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Reactivity of (β-Diketiminato)zinc Hydride toward Lewis Bases, Heterocumulenes and Cyclohexene Oxide

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Dedicated to Professor Dieter Fenske on the occasion of his 70th birthday

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The reaction of LZnH (**1**) {L = Mesnacnac = [(2,4,6-$Me_3C_6H_2$)-NC(Me)$]_2$CH} with 4-(dimethylamino)pyridine (dmap) yielded the Lewis acid–base adduct LZn(H)dmap (**2**), whereas LZn(Cl)dmap (**3**) was obtained from the equimolar reaction of LZnCl with dmap. In addition, reactions of **1** with di-*tert*-butylcarbodiimide [C(N*t*Bu)$_2$] and *tert*-butyl thioisocyanate (*t*BuNCS) proceeded with insertion of the heterocumulene into the Zn–H bond and formation of [LZn(*t*BuNC(H)N*t*Bu)] (**4**) and [LZn(*t*BuNC(H)S)] (**5**), whereas **1** reacted with Me_3SiN_3 with the elimination of Me_3SiH and formation of [LZnN_3]$_2$ (**6**). Moreover, the reaction of **1** with cyclohexene oxide (CHO) occurred with ring opening and formation of [LZnOCy]$_2$ (**7**) (Cy = cyclohexyl). Complexes **2**–**7** were characterized by multinuclear NMR (^{1}H, ^{13}C) and IR spectroscopy, elemental analyses and by single-crystal X-ray diffraction (**2**, **3**, **6**, **7**).

Introduction

Zinc hydride ZnH_2 and hydridozincates such as $LiZnH_3$ and Li_2ZnH_4 are powerful reducing reagents widely used in organic and inorganic chemistry.[1] However, the rather low thermal stability of ZnH_2 and its insolubility in organic solvents prompted the interest in more suitable heteroleptic organozinc hydrides of the general type RZnH.[2] Even though simple alkylzinc hydrides also show a limited thermal stability, they can be stabilized by coordination of an additional Lewis base as was found for RZnH(pyridine) (R = Et, Ph).[3] Moreover, chelating organic ligands such as scorpionato ($Tp^{p\text{-Tol,Me}}$)[4] and β-diketiminato (Mes′nacnac = [HC{C(Me)N(2,6-$Me_2C_6H_3$)}$_2$],[5] Mesnacnac,[6] Dipnacnac[7]) as well as sterically demanding terphenyl substituents [Ar′ = C_6H_3-2,6-(C_6H_3-2,6-*i*Pr_2)$_2$][8] were found to stabilize the desired class of compounds. In addition, a tetranuclear hydridozinc alkoxide complex (HZnO*t*Bu)$_4$ was reported by Driess et al.,[9] whereas a tetranuclear amidinatozinc hydride complex {C[C(N*i*Pr)$_2$ZnH]$_4$} was synthesized in our group by the reaction of the Cl-substituted derivative {C[C(N*i*Pr)$_2$ZnCl]$_4$} with CaH_2.[10]

We recently reported on the synthesis of (β-diketiminato)zinc halide complexes,[11] which were found to be suitable starting reagents for the synthesis of the corresponding zinc hydride RZnH.[6] MesnacnacZnH (**1**) was found to readily react with heterocumulenes such as CO_2, carbodiimides and isocyanates with insertion into the Zn–H bond and subsequent formation of the corresponding formato, formamidinato and formamido complexes, respectively.[12] Moreover, its reaction with DippnacnacAl(Me)-OH proceeded with elimination of H_2 and formation of a heterodimetallic, μ-O-bridged Al–Zn oxide complex, MesnacnacZnOAl(Me)Dippnacnac.[13]

Herein, we report on the reactions of MesnacnacZnH (**1**) with the strong Lewis base 4-(dimethylamino)pyridine (dmap), which occurred with adduct formation. In addition, reactions of MesnacnacZnH with di-*tert*-butylcarbodiimide [C(N*t*Bu)$_2$], *tert*-butyl thioisocyanate (*t*BuN=C=S), trimethylsilyl azide (Me_3SiN_3) and cyclohexene oxide (CHO) are reported.

Results and Discussion

Equimolar amounts of **1** and dmap were stirred at ambient temperature for 30 min and then stored at –30 °C for 48 h, yielding colourless crystals of LZn(H)dmap (**2**) in almost quantitative yield. An analogous reaction of LZnCl with an equimolar amount of dmap yielded the Cl-substituted adduct LZn(Cl)dmap (**3**) in quantitative yield (Scheme 1).

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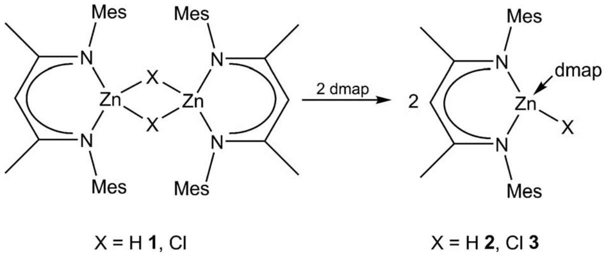


Scheme 1. Synthesis of **2** and **3**.

