Zinc Hydride

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Molecular Zinc Dihydride Stabilized by N-Heterocyclic Carbenes[**]

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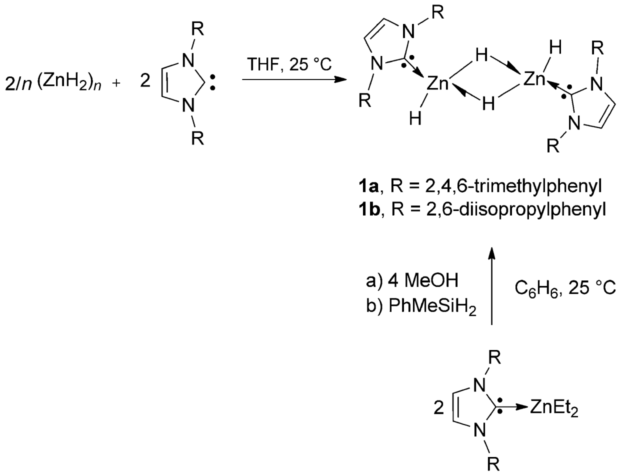
Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 65th birthday

Zinc dihydride, known for over 60 years,[1] has never been structurally characterized, possibly because of its polymeric nature and thermal instability. Gas-phase and matrix-isolation studies show that molecular zinc dihydride is linear with a d^{10} metal center bonded to two hydrido ligands.[2] In the condensed phase, however, only complexes with terminal or bridging zinc hydride units stabilized by mono(anionic) ligands such as nacnac,[3a–c] tris(4,4-dimethyl-2-oxazolinyl)-phenylborate,[3d] tris(2-pyridylthio)methyl,[3e] tris(3-*tert*-butylpyrazolyl)hydroborate,[3f,g] and other ligands[3h–j] have been reported. More recently, zinc hydride complexes have drawn attention as non-precious-metal catalysts for the coupling of silanes with protic substrates such as alcohols[4] as well as for the homogeneous hydrosilylation of carbon dioxide.[4b] Ill-defined compounds of the general type RZnH (R = H, alkyl) have been used in the hydrozincation reaction of olefins.[5] Despite the pronounced Lewis acidity of the zinc center, simple Lewis base adducts of monomeric zinc dihydride of composition $[ZnH_2(L)_2]$ with tetrahedral coordination and a filled valence shell have never been achieved. We report herein that zinc dihydride $(ZnH_2)_n$[1] can be stabilized as an N-heterocyclic carbene (NHC)[6] adduct and isolated as a thermally robust compound of composition $[\{ZnH_2(L)\}_2]$ (**1a**: L = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, IMes; **1b**: L = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, IPr).

When the carbenes IMes or IPr were added to polymeric $(ZnH_2)_n$ suspended in THF, the mixture dissolved within minutes to give a clear solution and after workup colorless crystals of **1a** or **1b** were isolated in 70% yield (Scheme 1). Both hydride compounds are soluble in aromatic solvents and THF and stable at 25 °C in benzene solution for days. The isolated crystals of **1a** and **1b** decompose only at temperatures above 170 and 195 °C, respectively, and can be stored for several months at −35 °C. Other Lewis bases such as PMe_3 and (4-dimethylamino)pyridine (DMAP) do not form ZnH_2 adducts. Both **1a** and **1b** can also be synthesized by the reaction of $[Zn(OMe)_2(L)]$, prepared by methanolysis of $[ZnEt_2(L)]$,[7] with $PhMeSiH_2$ (Scheme 1) and isolated in yields of over 80%.



Scheme 1. Synthesis of the NHC-stabilized zinc dihydrides **1a** and **b**.

