Cluster Compounds

DOI: 10.1002/ange.200804224

An Organozinc Hydride Cluster: An Encapsulated Tetrahydrozincate?**

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Organometallic compounds of zinc have been known since the work of Edward Frankland in the 1840s.[1] Despite his prediction that zinc hydride "may be obtained", it was not until about 100 years later that the first reports appeared.[2] Although there are now several reliable synthetic methods for the preparation of ZnH_2,[3] the nature of this white solid remains unknown; its low volatility and solubility suggest a polymeric structure.

Two important classes of compound containing zinc–hydrogen bonds emerged from this early work. Firstly, anionic zinc hydride species were identified in solution by spectroscopic techniques,[4] and isolated in partially characterized solids $M_2[ZnH_4]$ (M = Li, Na, K).[5] They have recently been investigated as reagents for selective reduction[6] and deprotometallation.[7] Bridging hydride species were found in crystal structure determinations of the hydridoalkylzincates $Na_2[Zn_2Et_4(\mu\text{-}H)_2]$ and $Na_3[Zn_2iPr_6(\mu\text{-}H)]$ (**1**, Figure 1).[8] Neutron diffraction studies on deuterium-substituted zincates $M_2[ZnD_4]$ and $M_3[ZnD_4(D)]$ (M = K, Rb, Cs), revealed the presence of $[ZnD_4]^{2-}$ dianions, with terminal Zn–D bond lengths in the range 1.632–1.704 Å.[9] Given current interest in related tetrahydroborates and -aluminates for the chemical storage of hydrogen,[10] further work on the chemistry of tetrahydrozincates may be expected in the future.

The second type of zinc hydride species are neutral and typically incorporate bulky ligands to limit aggregation (see Figure 1, **2**–**4**). Examples of structurally characterized compounds include monomeric pyrazolylhydroborates of the type [Zn(L)(H)] (**2**),[11] the dimeric diamino compound [{Zn(μ-L)(H)}$_2$] (**3a**),[12] hydride-bridged compounds [{Zn(L)(μ-H)}$_2$] (**3b**,**c**),[13,14] and cubanes [{Zn(L)H}$_{4-n}${Li(L)}$_n$] (**4**, n = 0–3).[15] Although current applications of these compounds are somewhat limited, hydridozinc alkoxide cubane clusters have recently been used to promote the hydrogenation of CO_2.[16]

We have recently described a new derivative of tris(trimethylsilyl)methane incorporating a bicyclic guanidine unit based on 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, hppH.[17] The neutral compound, RH (R = C(SiMe$_3$)$_2$(SiMe$_2$hpp)) is readily converted into the organolithium reagent RLi, which we have used as a ligand-transfer reagent in the synthesis of the alkylzinc bromide ZnRBr (**5**). Compound **5** is a member of a series of compounds [(Zn{C(SiMe$_3$)$_2$(SiMe$_2$L)}Br)$_2$] (L = NMe$_2$,[18] 2-pyridyl,[19] or hpp) in which the metallacycle increases sequentially from a four- to a five- to a six-membered ring (Figure 2).

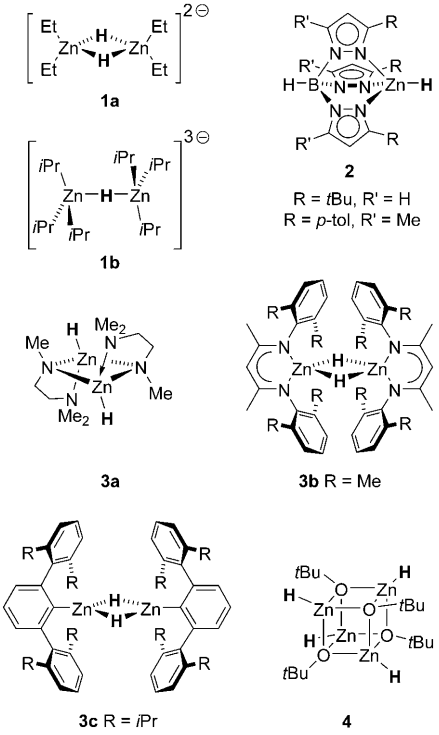

Figure 1. Zinc hydride species

In the solid state, all of these compounds are μ,μ′-dihalobridged dimers with distorted tetrahedrally coordinated metals and chelating κC,κN-alkyl ligands (Figure 2). No significant variation in Zn–C bond length occurs. In contrast, the Zn–N bond lengths decrease in the series NMe$_2$ > 2-pyridyl > hpp, reflecting both the greater strain in 4-membered rings, compared with 5- or 6-membered rings, and the greater basicity of the imino nitrogen in hpp than in the pyridyl ring. These data, as well as related data from a range of compounds of the form RML$_n$, [20] lead us to conclude that the bidentate ligand R is both more bulky and more tilted towards nitrogen ligation, than those previously studied.