The ^1H NMR spectra of **2** and **3** in C_6D_6 showed the expected resonances from the β-diketiminato ligand and the dmap base in the expected 1:1 molar ratio. In addition, the resonance of the Zn–H group, which was found at δ = 4.57 ppm for **1**, was observed at δ = 4.50 ppm. The IR spectrum of **2** did not show an absorption band from the Zn–H group as was observed for **1**. Pulsed gradient spin echo (PGSE) diffusion measurements of a solution of **2** at 25 °C in [D$_8$]toluene and [D$_8$]THF yielded hydrodynamic radii of 5.66(24) and 5.65(26) Å, respectively, which are slightly larger than that observed for **1** in [D$_8$]THF [5.26(26) Å]. Moreover, a second diffusion constant was measured [3.30(05) Å], which corresponds to that of pure dmap [3.53(15) Å]. These results indicate that **1** forms an equilibrium in solution between the dmap-coordinated adduct **2**, uncomplexed dmap and LZnH (**1**). Since the ^1H NMR spectrum of **2** only shows one set of resonances of the organic ligands, the exchange between the uncomplexed and complexed form in solution is fast on the NMR time scale.

Single crystals of **2** and **3** were obtained from solutions in toluene at ambient temperature. Complex **2** (Figure 1) crystallizes together with a toluene molecule in the monoclinic space group $P2_1/n$, whereas **3** (Figure 2) crystallizes without any additional solvent molecules in the space group $P\bar{1}$. The central bond lengths and bond angles within the Mesnacnac ligands in **2** and **3** are almost identical to those previously observed for **1** as well as LZnX (X = I, OMe, OEt, O*i*Pr) and L$_2$Zn.[14] The Zn–N bonds of the Mesnacnac ligand [**2**: 2.0188(14), 2.0121(14); **3**: 1.9956(9), 2.0037(9) Å] are significantly shorter than the Zn–N$_{\text{dmap}}$ bond [**2**: 2.0979(14); **3**: 2.0468(9) Å], as was expected because of the dative character of the latter. Moreover, the increased Lewis acidity of the Zn atom in **3** compared with **2**, which results from the more electronegative chlorine substituent, significantly influences the Zn–N$_{\text{dmap}}$ bond length as was expected. The endocyclic N1–Zn1–N2 bond angle [**2**: 94.58(6)°; **3**: 97.77(3)°] is smaller than the exocyclic N1–Zn1–N3 and N2–Zn1–N3 bond angles [**2**: 98.46(5), 101.57(6)°; **3**: 105.19(4), 109.07(4)°], hence leading to a distorted tetrahedral coordination sphere at the Zn atom. In addition, the higher steric demand of the Cl atom in **3** leads to wider Zn1–N1/2-C13/22 bond angles in **3** compared with **2** [**2**: 116.39(10), 117.27(10)°; **3**: 121.68(6), 122.66(7)°].

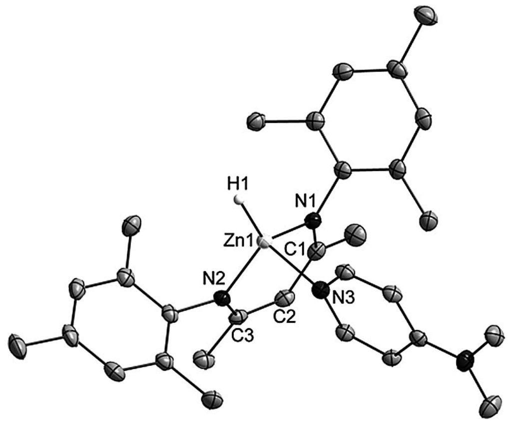


Figure 1. Solid-state structure of **2** (thermal ellipsoids are shown at 50% probability levels); H atoms are omitted for clarity except for Zn–H1. Selected bond lengths [Å] and angles [°]: Zn(1)–N(1) 2.0188(14), Zn(1)–N(2) 2.0121(14), Zn(1)–N(3) 2.0979(14), N(1)–C(1) 1.320(2), C(1)–C(2) 1.407(2), N(2)–C(3) 1.323(2), C(2)–C(3) 1.405(2); N(2)–Zn(1)–N(1) 94.58(6), N(2)–Zn(1)–N(3) 101.57(6), N(1)–Zn(1)–N(3) 98.46(5).

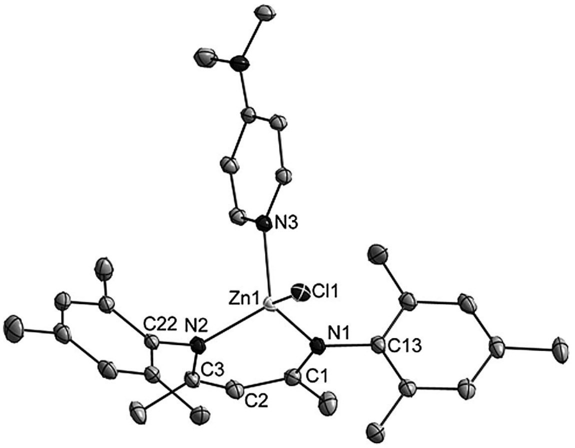
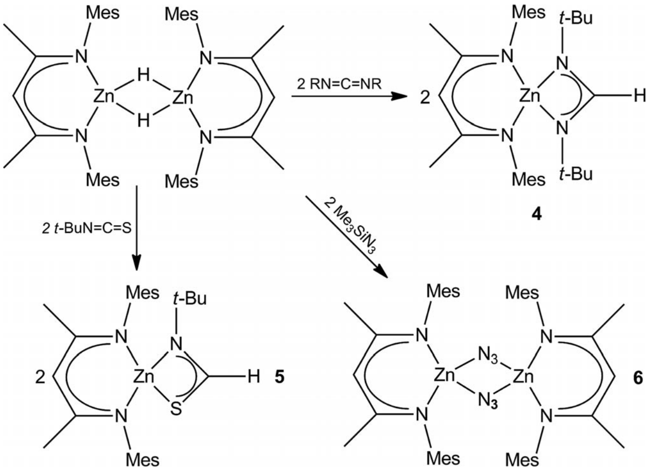