Crystals suitable for X-ray diffraction were obtained from benzene/pentane solution at 25 °C. Both compounds exist as dimers with a Zn_2H_4 core. Compound **1b** shows crystallographic C_i symmetry (Figure 1). Each zinc center is tetrahedrally coordinated by one IPr ligand and one terminal and two bridging hydrido ligands. *trans* Coordination of the NHC ligands minimizes steric interactions. The Zn⋯Zn distances in **1a** (2.4906(6) Å) and **1b** (2.4980(4) Å) are slightly longer than in $[\{2,6\text{-}(2,6\text{-}iPr_2C_6H_3)_2C_6H_3\}Zn(\mu\text{-}H)_2Zn\{2,6\text{-}(2,6\text{-}iPr_2C_6H_3)_2\text{-}C_6H_3\}]$.[8]

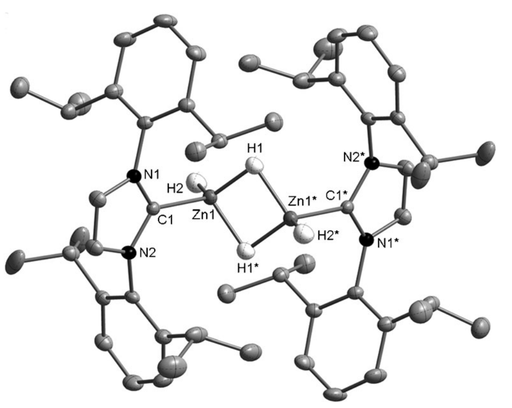


Figure 1. Molecular structure of **1b** in the solid state. Thermal ellipsoids are shown at the 50% probability level; hydrogen atoms are omitted except those of the Zn_2H_4 core.

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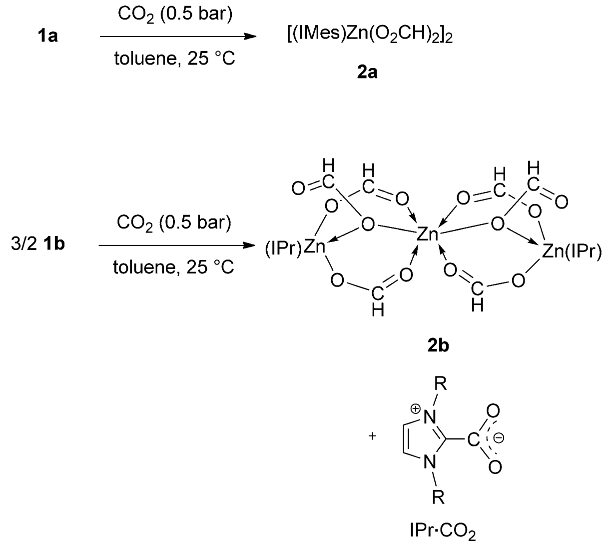
As expected, the terminal Zn−H bonds of 1.47(4) and 1.56(4) Å (**1a**) as well as 1.53(2) Å (**1b**) are shorter than the Zn−μ-H bonds (1.71(4)–1.81(3) Å in **1a** and 1.73(2) Å in **1b**). The $Zn-C_{NHC}$ bond lengths (**1a**: 2.052(3) and 2.054(3) Å; **1b**: 2.0573(17) Å) are in the range reported for other NHC adducts of zinc(II).[7b,9]

^1H NMR spectra of **1** exhibit only one set of signals for the NHC and hydrido ligands in agreement with C_2 symmetry in solution. Two singlets for the hydrido ligands in **1b** are observed at 2.23 and 3.57 ppm at 23 °C in C_6D_6. These signals are not observed for compound **1a** above 0 °C in $[D_8]$toluene. Below 0 °C two distinct signals are detected (2.39 and 3.97 ppm at −60 °C) for the bridging and terminal hydrides (see the Supporting Information). Coalescence of both hydride signals above +40 °C leads to a new signal (2.83 ppm at +80 °C). This fluxional behavior may be caused by an intramolecular dynamic exchange process or may also be explained by the dissociation into monomeric species. DOSY NMR experiments[10] in C_6D_6 at 25 °C show a smaller diffusion coefficient for **1a** than for the monomeric $[(IMes)ZnEt_2]$, consistent with the assumption that **1a** is dimeric in solution. In the $^{13}C\{^1H\}$ NMR spectra, the carbene carbon resonances are found at 188.48 (**1a**) and 191.97 ppm (**1b**), which agree with those in previously reported NHC compounds of zinc.[7,9] The IR spectra show an intense $\nu_{Zn\text{-}H}$ absorption at 1639 cm^{-1} for **1a** and at 1625 cm^{-1} for **1b**. The corresponding deuteride isotopomers show $\nu_{Zn\text{-}D}$ absorptions at 1177 cm^{-1} for **1a** and 1171 cm^{-1} for **1b**. The $\nu_{Zn\text{-}\mu\text{-}H}$ absorptions for **1** could not be reliably assigned due to overlap with the aromatic stretching modes of the NHC ligands.[8]

