Convenient synthesis and crystal structure of a monomeric zinc hydride complex with a three-coordinate metal center†

Jan Spielmann, Dirk Piesik, Bernd Wittkamp, Georg Jansen and Sjoerd Harder*

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Convenient syntheses for a β-diketiminate zinc hydride complex, that crystallizes as a monomer with a three-coordinate Zn atom, have been developed.

Despite the increasing interest in the use of zinc hydride complexes as reducing agents, models for zinc–enzymes or as possible precursors in material chemistry,[1] only a few well-defined examples are known. Recently, the first β-diketiminate zinc hydride,[2] $[(\text{Mes-nacnac})\text{ZnH}]_2$ (Mes-nacnac = $\text{CH}\{(\text{CMe})(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N})\}_2$) was prepared by reacting the corresponding zinc fluoride complex with Et_3SiH, a method that was earlier introduced to prepare the scorpionate complex $\text{Tp}^{p\text{-Tol,Me}}\text{ZnH}$.[3]

Our recent studies on the mechanism of hydrogen release in alkaline-earth metal amidoborane complexes,[4] directed our interest to investigations of related zinc amidoborane complexes. In one of our synthetic approaches we have reacted the potassium amidoborane, $\text{KN}(i\text{Pr})\text{HBH}_3$, which was obtained by deprotonation of $\text{H}_2\text{N}(i\text{Pr})\text{BH}_3$ with $\text{KN}(\text{SiMe}_3)_2$, with (DIPP-nacnac)ZnCl (DIPP-nacnac = $\text{CH}\{(\text{CMe})(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\}_2$) in THF (Scheme 1). This simple salt metathesis reaction, however, did not give the expected zinc amidoborane but instead the zinc hydride (DIPP-nacnac)ZnH could be isolated in good crystalline yield (71%).‡ Clean formation of this metal hydride is likely to proceed through β-hydride elimination and formation of various oligomeric "BN"-species (many signals could be seen in the NMR spectra).

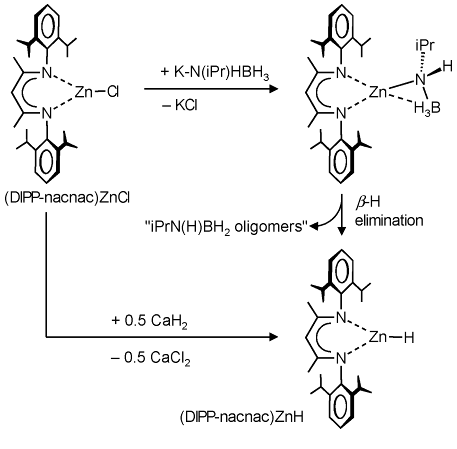
The crystal structure of (DIPP-nacnac)ZnH§ revealed a monomeric complex of approximate C_{2v} symmetry (Fig. 1). The hydride hydrogen atom has been located and was isotropically refined. The Zn–H bond distance of 1.46(2) Å is one of the shortest reported so far and equals that of 1.46(5) Å in $[(\text{Me}_3\text{PN})\text{ZnH}]_4$, a cubane-like tetramer with bridging N centers and terminal hydride functionalities.[5]

As the sum of the valence angles at the three-coordinate Zn center equals 360.0(7)°, the arrangement of the ligands around this metal center is perfectly planar. This trigonal coordination sphere is only distorted by the acute N1–Zn–N2 angle of 97.33(4)°, which is dictated by the chelating DIPP-nacnac ligand.