Figure 2. Solid-state structure of **3** (thermal ellipsoids are shown at 50% probability levels); H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn(1)–N(1) 1.9956(9), Zn(1)–N(2) 2.0037(9), Zn(1)–N(3) 2.0468(9), Zn(1)–Cl(1) 2.2337(3), N(1)–C(1) 1.3270(14), N(2)–C(3) 1.3258(13), C(1)–C(2) 1.4066(14), C(2)–C(3) 1.4077(14); N(1)–Zn(1)–N(2) 97.77(3), N(1)–Zn(1)–N(3) 105.19(4), N(2)–Zn(1)–N(3) 109.07(4), N(1)–Zn(1)–Cl(1) 120.74(3), N(2)–Zn(1)–Cl(1) 118.44(3), N(3)–Zn(1)–Cl(1) 104.74(3).

Because of our interest in reactions of organozinc complexes with heterocumulenes, we treated **1** with di-*tert*-butylcarbodiimide [C(N*t*Bu)$_2$] and *tert*-butyl isocyanate (*t*BuNCS). The reactions proceeded with insertion of the heterocumulene into the Zn–H bond and formation of the formamidinato {LZn[(*t*BuN)$_2$CH] (**4**)} and thioformamido {LZn[RN(S)CH] (**5**)} complexes, respectively, as was previously observed with (*i*PrN)$_2$C, *t*BuNCO and CO$_2$. In contrast, the reaction of **2** with trimethylsilyl azide (Me$_3$SiN$_3$) occurred with the elimination of Me$_3$SiH and formation of the azido-bridged dimer [LZnN$_3$]$_2$ (**6**) (Scheme 2).



Scheme 2. Synthesis of **4**–**6**.

The ^{1}H NMR spectra of **4** and **5** in C_6D_6 showed the expected resonances from the Mesnacnac ligand and the *tert*-butyl groups of the carbodiimide and thioisocyanate substituents. In addition, single resonances at $\delta = 7.30$ (**4**) and 8.40 (**5**) ppm, which are characteristic for a C–H group of a formamidinato and thioformamido backbone, respectively, clearly proved that the reactions proceeded with insertion of the heterocumulenes into the Zn–H bond. Comparable findings were previously reported for reactions of $[\text{DippnacnacMgH}]_2$ with $C(NCy)_2$[15] and DippnacnacSnH[16] as well as $[\text{DippnacnacFeH}]_2$ with $C(N\textit{i}Pr)_2$.[17] These reactions also occurred with insertion into the metal–H bond and subsequent formation of the corresponding formamidinato complexes, in which the formamidinato groups adopt an η^2-chelating binding mode. In contrast, the corresponding organocalcium hydride complex $[\text{DippnacnacCaH(thf)}]_2$ did not react with CO_2, $C(NR)_2$ or RNCO.[18]

The reaction of **1** with Me_3SiN_3 was expected to either proceed with insertion into the Zn–H bond and subsequent formation of the triazenido complex or with formation of a zinc azide complex as was recently reported by Holland et al. for the reaction of $[\text{LFeH}]_2$ with organic azides.[17] However, the ^{1}H NMR spectrum of **6** in C_6D_6 only showed the resonances from the Mesnacnac substituent, whereas the expected singlet for the trimethylsilyl group was not observed, indicating the formation of a zinc azide complex. Moreover, the IR spectrum of **6** showed two absorption bands from the asymmetric N–N–N stretching frequency $\nu_{as}(N_3)$ (2160, 2115 cm^{-1}), indicating the presence of an asymmetrically bridging μ-1,1-azido group.[19] Comparable values have been reported previously for zinc azide complexes.[20] Since the energy of the $\nu_{as}(N_3)$ band to a first approximation only depends on the degree of the symmetry of the azide group, the high energy indicates a large difference between the N_α–N_β and N_β–N_γ distances (Δd). The expected bands from the symmetric N–N–N stretching frequency (around 1300 cm^{-1}) and the N–N–N deformation mode (around 640 cm^{-1}) are overlapped by the absorption bands of the β-diketiminato group.

Single crystals of **6** were obtained from a solution in toluene at ambient temperature. Complex **6** (Figure 3) crystallizes in the triclinic space group $P\bar{1}$. The molecule is located on a centre of inversion. The C_3N_2Zn ring in **6** is almost planar (r.m.s. deviation from best plane 0.037 Å) with the Zn atoms slightly out of the plane [0.3938(12) Å deviation from the plane] as was observed in **1**, **2** and **3** as well as in $[\text{Mes'nacnacZn}(\mu\text{-H})]_2$,[5] DippnacnacZnH,[7] $\text{DippnacnacZnN(SiMe}_3)_2$[21] and $\text{DippnacnacZn}(\mu\text{-H})_2\text{-BH}_2$.[22] The C–C and C–N bond lengths as well as the N–C–C and C–C–C bond angles within the β-diketiminato backbone are nearly unchanged compared to those in LZnH (**1**), **2** and **3**. In contrast, the Zn1–N1 and Zn1–N2 bonds in **6** [1.9480(9) 1.9497(9) Å] are shorter than those in **2** [2.0188(14), 2.0121(14) Å], **3** [1.9956(9), 2.0037(9) Å] and the two polymorphs of dimeric $[\text{LZnH}]_2$ (**1**) [1.971(2), 1.975(2) Å; 2.0046(16), 2.0056(17) Å].[6] The azide group adopts an asymmetrically bridging μ-1,1 binding mode as was expected from the IR spectrum, with the Zn1–N3 and Zn1–N3#1 bond lengths differing by 0.04 Å [2.0652(9), 2.0265(9) Å]. The azide groups are almost linear [N3–N4–N5 179.30(13)°], and the N_α–N_β [1.2117(13) Å] and N_β–N_γ bond lengths [1.1391(14) Å] indicate a covalently bound azide, in accordance with the high energy of the asymmetric stretching mode in the IR spectrum (Δd = 0.0726 Å). Comparable Zn–N and N–N bond lengths were previously reported for zinc azides.[20b,20c,23] A CSD database search gave 26 zinc azides with bridging azide moieties.[24] The Zn–N_α bond length ranged from 1.946 to 2.249 Å, with a mean value of 2.089 Å. The central Zn_2N_2 four-membered ring in **6** is planar (inversion centre within the ring), and the Zn atoms adopt a distorted tetrahedral environment. The en-