Calculations on **1a** were carried out at the DFT level using the hybrid functional B3PW91. The optimized geometry agrees well with the experimental one (Zn···Zn distance 2.496 Å versus 2.4906(6) Å) and is obviously suitable to describe the $\{Zn(\mu\text{-}H)_2Zn\}$ core. In spite of the d^{10} configuration, a Zn···Zn interaction was indicated. To further investigate this, we carried out an NBO analysis. The Wiberg bond indices (WBI) showed pronounced Zn−H interactions (WBI = 0.42) along with a Zn−Zn interaction (WBI = 0.30). However, more detailed investigations at the NBO level reveal that the latter contribution results from the three-center interactions within the $\{Zn(\mu\text{-}H)_2Zn\}$ core and no significant donor–acceptor interaction between the two zinc atoms could be located, even at the second-order perturbation level. Therefore, the dimeric species is stabilized by two three-center bonding interactions rather than by any significant d^{10}–d^{10} interaction. In line with the theoretical calculations, comparison of the Zn···Zn distance in **1a** (2.4906(6) Å) with the reported Zn–Zn bonded compounds RZn−ZnR (R = $\{2,6\text{-}(2,6\text{-}i\text{Pr}_2C_6H_3)_2C_6H_3\}$ or C_5Me_5) (2.30–2.36 Å)[8,11] excludes a Zn−Zn bond in **1a**.

Compound **1a** did not react with D_2 (1 bar) in C_6D_6 at 50 °C over a period of several days. Compound **1b** did not show any H–D exchange either, but underwent partial decomposition to IPr and metallic zinc under evolution of H_2. The NHC ligands are labile in solution; a mixture of **1a** and **1b** in C_6D_6 at 23 °C shows new signals at 2.25 and 3.64 ppm in the ^1H NMR spectrum for the hydrido ligands in $[(ZnH_2)_2(IMes)(IPr)]$. This compound is also detected in the $^{13}C\{^1H\}$ NMR spectrum with signals for the carbene carbon atoms at 191.60 and 189.34 ppm. While **1a** did not react with IPr, **1b** readily underwent substitution with one equivalent of IMes to give $[(ZnH_2)_2(IMes)(IPr)]$ and with two equivalents of IMes to give **1a** along with free IPr.

The molecular hydrides **1** react with CO_2 (0.5 bar) at 25 °C to give formate species **2** in 59–79 % yield (based on NHCs) (Scheme 2). ^1H NMR analysis shows that all hydrido ligands have reacted within 2 h. Compound **1a** gave diformate **2a** and ESI mass spectrometric analysis suggests that this compound is dimeric (see the Supporting Information). The formate unit is characterized with one singlet at 7.99 ppm in the ^1H NMR spectrum and with one signal at 166.94 ppm in the $^{13}C\{^1H\}$ NMR spectrum. These chemical shifts are similar to those reported for $[\{(Mesnacnac)Zn(O_2CH)\}_2]$.[12] The integration ratio of formate to NHC ligands of 2:1 agrees with the formulation of the molecular structure. From the reaction of **1b** and CO_2, a formate was isolated which shows a ^1H NMR signal at 8.05 ppm and a $^{13}C\{^1H\}$ NMR signal at 167.71 ppm. Although these values are close to those found for **2a**, the 3:1 integration ratio for formate to NHC ligands indicates a different structure for **2b**.



Scheme 2. Reactions of **1a** and **1b** with CO_2.

Crystals of composition $\mathbf{2b}\cdot 2\,C_6H_5Cl\cdot C_6H_{14}$ suitable for molecular structure determination were obtained from hexane and chlorobenzene at 25 °C. Compound **2b** was found to be trinuclear with two different bridging modes μ_2-OCH(=O)-κO and μ_2-O_2CH-κO,O′ for the formate ligands (Figure 2). Similar coordination modes have been previously reported for zinc carboxylate compounds.[13] The central zinc atom Zn2 is octahedrally coordinated by six formate units, whereas the zinc atoms Zn1 and Zn3 are tetrahedrally coordinated by three formates and one IPr ligand. The two η^1-OCH(=O) ligands are in a *cis* arrangement; the coordination number of six leads to slightly longer Zn−O distances for Zn2 (average 2.09 Å, ranging from 2.046(4) to 2.137(4) Å)