At first sight, the monomeric nature of (DIPP-nacnac)ZnH is surprising. The closely related (Mes-nacnac)ZnH crystallized as a dimer with bridging hydride atoms (Zn–H = 1.766 Å).[2] The ionic radius of Zn^{2+} (four-fold coordination: 0.74 Å) is slightly larger than that for Mg^{2+} (four-fold coordination: 0.71 Å).[6] However, the complex (DIPP-nacnac)MgH is a strongly bound dimer with a Mg–H bond distance of 1.96(3) Å,[7] *i.e.* considerably longer than the Zn–H bond distance of 1.766 Å in $[(\text{Mes-nacnac})\text{ZnH}]_2$.[2] The magnesium hydride complex crystallizes even in the presence of THF as a dimeric solvate $[(\text{DIPP-nacnac})\text{MgH}\cdot\text{THF}]_2$.[7] This difference in structural behaviour is undoubtedly related to the significantly more covalent character of Zn complexes. The covalent radius for Zn (1.22 Å) is indeed smaller than that for Mg (1.41 Å).[8] A comparison of the related complexes $(\text{DIPP-nacnac})\text{MgN}(\text{SiMe}_3)_2$ and $(\text{DIPP-nacnac})\text{ZnN}(\text{SiMe}_3)_2$, which crystallize isomorphously,[9] shows that the bonds to Mg are on average 4.5% longer than those to Zn.

The crystal structure of monomeric (DIPP-nacnac)ZnH is reproduced well by DFT-calculations on the B97-D/TZV2P-level (Zn–N 1.996 Å; Zn–H 1.548 Å). At the same level of theory, however, a minimum was also found for the dimer $[(\text{DIPP-nacnac})\text{ZnH}]_2$ (Zn–N 2.034 Å; Zn–H 1.784 Å) which is even more stable than the monomer by 9.7 kcal mol^{-1} (corrected for ZPE). Similarly, calculations on $[(\text{Mes-nacnac})\text{ZnH}]_2$ reproduce its dimeric crystal structure (Zn–N 1.994 Å; Zn–H 1.768 Å). In this case, the slightly reduced ligand size results in a considerable preference for the dimer (19.8 kcal mol^{-1}).

As the calculation study indicates that, under gas phase conditions at 0 K, dimeric $[(\text{DIPP-nacnac})\text{ZnH}]_2$ is preferred over the monomeric species, we investigated the complex dissolved in toluene-d_8 with low-temperature ^{1}H NMR spectroscopy. Gradually cooling the sample to −80 °C did



Scheme 1

Fachbereich Chemie, Universitätsstrasse 5, 45117 Essen, Germany. E-mail: sjoerd.harder@uni-due.de; Fax: +49 201 1832621; Tel: +49 201 1833684

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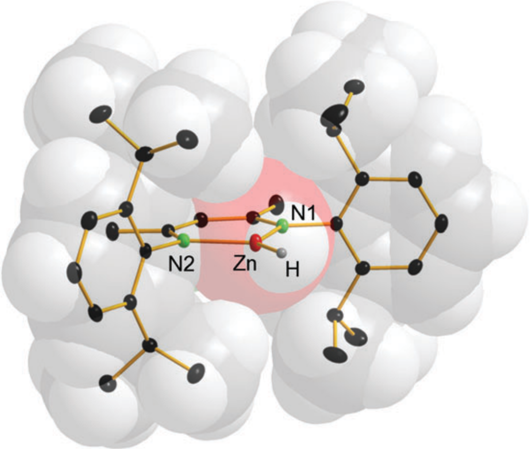

Fig. 1 The crystal structure of (DIPP-nacnac)ZnH (ORTEP plot with 50% probability; overlay with van der Waals radii). Selected bond distances (Å) and angles (°): Zn–N1 1.950(1); Zn–N2 1.952(1); Zn–H 1.46(2); N1–Zn–N2 97.33(4); N1–Zn–H 131.5(7); N2–Zn–H 131.2(7).

not give rise to the appearance of another set of signals that could be assigned to a dimeric species. However, a significant shift of the signals for the hydride ($\Delta\delta = 0.31$ ppm) and the *i*Pr-methyl group directed towards the hydride ($\Delta\delta = 0.09$ ppm) was observed, *i.e.* those groups most affected by possible dimer formation (all other signals hardly shifted). This indicates a possible monomer–dimer equilibrium which at higher temperatures shifts to the monomer side on account of entropy. From pulsed gradient spin echo (PGSE) diffusion measurements[10] on a solution of (DIPP-nacnac)ZnH in toluene-d_8 at 20 °C, a hydrodynamic radius of 5.2(1) Å could be deduced. As measurements on monomeric (DIPP-nacnac)ZnMe gave an equal hydrodynamic radius, (DIPP-nacnac)ZnH in toluene at 20 °C is largely monomeric.