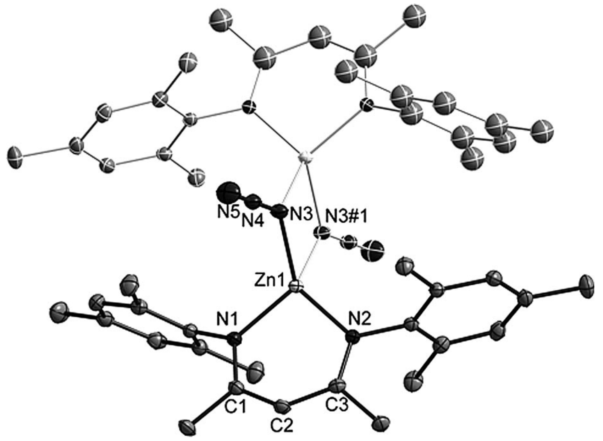
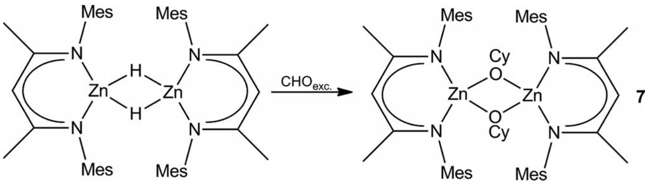


Figure 3. Solid-state structure of **6** (thermal ellipsoids are shown at 50% probability levels), asymmetric unit highlighted in dark bonds; H atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°] (#1: $-x + 2, -y + 1, -z + 1$): Zn(1)–N(1) 1.9480(9), Zn(1)–N(2) 1.9497(9), Zn(1)–N(3)#1 2.0265(9), Zn(1)–N(3) 2.0652(9), N(1)–C(1) 1.3344(13), N(2)–C(3) 1.3283(13), N(3)–N(4) 1.2117(13), N(4)–N(5) 1.1391(14), C(1)–C(2) 1.4051(15), C(2)–C(3) 1.4081(15); N(1)–Zn(1)–N(2) 99.49(4), N(1)–Zn(1)–N(3)#1 124.39(4), N(2)–Zn(1)–N(3)#1 116.04(4), N(1)–Zn(1)–N(3) 117.35(4), N(2)–Zn(1)–N(3) 119.71(4), N(3)#1-Zn(1)–N(3) 81.28(4), N(5)–N(4)–N(3) 179.30(13).

docyclic N1–Zn1–N2 bond angle [99.49(4)°] is significantly larger than the endocyclic N3–Zn1–N3#1 bond angle [81.28(4)°].

In order to reveal the mechanism for the formation of **7**, the reaction of MesnacnacZnH with an excess of Me$_3$SiN$_3$ was monitored in situ by ^{29}Si{^{1}H} NMR spectroscopy. After 2 h, a sharp resonance from the formation of Me$_3$SiH at $\delta = -16.3$ ppm was observed. In contrast, the reaction between [LFeH]$_2$ and Me$_3$SiN$_3$ proceeded with the formation of Me$_3$SiSiMe$_3$, most likely by a coupling reaction of two trimethylsilyl radicals, whereas that with AdN$_3$ (Ad = adamantyl) yielded the triazenido complex LFe(η^2-HNNNAd).[17]

Zinc complexes have found wide technical application in CO$_2$/epoxide copolymerization reactions in the last decade.[25] In order to investigate the capability of **1** to serve as a catalyst in CO$_2$/CHO (cyvlohexene oxide) copolymerization reactions, several reactions were performed. Unfortunately, **1** did not show any catalytic activity in these reactions. However, the reaction of **1** with CHO yielded a colourless crystalline solid **7**. The ^{1}H NMR spectrum of **7** in C$_6$D$_6$ showed the expected resonances from the Mesnacnac substituent and a cyclohexane group in a 1:1 molar ratio (Scheme 3).



Scheme 3. Synthesis of **7**.

