carmona, E.; Gutierrez-Puebla, E.; Monge, A. *Science* **2004**, *305*, 1136-1138. (b) del Río, D.; Galindo, A.; Resa, I.; Carmona, E. *Angew. Chem. Int. Ed.* **2005**, *44*, 1244-1247. (c) Carmona, E.; Galindo, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 6526-6536.
- (2) It should be noted that Zn_2H_2 , the first molecular zinc complex with a Zn-Zn bond, was trapped in an Ar matrix at 12 K. Zn_2H_2 was characterized by vibrational spectroscopy and theoretical calculations. (a) Wang, X.; Andrews, L. *J. Phys. Chem. A* **2004**, *108*, 11006-11013. (b) Greene, T. M.; Brown, W.; Andrews, L.; Downs, A. J.; Chertihin, G. V.; Runeberg, N.; Pyykkö, P. *J. Phys. Chem.* **1995**, *99*, 7925-7934.
- (3) Grirrane, A.; Resa, I.; Rodriguez, A.; Carmona, E.; Alvarez, E.; Gutierrez-Puebla, E.; Monge, A.; Galindo, A.; del Río, D.; Andersen, R. A. *J. Am. Chem. Soc.* **2007**, *129*, 693-703.
- (4) Wang, Y.; Quillian, B.; Wei, P.; Wang, H.; Yang, X.-J.; Xie, Y.; King, R. B.; Schleyer, P. v. R.; Schaefer III, H. F.; Robinson, G. H. *J. Am. Chem. Soc.* **2005**, *127*, 11944-11945.
- (5) (a) Zhu, Z.; Wright, R. J.; Olmstead, M. M.; Rivard, E.; Brynda, M.; Power, P. P. *Angew. Chem. Int. Ed.* **2006**, *45*, 5807-5810. (b) Zhu, Z.; Brynda, M.; Wright, R. J.; Fischer, R. C.; Merrill, W. A.; Rivard, E.; Wolf, R.; Fettingner, J. C.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2007**, *129*, 10847-10857.
- (6) Yang, X.-J.; Yu, J.; Liu, Y.; Xie, Y.; Schaefer III, H. F.; Liang, Y.; Wu, B. *Chem. Commun.* **2007**, 2363-2365.
- (7) Tsai, Y.-C.; Lu, D.-Y.; Lin, Y.-M.; Hwang, J.-K.; Yu, J.-S. K. *Chem. Commun.* **2007**, 4125-4127.
- (8) Fedushkin, I. L.; Skatova, A. A.; Ketkov, S. Y.; Eremenko, O. V.; Piskunov, A. V.; Fukin, G. K. *Angew. Chem. Int. Ed.* **2007**, *46*, 4302-4305.

- (9) (a) Zhu, Z.; Fischer, R. C.; Fetting, J. C.; Rivard, E.; Brynda, M.; Power, P. P. *J. Am. Chem. Soc.* **2006**, *128*, 15068-15069.
- (10) Green, S. P.; Jones, C.; Stasch, A. *Science* **2007**, *318*, 1754-1757.
- (11) (a) Kan, Y. *J. Mol. Struct. Theochem* **2007**, *805*, 127-132. (b) Velazquez, A.; Fernández, I.; Frenking, G.; Merino, G. *Organometallics* **2007**, *26*, 4731-4736. (c) Philpott, M. R.; Kawazoe, Y. *Chem. Phys.* **2007**, *333*, 201-207. (d) Pandey, K. N. *J. Organomet. Chem.* **2007**, *692*, 1058-1063. (e) Wang, H.; Yang, C.; Wan, B.; Han, K.-L. *J. Theor. Comp. Chem.* **2006**, *5*, 461-473. (f) Philpott, M. R.; Kawazoe, Y. *J. Mol. Struct. Theochem* **2006**, *776*, 113-123. (g) Kress, J. W. *J. Phys. Chem. A* **2005**, *109*, 7757-7763. (h) Xie, Y.; Schaefer III, H. F.; King, R. B. *J. Am. Chem. Soc.* **2005**, *127*, 2818-2819.
- (12) Schuchmann, D.; Westphal, U.; Schulz, S.; Flörke, U.; Bläser, D.; Boese, R. *Angew. Chem. Int. Ed.*, **2009**, *48*, 807-810.
- (13) Green, S. P.; Jones, C.; Stasch, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 9079-9083.
- (14) Hao, H.; Cui, C.; Roesky, H. W.; Bai, G.; Schmidt, H.-G.; Noltemeyer, M. *Chem. Commun.* **2001**, 1118-1119.
- (15) The formation of (Mesnacnac)₂Zn can be excluded since the ¹H and ¹³C resonances of this Zn(II) complex are significantly shifted compared to those observed for **3**. Schulz, S.; Eisenmann, T.; Bläser, D.; Boese, R. manuscript submitted.
- (16) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738-8749.
- (17) Schulz, S.; Eisenmann, T.; Westphal, U.; Schmidt, S.; Flörke, U. *Z. Anorg. Allg. Chem.*, in the press.
- (18) Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, *46*, 467.
- (19) Sheldrick, G. M. Universität Göttingen, 1997.

for table of contents use only

The reaction of Cp^*_2Zn_2 **1** with MesnacnacH occurred with elimination of Cp^*H and subsequent formation of $(\text{Mesnacnac})_2\text{Zn}_2$, demonstrating the capability of **1** to serve as building block for the synthesis of novel zinc-zinc bonded complexes.

This text is made available via DuEPublico, the institutional repository of the University of Duisburg-Essen. This version may eventually differ from another version distributed by a commercial publisher.

DOI: 10.1021/om801155j

URN: urn:nbn:de:hbz:464-20201030-101533-7

This document is the Accepted Manuscript version of a Published Work that appeared in final form in: *Organometallics* 2009, 28, 5, 1590–1592, copyright © American Chemical Society after peer review and technical editing by the publisher.

To access the final edited and published work see <https://doi.org/10.1021/om801155j>

All rights reserved.