(DIPP-nacnac)ZnH is the first monomeric zinc hydride complex with a three-coordinate Zn center. All other complexes with a terminal Zn–H functionality show four-fold coordination at Zn and the only other zinc hydride complex with a three-coordinate Zn center is a dimer with bridging hydride atoms: [(2,6-DIPP-phenyl)ZnH]$_2$.[11]

The monomeric nature of (DIPP-nacnac)ZnH and its low metal coordination number make this complex an interesting precursor in reduction chemistry, catalysis, material chemistry or for mimicking zinc–enzyme processes. Therefore we developed an even more attractive synthetic route for this potentially useful complex.

Salt metathesis between the well-accessible (DIPP-nacnac)-ZnCl and a metal hydride would be preferable over both the amidoborane, and the zinc fluoride/silane routes.[2,3] In such syntheses highly reactive metal hydrides like NaH or KH are usually used. In recent years, however, there has been an increased interest in implementing cheaper, more inert, metal hydrides like LiH and CaH$_2$. Both hydrides show extremely high lattice energies and do not react with a large variety of functional groups (hence the application of CaH$_2$ as a versatile drying agent for many organic liquids). Other operational advantages arise from their easy handling and safe storage without deterioration. Noyori *et al.* discovered that the combination of basically inert LiH and catalytic amounts of ZnCl$_2$ can be used as a reagent in reduction chemistry.[12] Additionally, a recent report appeared on the use of the CaH$_2$–ZnBr$_2$ combination in the reduction of imines.[13] This prompted us to react a solution of (DIPP-nacnac)ZnCl in THF with commercially available CaH$_2$, the cheapest available metal hydride. We found quantitative conversion of the chloride to (DIPP-nacnac)ZnH (Scheme 1) and the raw product is essentially pure.

The convenient synthesis and the good accessibility of the hydride functionality in (DIPP-nacnac)ZnH encourages further exploration of this complex.

Notes and references

‡ For (DIPP-nacnac)ZnH: mp 211 °C. Anal. Calc. (Found) for $C_{29}H_{42}N_2Zn$: C 71.96 (71.89); H 8.75 (8.94)%. ^{1}H NMR (C_6D_6, 300 MHz): δ 1.11 (d, $^3J_{(H,H)} = 6.9$ Hz, 12H, *i*Pr), 1.27 (d, $^3J_{(H,H)} = 6.9$ Hz, 12H, *i*Pr), 1.68 (s, 6H, Me backbone), 3.18 (sept, $^3J_{(H,H)} = 6.9$ Hz, 4H, *i*Pr), 4.39 (s, 1H, ZnH), 5.02 (s, 1H, H backbone), 7.12 (m, 6H, aryl). ^{13}C NMR (C_6D_6, 75 MHz): 23.2 (*i*Pr-Me), 23.5 (Me backbone), 24.8 (*i*Pr-Me), 28.4 (*i*Pr-CH), 96.0 (*C*H backbone), 123.9 (aryl), 126.2 (aryl), 141.8 (aryl), 144.6 (aryl), 168.1 (*C*Me backbone).

§ Crystal data for (DIPP-nacnac)ZnH: $C_{29}H_{42}N_2Zn$, $M = 484.04$, monoclinic, space group $P2_1/n$, $a = 12.639(3)$, $b = 15.856(3)$, $c = 14.020(3)$ Å, $\beta = 105.528(10)°$, $U = 2707.1(10)$ Å^3, $Z = 4$, $D_c = 1.188$ g cm^{-3}, $F(000) = 1040$, μ(Mo Kα) = 0.925 mm^{-1}, $3.8 \leq 2\theta \leq 61.0°$, 50 265 reflections measured, 7976 unique ($R_{\text{int}} = 0.045$) were used in all calculations, $R_1 = 0.0278$ [$I > 2\sigma(I)$] and w$R_2 = 0.0777$ (all data); max/min. residual electron density: 0.41/−0.35.

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