Single crystals of **7** were obtained from a solution in toluene at 50 °C upon slow cooling to ambient temperature. Complex **7** (Figure 4) crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit contains two independent molecules placed on inversion centres. Complex **7** forms an asymmetrically alkoxido-bridged dimer in the solid state with a (necessarily) planar four-membered Zn$_2$O$_2$ ring and fourfold-coordinated Zn atoms, which adopt a distorted tetrahedral coordination sphere. Analogous structural motifs were observed in simple Mesnacnac zinc alkoxide complexes LZnOR (R = Me, Et, *i*Pr).[14b] The central bond lengths and bond angles within the envelope-shaped C$_3$N$_2$Zn heterocycles [r.m.s. deviation from C$_3$N$_2$ best plane: 0.039 Å, 0.0455 Å; deviation Zn from best plane: Zn1 0.633(3) Å, Zn2 0.690(3) Å] are comparable to those observed for **2** and **6** and values previously reported for (β-diketiminato)zinc complexes. In addition, the Zn–O bond lengths [2.008(2), 1.952(2), 2.000(2), 1.9447(19) Å] in **7**, which are comparable to the Zn–N bond lengths [1.994(2), 1.995(2), 1.990(2), 2.002(2) Å], are typical for dimeric zinc alkoxides. The endocyclic O–Zn–O bond angles [82.77(9), 81.87(8)°] are smaller than the N–Zn–N bond angles [95.68(10), 95.90(9)°] and comparable to the endocyclic N–Zn–N bond angle [81.28(4)°] observed for **6**. The Zn–O–Zn bond angles [97.23(9), 98.13(8)°] in **7** and the Zn–N–Zn bond angle [98.72(4)°] in **7** are also comparable.

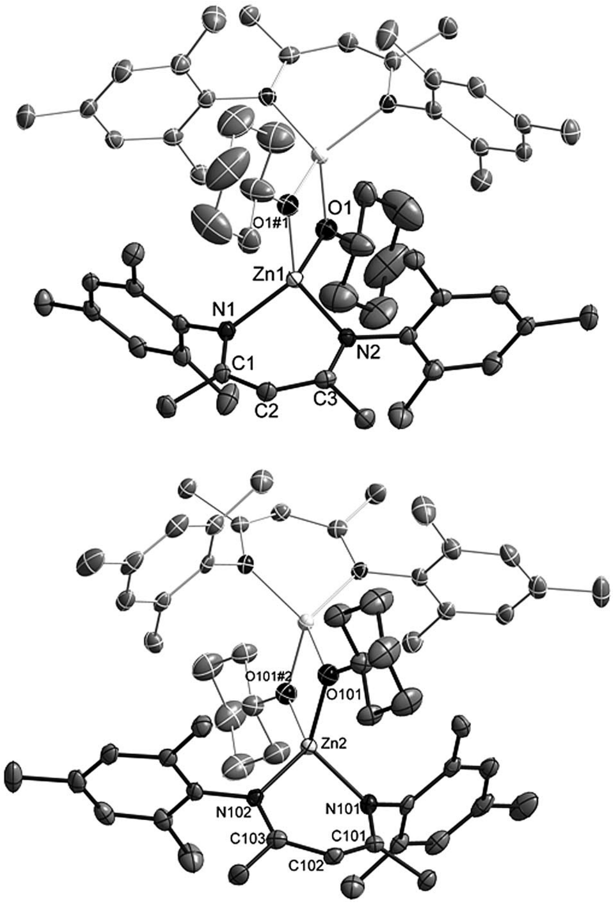


Figure 4. Solid-state structure of **7** (thermal ellipsoids are shown at 50% probability levels), asymmetric unit highlighted in dark bonds; H atoms are omitted for clarity. The arrangement of the molecules does not represent their actual arrangement in the crystal packing. Selected bond lengths [Å] and angles [°] (#1: $-x$, $-y+2$, $-z$; #2: $-x+1$, $-y+1$, $-z$): Zn(1)–O(1) 2.008(2), Zn(1)–O(1)#1 1.952(2), Zn(1)–N(1) 1.995(2), Zn(1)–N(2) 1.994(2), N(1)–C(1) 1.331(4), N(2)–C(3) 1.327(4), C(1)–C(2) 1.407(4), C(2)–C(3) 1.399(4), Zn(2)–O(101) 2.000(2), Zn(2)–O(101)#2 1.9447(19), Zn(2)–N(101) 1.990(2), Zn(2)–N(102) 2.002(2), N(101)–C(101) 1.333(3), N(102)–C(103) 1.330(4), C(101)–C(102) 1.404(4), C(102)–C(103) 1.407(4); O(1)#1–Zn(1)–N(2) 117.21(9), O(1)#1–Zn(1)–N(1) 128.37(9), N(2)–Zn(1)–N(1) 95.68(10), O(1)#1–Zn(1)–O(1) 82.77(9), N(2)–Zn(1)–O(1) 115.72(9), N(1)–Zn(1)–O(1) 118.94(9), O(101)#2–Zn(2)–N(101) 122.73(9), O(101)#2–Zn(2)–O(101) 81.87(8), N(101)–Zn(2)–O(101) 118.76(9), O(101)#2–Zn(2)–N(102) 124.02(9), N(101)–Zn(2)–N(102) 95.90(9), O(101)–Zn(2)–N(102) 115.53(9).

Conclusions

MesnacnacZnH (**1**) reacts with Lewis bases such as 4-(dimethylamino)pyridine with the formation of the corresponding Lewis acid–base adduct. Reactions with heterocumulenes and with cyclohexene oxide occurred with insertion into the Zn–H bond, whereas the reaction with Me_3SiN_3 proceeded with the elimination of trimethylsilane and subsequent formation of the azido-bridged dimer $[LZnN_3]_2$ (**6**), in which the azido groups adopt μ-1,1 bridging positions.

Experimental Section

General Procedures: All manipulations were performed under Ar. Solvents were carefully dried with Na/K and degassed prior to use. *t*BuNCS, $(tBuN)_2C$, dmap, Me_3SiN_3 and CHO were commercially available and used as received. ^1H NMR, $^{13}C\{^1H\}$ NMR and $^{29}Si\{^1H\}$ NMR spectra were recorded with a Bruker DMX 300 spectrometer and are referenced to internal C_6D_5H (^1H NMR: δ = 7.154 ppm; ^{13}C NMR: δ = 128.0 ppm) and Me_4Si (^{29}Si NMR: δ = 0.0 ppm). IR spectra were recorded with an ALPHA-T FTIR spectrometer equipped with a single-reflection ATR sampling module. Melting points were measured in sealed capillaries. Elemental analyses were performed at the Elementaranalyse-Labor of the University of Essen.

