

Reactions of a β -Diketiminato Zinc Hydride Complex with Heterocumulenes

Stephan Schulz,* Tamara Eisenmann, Sarah Schmidt, Dieter Bläser, Ulrich Westphal, and Roland Boese

Received (in XXX, XXX) Xth XXXXXXXXXX 200X, Accepted Xth XXXXXXXXXX 200X

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

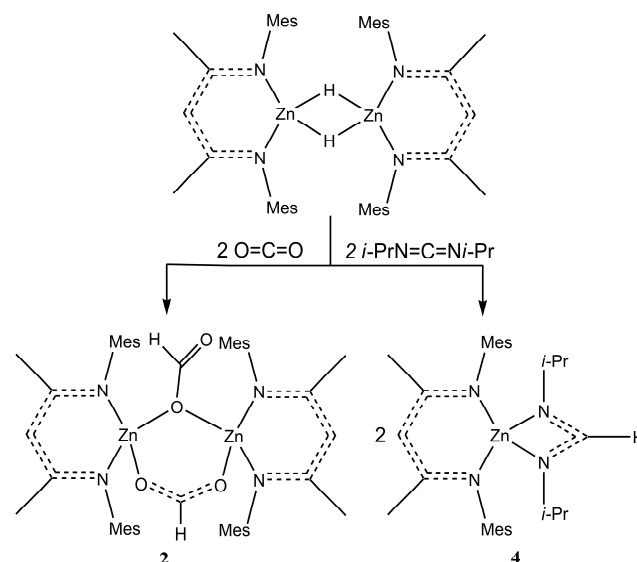
The β -diketiminato zinc hydride MesnacnacZnH (**1**) reacts with CO₂, C(Ni-Pr)₂ and *t*-BuNCO at ambient temperature with insertion into the Zn-H bond and subsequent formation of the corresponding formate (**2**), formamido (**3**) and formamidinato (**4**) complexes.

The effective utilization of abundant, renewable, nontoxic and inexpensive CO₂ as C₁-feedstock still is an important target in respect to the current environmental concerns facing our planet.[1] Unfortunately, the high stability of CO₂ has limited its use in industrial syntheses, so far, but zinc complexes have been demonstrated in the past to be of potential interest for this purpose. Zinc alkoxide and carboxylate complexes were found to serve as *living single-site catalysts* for the ring-opening polymerization (ROMP) of lactide [2] and the copolymerization of epoxides and carbon dioxide [3] yielding biodegradable aliphatic polycarbonates. Moreover, bimetallic calcium/zinc complexes supported by a bridged β -diketiminato ligand are effective catalysts for terpolymerization reactions of epoxide, cyclic anhydrides and CO₂ [4] as well as for epoxide/CO₂ copolymerization.[5]

In order to investigate the mechanism of the CO₂ activation in more detail, several reactions of zinc alkoxides RZnOR' and amides RZnNR'₂ with CO₂ have been investigated experimentally[6] and by theoretical calculations.[7] These reactions typically proceeded with insertion into the Zn-N and Zn-O bond and subsequent formation of zinc carbamate and carbonate complexes. In addition, pyrazolylborate zinc hydrides were found to react with CO₂ and heterocumulenes such as CS₂ and isothiocyanates RNCS with insertion into the Zn-H bond and formation of the mononuclear Zn complexes.[8] whereas no reaction was observed with cyclohexyl carbodiimide.[9] Very recently, *Driess et al.* reported on the formation of zinc formates *via* Li-promoted hydrogenation of CO₂ using heterobimetallic hydrido zinc alkoxide clusters of the type [(HZnOt-Bu)_{4-n}(LiOt-Bu)_n] (n = 0 – 3). Li ions were found to play a distinguished role on the activity of the Zn-H moiety since [(HZnOt-Bu)₄] only showed a very low hydride transfer (reduction) activity of CO₂ at Zn-H sites whereas [(HZnOt-Bu)₃(LiOt-Bu)] reduces CO₂ at atmospheric pressure and ambient temperature with formation of the corresponding formate complex. In addition, ZnH₂ completely failed to react with CO₂. [10]