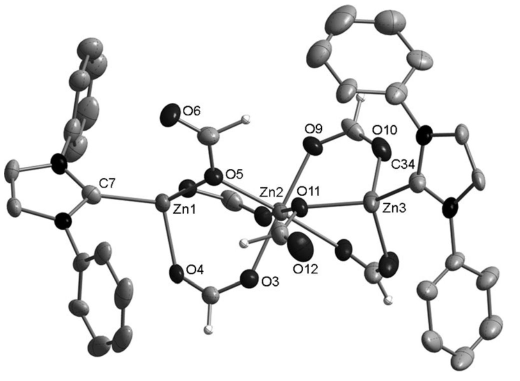


Figure 2. Molecular structure of **2b** in the solid state. Thermal ellipsoids are shown at the 50% probability level; isopropyl groups and hydrogen atoms except for those of the formate moieties are omitted for clarity.

than for Zn1 or Zn3 (average 1.97 Å ranging from 1.952(4) to 1.984(4) Å). No bonding interaction of the CH(=O) moieties with the zinc centers was observed (Zn1–O6 3.141(5); Zn3–O12 2.941(5) Å). The C–O bond lengths within these η^1-formate ligands indicate localized single and double bonds (1.310(7), 1.300(7) and 1.202(8), 1.210(8) Å, respectively). The intermetallic Zn···Zn distances (Zn1···Zn2 3.3231(10), Zn2···Zn3 3.3312(11) Å) are slightly longer than those in structurally similar compounds [Zn_3(crotonate)$_6$(quinoline)$_2$][13a] (3.26 Å) and [$Zn_2(bpy)_2(MeCO_2)_3$]$^+$ (3.275(2) Å).[13b]

The ^1H NMR spectra of **2b** in [D_8]toluene show only one formate resonance at temperatures down to −80 °C most likely due to fast exchange between the two bridging modes.

As pure ZnH_2 was reported to be inert toward CO_2,[14] it is most likely that **1b** first forms [(IPr)Zn($O_2CH)_2$] analogous to **2a** by means of hydride transfer to CO_2. The formation of **2b** is the result of the dissociation of one IPr ligand. The released IPr is trapped by CO_2 to give the adduct IPr•CO_2 as shown by ^1H and $^{13}C\{^1H\}$ NMR spectral analysis; this compound was described previously in the literature.[15]

Compounds **1** catalyze the methanolysis of silanes $PhSiH_3$ and $PhMeSiH_2$ (0.5 mol %, 25 °C). ^1H NMR spectroscopic analysis showed that $PhSiH_3$ and $PhMeSiH_2$ were completely and selectively converted into $PhSi(OMe)_3$ and $PhMeSi(OMe)_2$ within 10 min (Scheme 3). No traces of differently substituted products were observed. These preliminary results indicate that compounds **1** have higher catalytic activity than [tris(4,4-dimethyl-2-oxazolinyl)phenylborate]zinc hydride (10 mol %, 45 °C, 10 h).[4a] Compounds **1** show activity comparable with that reported for [(κ^3-Tptm)ZnH].[4b]

$$PhSiH_3 + 3\,MeOH \xrightarrow[C_6D_6,\ 25\,°C \atop 10\ min]{0.5\ mol\%\ \mathbf{1}} PhSi(OMe)_3 + 3\,H_2$$

$$PhMeSiH_2 + 2\,MeOH \xrightarrow[C_6D_6,\ 25\,°C \atop 10\ min]{0.5\ mol\%\ \mathbf{1}} PhMeSi(OMe)_2 + 2\,H_2$$

Scheme 3. Catalytic methanolysis of silanes.

In conclusion, we have isolated and fully characterized[16] the first molecular zinc dihydrides as NHC adducts which are thermally robust and amenable to reactivity studies in solution. Reaction with CO_2 gave zinc formates which are relevant as intermediate in the ZnO-catalyzed synthesis of methanol.[17] Compounds **1** show excellent catalytic activity in the methanolysis of silanes.

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[16] CCDC 916779 (**1a**), 916780 (**1b**), and 916781 (**2b**) 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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