The reaction between [RZnBr] **5** and an excess of NaH, following Power's procedure,[14] afforded colorless crystals **6**. The ^{1}H NMR spectrum displayed a singlet at δ = 5.10 ppm, indicating that **6** contained a zinc hydride species. This singlet

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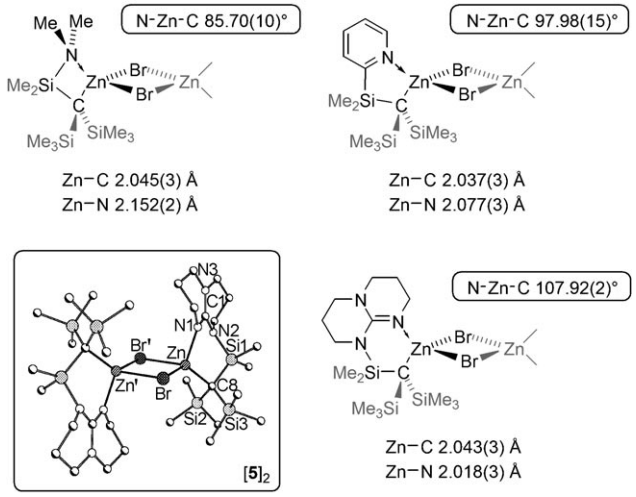


Figure 2. Molecular structure of **5**, and comparison of key bond lengths and angles in related [{Zn(C{SiMe$_3$}$_2${SiMe$_2$L})Br}$_2$] dimers. Hydrogen atoms are omitted to aid clarity. Selected bond lengths [Å] and angles [°] in [**5**]$_2$: Zn–Br 2.5224(5), Zn–Br′ 2.5963(5), C1–N1 1.323(4), C1–N2 1.371(4), C1–N3 1.360(4); N1-Zn-C8 107.92(12), N1-Zn-Br 108.52(8), C8-Zn-Br 124.88(9), N1-Zn-Br′ 101.74(8), C8-Zn-Br′ 123.84(10), Br-Zn-Br′ 86.659(16), Zn-Br-Zn′ 93.341(16).

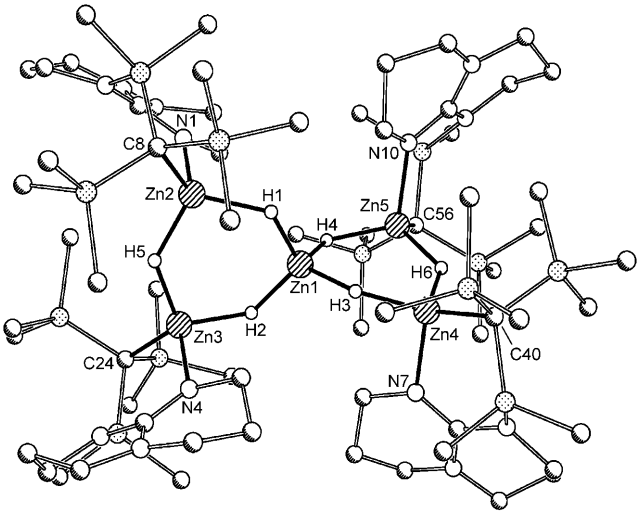
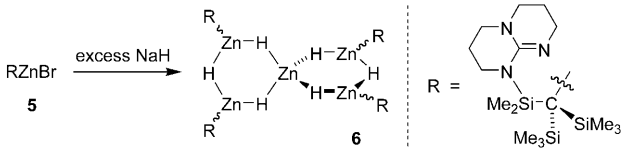


Figure 3. Molecular structure of [ZnH$_4$(RZn(H)ZnR)$_2$] **6**. Some hydrogen atoms are omitted to aid clarity. Selected bond lengths [Å]: Zn2–C8 2.083(5), Zn2–N1 2.065(4), Zn3–C24 2.075(5), Zn3–N4 2.065(4), Zn4–C40 2.074(5), Zn4–N7 2.059(4), Zn5–C56 2.067(5), Zn5–N10 2.059(4).