We became only recently interested in organozinc hydrides RZnH and reported on the synthesis of MesnacnacZnH (**1**) (Mesnacnac = [HC{C(Me)N(2,4,6-Me₃C₆H₂)₂}]₂) containing a sterically demanding N,N'-chelating β -diketiminato

group.[11] **1**, which was synthesized according to a procedure established by *Harder et al.* by reaction of MesnacnacZnCl with KN(*i*-Pr)HBH₃, [12] represents one of the rare examples of structurally characterized organozinc hydrides.[13] Even though **1** forms a hydride-bridged dimer in the solid state, pulsed gradient spin echo (PGSE) diffusion measurements at 25 °C of solutions of **1** in different solvents indicated, that **1** is monomeric in solution. Herein we report on reactions of **1** with CO₂, C(Ni-Pr)₂ and *t*-BuNCO.



Scheme 1 Synthesis of **2** and **4**

Reaction of **1** with CO₂ under very mild reaction conditions (ambient temperature, CO₂ under normal pressure) for 2 hours resulted in an almost quantitative formation of **2**. *In situ* monitoring of the reaction by ¹H NMR spectroscopy showed a continuously decreasing resonance at 4.57 ppm (Zn-H) and a steadily increasing new singlet at 8.01 ppm due to the formation of the O₂C-H group. IR spectra of pure **2** shows two absorption bands due to $\nu_{as}(\text{CO})$ and $\nu_{sy}(\text{CO})$. The difference $\Delta\nu$ between both is typically used to classify the binding mode of the formate group, with a large difference of about 200 cm⁻¹ indicating a η^1 -coordination, whereas difference of 100 cm⁻¹ are typical for bridging and chelating formate groups. **2** shows a difference of 99 cm⁻¹, which points to a bridging/chelating mode as observed in the solid state structure. No further symmetrical or asymmetrical CO absorption bands could be identified; however, they might be overlapped by absorption bands of the diketiminato group as a

comparison of **2** with the starting hydride showed (see supporting information file).

The molecular structure of **2** in the solid state was investigated by single crystal X-ray diffraction. **2** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. **2** forms an unsymmetrically bridged dimer exhibiting two different coordination modii of the formato unit. The two Zn atoms are linked by two HCO₂ units, with one formato group serving as bridging bidentate (syn-syn) μ - η^2 -O₂CH ligand and the second group adopting a bridging μ - η^1 -OC(O)H coordination mode. The presence of only a single resonance for the formato moiety in the ¹H NMR spectrum of **2** points to the presence of a monomeric complex in solution as was observed for the starting hydride complex. Moreover, a pulsed gradient spin echo (PGSE) diffusion measurement of a solution of **2** in C₆D₆ at 25 °C yields a hydrodynamic radi of 5.48 Å, which is very similar to that observed for monomeric MesnacnacZnH in [D₈]THF (5.26 Å), also indicating **2** to be monomeric in solution. Unfortunately, temperature-dependent ¹H NMR spectroscopic studies were hindered by the extremely low solubility of **2** in solvents such as [D₈]THF and [D₈]Toluene at temperatures below -10 °C.

DFT calculations were performed to evaluate the relative stabilities of monomeric versus dimeric **2**. However, the unsymmetrically bridged form as was observed experimentally doesn't represent an energy minimum. Instead, the symmetrically bridged dimer containing two μ - η^2 -O₂CH groups is energetically favored by 24.2 kcal/mol compared to the monomer (see supporting information file).

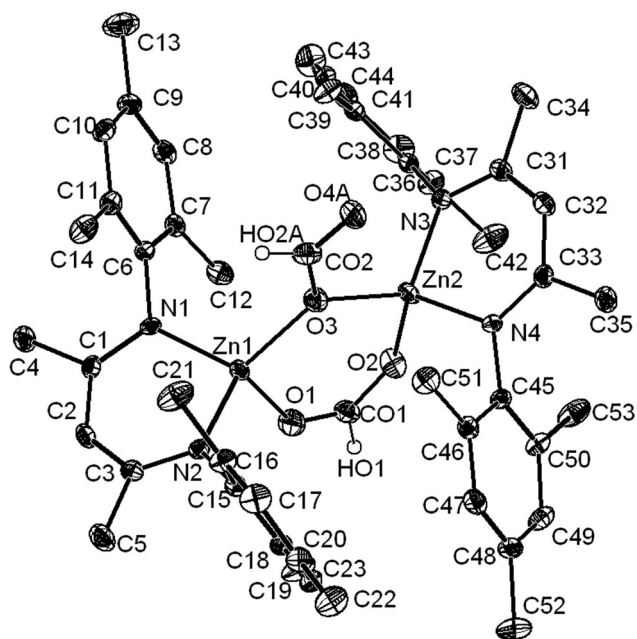


Fig. 1 Solid state structure of **2**; H atoms are omitted for clarity.

