Reactions of a β-diketiminate zinc hydride complex with heterocumulenes†

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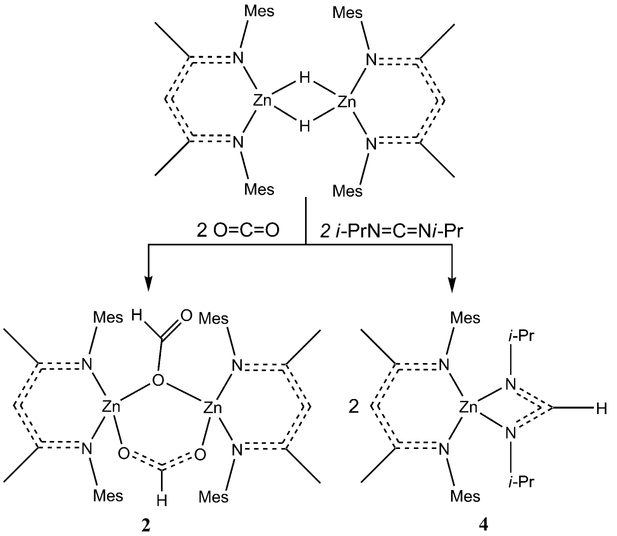
The β-diketiminate zinc hydride MesnacnacZnH (1) reacts with CO_2, C(N*i*-Pr)$_2$ and *t*-BuNCO at ambient temperature with insertion into the Zn–H bond and subsequent formation of the corresponding formato (2), formamido (3) and formamidinato (4) complexes.

The effective utilization of abundant, renewable, nontoxic and inexpensive CO_2 as C_1-feedstock still is an important target in respect to the current environmental concerns facing our planet.[1] Unfortunately, the high stability of CO_2 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-diketiminate ligand are effective catalysts for terpolymerization reactions of epoxide, cyclic anhydrides and CO_2[4] as well as for epoxide/CO_2 copolymerization.[5]

In order to investigate the mechanism of the CO_2 activation in more detail, several reactions of zinc alkoxides RZnOR′ and amides RZnNR′$_2$ with CO_2 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 CO_2 and heterocumulenes such as CS_2 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 CO_2 using heterobimetallic hydridozinc alkoxide clusters of the type [(HZnO*t*-Bu)$_{4-n}$(LiO*t*-Bu)$_n$] (n = 0–3). Li ions were found to play a distinguished role on the activity of the Zn–H moiety since [(HZnO*t*-Bu)$_4$] only showed a very low hydride transfer (reduction) activity of CO_2 at Zn–H sites whereas [(HZnO*t*-Bu)$_3$(LiO*t*-Bu)] reduces CO_2 at atmospheric pressure and ambient temperature with the formation of the corresponding formato complex. In addition, ZnH_2 completely failed to react with CO_2.[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-$Me_3C_6H_2$)}$_2$]) 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)HBH_3,[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 CO_2, C(N*i*-Pr)$_2$ and *t*-BuNCO (Scheme 1).

Reaction of **1** with CO_2 under very mild reaction conditions (ambient temperature, CO_2 under normal pressure) for 2 hours resulted in an almost quantitative formation of **2**. *In situ* monitoring of the reaction by ^{1}H 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 O_2C–H group. IR spectra of pure **2** show two absorption bands due to ν_{as}(CO) and ν_{sy}(CO). The difference Δν between both is typically used to classify the binding mode of the formiate group, with a large difference of about 200 cm^{-1} indicating a η^1-coordination, whereas difference of 100 cm^{-1} is typical for bridging and chelating



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

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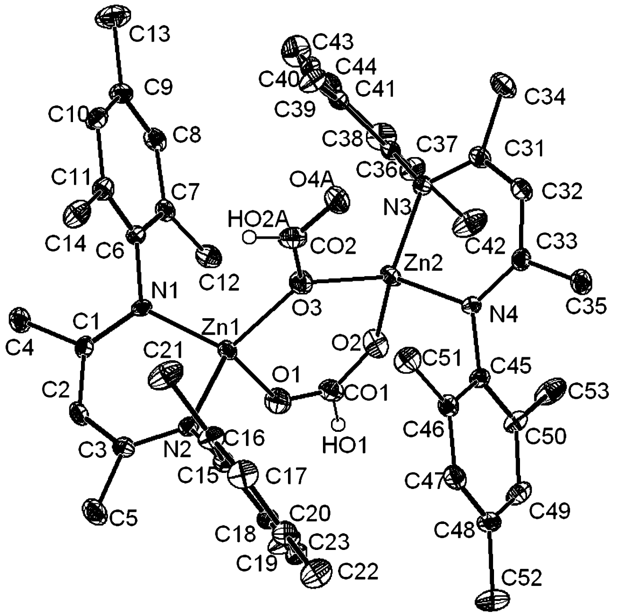

Fig. 1 Solid state structure of **2**; H atoms are omitted for clarity.

formiate groups. **2** shows a difference of 99 cm^{-1}, which points to a bridging/chelating mode as observed in the solid state structure (Fig. 1). 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 ESI†).

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 HCO_2 units, with one formato group serving as bridging bidentate (*syn–syn*) μ-η^2-O_2CH 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 C_6D_6 at 25 °C yields a hydrodynamic radius of 5.48 Å, which is very similar to that observed for monomeric MesnacnacZnH in $[D_8]$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 $[D_8]$THF and $[D_8]$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-O_2CH groups is energetically favored by 24.2 kcal mol^{-1} compared to the monomer (see ESI†).

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 C_3N_2Zn rings in **2** are almost planar with the Zn atoms slightly out of the plane as was observed in $[MesnacnacZn(\mu\text{-}H)]_2$ 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 $(i\text{-}PrN)_2C$ 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 CO_2, 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 (Fig. 2). **4** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell.

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 C_3N_2Zn ring is significantly larger than the N3–Zn1–N4 bond angle (65.7(2)°) within the four-membered CN_2Zn 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

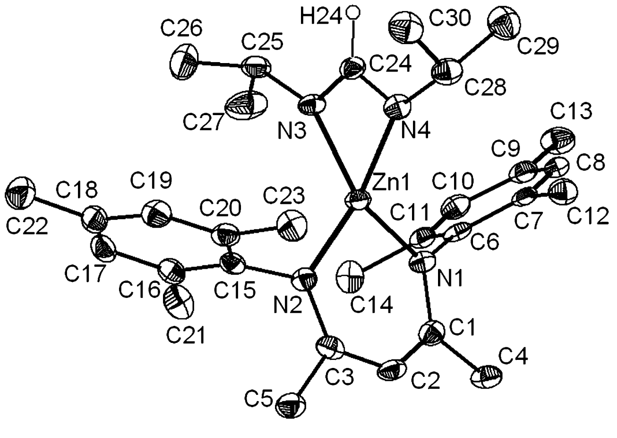

Fig. 2 Solid state structure of **4**; H atoms are omitted for clarity.

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 C_3N_2Zn 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 $[\text{DippnacnacMgH}]_2$, 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 $[\text{DippnacnacCaH(thf)}]_2$ with several unsaturated substrates, but unfortunately no reaction with CO_2, $C(NR)_2$ or RNCO were reported.[16] In contrast, Holland *et al.* very recently reported on reactions of β-diketiminato stabilized iron hydrides with both CO_2 and $C(N\textit{i}\text{-Pr})_2$. These reactions also yielded a formamidinato complex with a chelating η^2-$(NR)_2CH$ unit, whereas the formato complexes showed two bridging bidentate μ-O_2CH ligands.[17]

MesnacnacZnH was found to react with CO_2 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.

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