[MesnacnacZn(H)dmap] (2): A solution of dmap (60 mg, 0.5 mmol) in THF (10 mL) was added to a solution of **1** (200 mg, 0.25 mmol) in THF (20 mL) and stirred at ambient temperature for 1 h. The solution was concentrated to 5 mL and stored at ambient temperature. Colourless crystals of **2** were formed within 24 h and isolated by filtration. Yield (isolated crystals) 0.24 g (92%). M.p. 205 °C. $C_{30}H_{40}N_4Zn$ (522.03): calcd. C 69.02, H 7.72, N 10.73; found C 69.08, H 7.70, N 10.67. ^1H NMR (300 MHz, C_6D_6, 298 K): δ = 1.60 [s, 6 H, C(CH_3)], 1.93 (s, 12 H, *o*-CH_3), 2.17 (s, 6 H, *p*-CH_3), 3.00 [s, 6 H, N(CH_3)] 4.50 (s, 1 H, Zn*H*), 4.72 (s, 1 H, *CH*), 6.55 (dd, $^3J_{HH}$ = 5.1, $^4J_{HH}$ = 1.5 Hz, 2 H, *m*-Py*H*), 6.74 (s, 4 H, Ar*H*), 8.08 (dd, $^3J_{HH}$ = 5.1, $^4J_{HH}$ = 1.5 Hz, 2 H, *o*-Py*H*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = 19.1 (*o*-CH_3), 20.9 (β-CCH_3), 23.2 (*p*-CH_3), 38.1 [N(CH_3)$_2$], 93.1 (γ-*C*), 106.5 (*m*-Py), 129.8 (*m*-Ar), 131.6 (*o*-Ar), 132.5 (*p*-Ar), 147.5 (*p*-Py), 154.7 (*ipso*-Py), 168.5 (γ-*C*) ppm. ATR-IR: $\tilde{\nu}$ = 2913, 2853, 2300, 1526, 1455, 1398, 1260, 1203, 1148, 1078, 1014, 856, 767, 632, 568, 502, 435, 394 cm^{-1}.

[MesnacnacZn(Cl)dmap] (3): A solution of dmap (30 mg, 0.26 mmol) in THF (10 mL) was added to a solution of **1** (100 mg, 0.13 mmol) in THF (20 mL) and stirred at room temperature for 1 h. The solution was concentrated to 5 mL and stored at ambient temperature. All volatiles were removed under reduced pressure, and the resulting solid was dissolved in hexane (10 mL) and stored at 0 °C. Colourless crystals of **3** were formed within 24 h and isolated by filtration. Yield (isolated crystals) 0.11 g (85%). M.p. 245 °C. $C_{30}H_{39}ClN_4Zn$ (556.49): calcd. C 64.75, H 7.06, N 11.75; found C 64.60, H 7.01, N 11.63. ^1H NMR (300 MHz, C_6D_6, 298 K): δ = 1.78 [s, 6 H, C(CH_3)], 1.88 (s, 6 H, *o*-CH_3), 1.99 (s, 6 H, *o*-CH_3), 2.15 (s, 6 H, *p*-CH_3), 2.73 [s, 6 H, N(CH_3)] 4.96 (s, 1 H, *CH*), 5.61 (dd, $^3J_{HH}$ = 5.0, $^4J_{HH}$ = 1.5 Hz, 2 H, *m*-Py*H*), 6.74 (s, 2 H, Ar*H*), 6.91 (s, 2 H, Ar-*H*), 8.12 (dd, $^3J_{HH}$ = 5.0, $^4J_{HH}$ = 1.5 Hz, 2 H, *o*-Py*H*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = 19.0 (*o*-CH_3), 19.9 (*o*-CH_3), 21.3 (β-CCH_3), 23.7 (β-CCH_3), 26.2 (*p*-CH_3), 38.3 [N(CH_3)$_2$], 93.9 (γ-*C*), 106.7 (*m*-Py), 129.2 (*m*-Ar), 130.5 (*o*-Ar), 131.1 (*o*-Ar), 133.6 (*p*-Ar), 133.8 (*p*-Ar), 146.2 (*p*-Py), 149.2 (*p*-Py), 155.2 (*ipso*-Py), 167.9 (γ-*C*) ppm. ATR-IR: $\tilde{\nu}$ = 2962, 2916, 2857, 1615, 1543, 1518, 1444, 1392, 1261, 1224, 1199, 1146, 1067, 1013, 857, 813, 744, 631, 569, 534, 502 cm^{-1}.