The Zn-O bond lengths within the bridging bidentate moiety are almost identical (Zn1-O3 1.971(2); Zn2-O3 1.986(2) Å), whereas the Zn-O distances within the μ - η^1 -bridged unit differ by almost 0.04 Å (Zn1-O1 2.039(3); Zn2-O2 1.995(3) Å). Comparable structural motifs with two metal centers bridged by two formato groups with as-described

coordination modii have been previously observed.[14] The C-O distances within the formato groups differ significantly. The bridging bidentate moiety (CO1-O1 1.233(4), CO2-O2 1.236(4) Å) almost shows equal C-O bond lengths whereas the bridging monodentate unit exhibits a long (CO2-O3 1.332(5) Å) and a short C-O bond (CO2-O4A 1.165(7) Å) indicating a terminal C=O double bond. Both the terminal O-atom and the H-atom are disordered over two sites (SOF 0.5). The C₃N₂Zn rings in **2** are almost planar with the Zn atoms slightly out of the plane as was observed in [MesnacnacZn(μ -H)]₂ and the C-C, C-N and Zn-N bond lengths within the rings are almost identical compared to the starting zinc hydride complex.[11]

In order to evaluate the reactivity of the zinc hydride in more detail, reactions of **1** with heterocumulenes such as (*i*-PrN)₂C and *t*-BuNCO were investigated. These reactions were also performed at ambient temperature and resulted in an almost quantitative formation of the corresponding formamido (**3**) and formamidinato (**4**) complexes, respectively.

Both reactions were monitored by ¹H NMR spectroscopy. As was observed for the reaction with CO₂, the Zn-H resonance of **1** steadily decreased over a period of 30 min and new resonances at 7.91 (**3**) and 7.30 ppm (**4**) occurred.

Colorless crystals of **4** suitable for a single crystal structure determination were obtained from a solution in *n*-hexane. **4** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell.

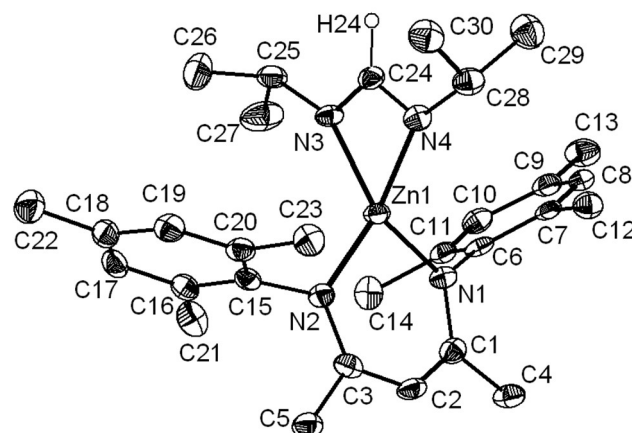


Fig. 2 Solid state structure of **4**; H atoms are omitted for clarity

The formamidinato unit serves as chelating η^2 -(NR)₂CH substituent with the Zn-N bond lengths significantly differing (Zn1-N3 2.024(3); Zn1-N4 2.092(4) Å), which most likely indicates some sterical stress within this complex. The central Zn atom adopts a distorted tetrahedral coordination sphere. The endocyclic N1-Zn1-N2 bond angle (97.2(2)°) within the six-membered C₃N₂Zn ring is significantly larger than the N3-Zn1-N4 bond angle (65.7(2)°) within the four-membered CN₂Zn ring and the Zn-N bond lengths within the six-membered ring are significantly shorter (Zn1-N1 1.968(4); Zn1-N2 1.970(4) Å) than in the four-membered ring (Zn1-N3 2.024(3); Zn1-N4 2.092(4) Å). The N-C bond lengths of the formamidinato group (C24-N3 1.314(6), C24-N4 1.311(6) Å) indicate perfect delocalization of the π -electrons. As was

observed for **2**, the Zn atom in the C₃N₂Zn ring in **4** is slightly out of the plane and the C-C, C-N and Zn-N bond lengths within the rings again are almost identical compared to those of the starting zinc hydride complex.

MesnacnacZnH easily reacts with heterocumulenes under very mild reaction conditions and its reactivity is more pronounced compared to the corresponding organomagnesium hydride [DippnacnacMgH]₂, which was found to react with cyclohexyl carbodiimide C(NCy)₂ with insertion into the Mg-H bond whereas the reaction with *t*-BuNCO only gave a mixture of unidentified products.[15] Harder et al. recently reported on the reactions of an organocalcium hydride [DippnacnacCaH(thf)]₂ with several unsaturated substrates, but unfortunately no reaction with CO₂, C(NR)₂ or RNCO were reported.[16] In contrast, Holland et al. very recently reported on reactions of β -deketiminato stabilized iron hydrides with both CO₂ and C(Ni-Pr)₂. These reactions also yielded a formamidinato complex with a chelating η^2 -(NR)₂CH unit, whereas the formato complexes showed two bridging bidentate μ -O₂CH ligands.[17]

Conclusion. MesnacnacZnH was found to react with CO₂ and other heterocumulenes under very mild reaction conditions with insertion into the Zn-H bond. Further studies on its reactivity toward other small molecules including other heterocumulenes as well as C-C and C-X multiple bonded species are currently under investigation.

Notes and references

University of Duisburg-Essen, Universitätsstr. 5-7, S07 S03 C30, 45117 Essen, Germany. Fax: Int (+)201 1833830; Tel: Int (+)201 1834635; E-mail: stephan.schulz@uni-due.de

† Electronic Supplementary Information (ESI) available: Experimental procedure, characterization of **2**, **3**, and **4**, IR spectroscopic studies as well as computational calculations. See DOI: 10.1039/b000000x/

‡ CCDC 776239 (**2**) and 776240 (**4**) 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.

A. Name, B. Name and C. Name, *Journal Title*, 2000, **35**, 3523; A. Name, B. Name and C. Name, *Journal Title*, 2000, **35**, 3523.

- 1 H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielsen, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults and W. Tumas, *Chem. Rev.* 2001, **101**, 953.
- 2 M. H. Chisholm, J. C. Gallucci and K. Phomphrai, *Inorg. Chem.* 2005, **44**, 8004; A. P. Dove, V. C. Gibson, E. L. Marshall, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.* 2004, 570; L. R. Rieth, D. R. Moore, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.* 2002, **124**, 15239; M. H. Chisholm, J. C. Huffman and K. Phomphrai, *J. Chem. Soc., Dalton Trans.* 2001, 222; B. J. O'Keefe, M. A. Hillmeyer and W. B. Tolman, *J. Chem. Soc., Dalton Trans.* 2001, 2215; M. Cheng, A. B. Attygalle, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.* 1999, **121**, 11583. For a review article see: J. Wu, T.-L. Yu, C.-T. Chen and C.-C. Lin, *Coord. Chem. Rev.* 2006, **250**, 602.
- 3 D. R. Moore, M. Cheng, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.* 2003, **125**, 11911; D. R. Moore, M. Cheng, E. B. Lobkovsky and G. W. Coates, *Angew. Chem., Int. Ed.* 2002, **41**,