[MesnacnacZn(*t*BuNC(H)N*t*Bu)] (4): A solution of $(tBuC)_2N$ (38 mg, 0.26 mmol) in THF (15 mL) was added to a solution of **1** (100 mg, 0.13 mmol) in THF (20 mL) and stirred at ambient temperature for 1 h. Thereafter, the solvent was evacuated in vacuo. Yield (isolated crystals) 0.13 g (95%). M.p. 230 °C. $C_{32}H_{48}N_4Zn$ (554.13): calcd. C 69.36, H 8.73, N 10.11; found C 69.21, H 8.65, N 10.02. ^1H NMR (300 MHz, [D$_8$]THF, 298 K): δ = 0.84 [s, 18 H, C(CH_3)$_3$], 1.67 [s, 6 H, C(CH_3)], 2.20 (s, 12 H, *o*-CH_3), 2.21 (s, 6 H, *p*-CH_3), 4.86 (s, 1 H, *CH*), 6.74 (s, 4 H, Ar*H*), 7.30 (HCN_2) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_8$]THF, 298 K): δ = 19.6 (*o*-CH_3), 20.9 (β-CCH_3), 23.2 (*p*-CH_3), 32.5 [C(CH_3)$_3$], 50.7 [*C*(CH_3)$_3$], 94.6 (γ-*C*), 129.4 (*m*-Ar), 132.3 (*o*-Ar), 133.8 (*p*-Ar), 168.3 (γ-*C*) ppm. ATR-IR: $\tilde{\nu}$ = 2960, 2914, 2858, 2132, 2101, 1546, 1522, 1452, 1397, 1357, 1259, 1200 1148, 1092, 1072, 1016, 857, 798, 752, 631, 598 568, 503, 470 cm^{-1}.

[MesnacnacZn(*t*BuNC(H)S)] (5): *t*BuNCS (0.04 g, 0.38 mmol) was added at ambient temperature by syringe to a solution of **1** (0.15 g, 0.19 mmol) in THF (30) and stirred for an additional 2 h. Thereafter, the solvent was evaporated in vacuo. Yield (isolated crystals) 0.16 g (84%). M.p. 175 °C. $C_{28}H_{39}N_3SZn$ (515.07): calcd. C 65.29, H 7.63, N 8.16; found C 65.36, H 7.59, N 8.09. ^1H NMR (300 MHz, C_6D_6, 298 K): δ = 0.60 [s, 9 H, C(CH_3)$_3$], 1.65 [s, 6 H, C(CH_3)], 2.12 (s, 6 H, *p*-CH_3), 2.39 (s, 12 H, *o*-CH_3), 4.90 (s, 1 H, *CH*), 6.74 (s, 4 H, Ar*H*), 8.40 (s, 1 H, NCS*H*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = 18.2 (*o*-CH_3), 19.2 (β-CCH_3), 20.8 (*p*-CH_3), 23.0 [C(CH_3)$_3$], 28.8 [*C*H(CH_3)$_2$], 94.4 (γ-*C*), 129.0 (*m*-Ar), 129.4 (*o*-Ar), 133.7 (*p*-Ar), 145.2 (*ipso*-Ar), 167.0 (*C*NS), 168.3 (γ-C) ppm. ATR-IR: $\tilde{\nu}$ = 2963, 2916, 1621, 1549, 1517, 1451, 1394, 1259, 1200, 1085, 856, 793, 567, 503, 388 cm^{-1}.

[MesnacnacZn-μ-N$_3$]$_2$ (6): A solution of **1** (0.25 g, 0.31 mmol) in THF (30 mL) was treated with Me_3SiN_3 (0.07 g) and stirred at ambient temperature for 12 h. All volatiles were removed under reduced pressure, and the resulting solid was dissolved in toluene (10 mL) and stored at –30 °C. Colourless crystals of **6** were formed within 24 h and isolated by filtration. Yield (isolated crystals) 0.26 g (96%). M.p. 180 °C. $C_{46}H_{58}N_{10}Zn_2$ (881.77):calcd. C 62.66, H 6.63, N 15.88; found C 62.49, H 6.51, N 15.76. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 1.39 [s, 6 H, C(CH_3)], 2.01 (s, 12 H, *o*-CH_3), 2.34 (s, 6 H, *p*-CH_3), 4.71 (s, 1 H, *CH*), 6.74 (s, 4 H, Ar-*H*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = 7.6 (o-CH_3), 21.4 (β-CCH_3), 22.8 (*p*-CH_3), 129.8 (*m*-Ar), 131.3 (o-Ar), 133.0 (*p*-Ar), 144.5 (*ipso*-Ar), 169.0 (γ-C) ppm. $^{29}Si\{^1H\}$ NMR (75 MHz, [D$_8$]-THF, 25 °C): δ = –16.3 (Me_3SiH), 16.1 (Me_3SiN_3) ppm. ATR-IR: $\tilde{\nu}$ = 2961, 2921, 2858, 2160, 2115, 2059, 1728, 1552, 1522, 1401, 1260, 1204, 1073, 1016, 839, 796, 745 cm^{-1}.

[MesnacnacZn-μ-OCy]$_2$ (7): A solution of **1** (0.30 g, 0.4 mmol) and CHO (0.15 g, 1.5 mmol) in toluene (20 mL) was stored at 50 °C for 3 d, yielding colourless crystals of **7**, which were isolated by filtration. Yield 0.24 g (64%). M.p. 346 °C (dec.). $C_{58}H_{80}N_4O_2Zn_2$ (996.04): calcd. C 69.94, H 8.09, N 5.62; found C 69.89, H 8.10, N 5.58. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ = 0.90–1.02 [m (br.), 2 H, H(4)], 1.13–1.26 [m (br.), 4 H, H(3/5)], 1.50 (s, 6 H, β-CCH_3), 1.72 [d (br.), 4 H, H(3/5)$_{eq}$], 2.10 (s, 12 H, *o*-CH_3), 2.36 (s, 6 H, *p*-CH_3), 3.24 [m (br.), 1 H, H(1)], 4.87 (s, 1 H, γ-*CH*), 7.00 (s, 4 H, *m*-*H*) ppm. Because of the very low solubility of **7** in C_6D_6 and [D$_8$]THF, the resonances are rather broad, in particular those of the Cy (Cy = cyclohexyl) group. As a consequence, it was not possible to distinguish between the equatorial and axial H atoms of the Cy group. Moreover, a $^{13}C\{^1H\}$ NMR spectrum could not be recorded. IR: $\tilde{\nu}$ = 2916, 2849, 1541, 1519 1477, 1452, 1394, 1365, 1259, 1228, 1199, 1148, 1076, 1019, 974, 855, 754, 728, 592, 568, 552, 504, 427 cm^{-1}.

Single-Crystal X-ray Analyses: Crystallographic data of **2**, **3**, **6** and **7**, which were collected with a Bruker AXS D8 Kappa dif-

Table 1. Crystallographic data for **2**, **3**, **6** and **7**.

	2	**3**	**6**	**7**
Empirical formula	$C_{30}H_{40}N_4Zn$	$C_{30}H_{39}ClN_4Zn$	$C_{46}H_{58}N_{10}Zn_2{\cdot}2C_7H_8$	$C_{58}H_{80}N_4O_2Zn_2$
M_r [g mol^{-1}]	522.03	556.47	1066.03	996.0
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a [Å]	7.9641(2)	8.1153(2)	9.2569(4)	13.0401(4)
b [Å]	28.7478(7)	12.4514(4)	12.0857(5)	19.4242(6)
c [Å]	12.3878(3)	16.4631(5)	13.4593(5)	20.7932(6)
a [°]	90	68.769(2)	101.770(2)	90
β [°]	96.1120(10)	80.746(1)	109.520(2)	94.3590(10)
γ [°]	90	85.334(1)	90.798(2)	90
V [Å^3]	2820.07(12)	1529.97(8)	1383.88(10)	5251.5(3)
Z	4	2	1	4
T [K]	103(1)	100(1)	100(1)	103(1)
λ [Å]	0.71073	0.71073	0.71073	0.71073
μ [mm^{-1}]	0.985	0.913	0.914	0.958
$D_{\text{calcd.}}$ [g cm^{-3}]	1.230	1.208	1.279	1.260
$2\theta_{\max}$ [°]	52.9	61.1	60.0	50.1
Crystal size [mm]	0.28 × 0.23 × 0.20	0.32 × 0.23 × 0.08	0.35 × 0.17 × 0.15	0.15 × 0.13 × 0.07
Number of reflections	33157	64274	29768	56415
Number of unique reflections	5782	9276	7943	9264
R_{int}	0.0166	0.0257	0.0193	0.0366
Number of parameters refined/restraints	320/0	325/0	325/0	595/0
R_1[a]	0.0302	0.027	0.0249	0.0407
wR_2[b]	0.0760	0.0787	0.0682	0.1034
Gof[c]	1.110	1.084	1.038	1.029
Max./min. transmission	0.75/0.67	0.75/0.67	0.75/0.63	0.75/0.67
Final max/min. $\Delta\rho$ [e Å^{-3}]	0.345/–0.290	0.515/–0.259	0.443/–0.227	1.359/–0.598

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ [for $I > 2\sigma(I)$]. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] Goodness of fit = $\{\Sigma[w(|F_o^2| - |F_c^2|)^2]/(N_{\text{observns}} - N_{\text{params}})\}^{1/2}$. $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ with $P = [F_o^2 + 2F_c^2]/3$, a and b are constants chosen by the program.

fractometer (Mo-K_α radiation, λ = 0.71073 Å), are summarized in Table 1. The structures were solved by direct methods (SHELXS-97)[26] and refined by full-matrix least-squares on F^2. Absorption corrections were performed semiempirically from equivalent reflections on the basis of multi-scans (Bruker AXS APEX2). All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97, Program for Crystal Structure Refinement)[27] on idealized geometries with the 1.2-fold (1.5-fold for methyl groups) isotropic displacement parameters of the equivalent U_{ij} values of the corresponding carbon atoms. H1 of **2** was taken from a difference Fourier map and refined freely. In the refinement of **3** several peaks of 1.6–2.8 Å^3 remained, which were attributed to hexane molecules highly disorderd over an inversion centre. Refining the peaks as carbon atoms with reduced SOF yielded R_1 = 0.0344, but no reasonable arrangement of the atoms could be refined properly. Consequently, the final refinement was performed with solvent-free reflection data taken from PLATON/squeeze.[28] CCDC-872730 (**2**), CCDC-872731 (**3**), CCDC-872733 (**6**), CCDC-872732 (**7**) 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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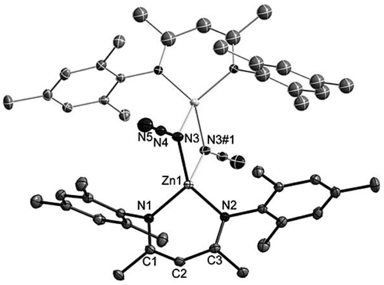
(β-Diketiminato)zinc Hydride

MesnacnacZnH {Mesnacnac = [(2,4,6-$Me_3C_6H_2$)NC(Me)$]_2$CH} reacts with 4-(dimethylamino)pyridine (dmap) upon adduct formation, whereas reactions with (tBuN)$_2$C, tBuNCS and CHO proceed with insertion into the Zn–H bond. In contrast, Me_3SiN_3 was found to react with MesnacnacZnH with the formation of MesnacnacZn(N_3), which forms an azido-bridged dimer in the solid state.



Reactivity of (β-Diketiminato)zinc Hydride toward Lewis Bases, Heterocumulenes and Cyclohexene Oxide

Keywords: N ligands / Zinc / Insertion / Cumulenes / Lewis acids