- 2599; M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.* 2001, **123**, 8738; M. Cheng, N. A. Darling, E. B. Lobkovsky and G. W. Coates, *J. Chem. Soc., Chem. Commun.* 2000, 2007; M. Cheng, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.* 1998, **120**, 11018; B. Y. Liu, C. Y. Tian, L. Zhanq, W. D. Yan and W. J. Zhanq, *J. Polym. Sci. Part A: Polym. Chem.* 2006, **44**, 6243; M. Kröger, C. Folli, O. Walter and M. Döring, *Adv. Synth. Cat.* 2006, **348**, 1908.
- 4 R. C. Jeske, J. M. Rowley and G. W. Coates, *Angew. Chem., Int. Ed.* 2008, **47**, 6041
- 5 D. F.-J. Piesik, S. Range and S. Harder, *Organometallics* 2008, **27**, 6178
- 6 Y. Tang, W. S. Kassel, L. N. Zakharov, A. L. Rheingold and R. A. Kemp, *Inorg. Chem.* 2005, **44**, 359; J. Notni, S. Schenk, H. Görls, H. Breitzke and E. Anders, *Inorg. Chem.* 2008, **47**, 1382; D. Domide, E. Kaifer, J. Mautz, O. Walter, S. Behrens and H.-J. Himmel, *Eur. J. Inorg. Chem.* 2008, 3177; P. F. Haywood, M. R. Hill, N. K. Roberts, D. C. Craig, J. J. Russell and R. N. Lamb, *Eur. J. Inorg. Chem.* 2008, 2024; M. B. Hursthouse, M. A. Malik, M. Motevalli and P. O'Brien, *J. Chem. Soc., Chem. Commun.* 1991, 1690; I. Abrahams, M. A. Malik, M. Motevalli and P. O'Brien, *J. Chem. Soc., Dalton Trans.* 1995, 1043.
- 7 H. J. Himmel, *Eur. J. Inorg. Chem.* 2007, 675.
- 8 R. Han, I. B. Gorrell, A. G. Looney and G. Parkin, *J. Chem. Soc., Chem. Commun.* 1991, 717; M. Rombach, H. Brombacher and H. Vahrenkamp, *Eur. J. Inorg. Chem.* 2002, 153.
- 9 H. Brombacher, Ph.D. Thesis, University of Freiburg, 2003.
- 10 K. Merz, M. Moreno, E. Löffler, L. Khodeir, A. Rittermeier, K. Fink, K. Kotsis, M. Muhler and M. Driess, *Chem. Commun.* 2008, 73
- 11 S. Schulz, T. Eisenmann, D. Schuchmann, M. Bolte, M. Kirchner, R. Boese, J. Spielmann and S. Harder, *Z. Naturforsch.* 2009, **64b**, 1397.
- 12 J. Spielmann, D. Piesik, B. Wittkamp, G. Jansen and S. Harder, *Chem. Commun.* 2009, 3455
- 13 A. J. de Koning, J. Boersma and G. J. M. van der Kerk, *J. Organomet. Chem.* 1978, **155**, C5; W. Kläui, U. Schilde and M. Schmidt, *Inorg. Chem.* 1997, **36**, 1598; H. Hao, C. Cui, H. W. Roesky, G. Bai, H.-G. Schmidt and M. Noltemeyer, *Chem. Commun.* 2001, 1118; Z. Zhu, R. J. Wright, M. M. Olmstead, E. Rivard, M. Brynda and P. P. Power *Angew. Chem. Int. Ed.* 2006, **45**, 5807.
- 14 W. B. Tolman, A. Bino and S. J. Lippard, *J. Am. Chem. Soc.* 1989, **111**, 8522; W. B. Tolman, S. Liu; J. G. Bentsen and S. J. Lippard, *J. Am. Chem. Soc.* 1991, **113**, 152; A. Escuer, B. Cordero, X. Solans, M. Font-Bardia and T. Calvet, *Eur. J. Inorg. Chem.* 2008, 5082; R. F. Baggio, P. K. De Perazzo and G. Polla *Acta Cryst.* 1985, **C41**, 194; A. Goeta, R. Baggio and D. Stoilova, *Vibrational Spectroscopy* 2004, **34**, 293.
- 15 S. J. Bonyhady, S. P. Green, C. Jones, S. Nembenna and A. Stasch *Angew. Chem. Int. Ed.* 2009, **48**, 2973.
- 16 J. Spielmann, S. Harder *Chem. Eur. J.* 2007, **13**, 8928; J. Spielmann, S. Harder *Eur. J. Inorg. Chem.* 2008, 1480; J. Spielmann, F. Buch, S. Harder *Angew. Chem. Int. Ed.* 2008, **47**, 9434.
- 17 Y. Yu, A. R. Sadique, J. M. Smith, T. R. Dugan, R. E. Cowley, W. W. Brennessel, C. J. Flaschenriem, E. Bill, T. R. Cundari and P. L. Holland, *J. Am. Chem. Soc.* 2008, **130**, 6624.

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: 10.1039/C0CC01329C

URN: urn:nbn:de:hbz:464-20201104-090808-9

Accepted Manuscript. The final article was published in: Chemical Communications, 2010,46, 7226-7228 and is available at: <https://doi.org/10.1039/C0CC01329C>

All rights reserved.