broadened as the sample in [D$_8$]toluene was cooled to −80 °C, but there was no further resolution. Although no clear Zn–H stretches were discernible in the IR spectrum, the appearance of a broad underlying feature centered at approximately 1500 cm^{-1}, in the region associated with Zn–(μ-H)–Zn stretching frequencies,[4,21] was evident from comparison with the corresponding spectrum of **5**.[22] The EI mass spectrum showed peaks corresponding to species containing one Zn atom, and smaller peaks from species with two or three Zn atoms. These results suggested that, in contrast to the recent important work leading to formation of compounds containing Zn–Zn bonds,[14,23] an oligomeric hydride-bridged species had been formed (Scheme 1). Compound **6** was thermally stable in solution up to 80 °C and in the solid state up to the sharp melting point at 145–147 °C, in contrast to ZnH_2 which decomposes to Zn metal and hydrogen at 90 °C.[3]



Scheme 1. Synthesis of oligomeric organozinc hydride species **6** from alkylzinc bromide **5**.

The crystal structure of **6** showed that the formula unit was [Zn$_5$R$_4$H$_6$],[24] composed of several structural components hitherto unknown within zinc hydride chemistry (Figure 3). The core of the molecule contains five zinc atoms with distorted tetrahedral coordination in a spirocyclic [Zn{(μ-H)Zn}$_4$(μ-H)$_2$]$^{4+}$ array, in which two {Zn(μ-H)}$_3$-rings are fused at Zn1. Four κC,κN-alkyl ligands are bonded to the outermost zinc atoms, with longer Zn–C and Zn–N bonds than those in **5**, reflecting the weaker Lewis acidity of the metal in **6**. Each six-membered {Zn(μ-H)}$_3$-ring adopts a shallow skew-boat conformation, with a dihedral angle of 77° between the mean Zn$_3$-planes. Only three examples of dimeric cyclo-{Zn(μ-H)}$_2$ units have been structurally characterized,[8,13,14] and **6** is the first example of a compound with a cyclo-{Zn(μ-H)}$_3$ unit.

The resulting Zn···Zn separations in **6** (3.156–3.195 Å) are considerably longer than those for either unsupported Zn–Zn bonds (2.305(3)–2.3591(9) Å)[14,23] or doubly bridged compounds containing the {Zn(μ-H)$_2$Zn} fragment (2.4084(3)–977(4) Å).[8,13,14] Uncertainty in the hydrogen positions makes it impossible to ascertain whether the zinc–hydrogen bond lengths within the central {ZnH$_4$} unit are significantly different from those to the four peripheral zinc atoms (Figure 4).

It is probable that the distortion of the coordination from tetrahedral at the central zinc atom arises from interligand interactions, which give an approximate C_2 axis through H5···Zn1···H6. The six-membered {Zn(μ-H)}$_3$ rings are reminiscent of the {Ga(μ-H)}$_3$ rings in [(R$_2$GaH)$_3$] (R = Me, Et, *i*Pr, *t*Bu)[25] or [(R$_2$AlH)$_3$] (R = Me,[26] *t*Bu[27]). The structure of **6** can thus be considered as a fragment of polymeric zinc hydride, the growth of which has been restricted by the bulky ligands R. Alternatively **6** may be viewed as a triple ion comprising a central {ZnH$_4$}$^{2-}$ dianion, as found in M$_2$[ZnH$_4$] and M$_3$[ZnH$_4$(H)],[9] and two {RZn(μ-H)ZnR}$^+$ cations.

The initial product of the reaction between [RZnBr] and NaH has the probable composition [RZnH]. Capture of this species by ZnH_2, generated by the excess of NaH, would lead to formation of **6**. Alternatively the formation of **6** could involve zincate species, such as Na[ZnH$_2$R]. It was shown previously that the cluster [Ph$_2$Zn$_3$H$_4$(tmeda)] was formed from [{(PhZnH)$_2$(tmeda)}$_2$] by a Schlenk rearrangement with

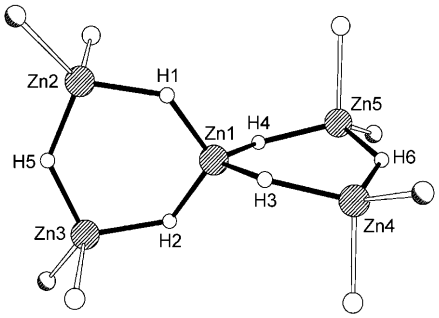


Figure 4. Structure of the core of **6**. Selected bond lengths [Å] and angles [°]: Zn1–H1 1.75(5), Zn1–H2 1.74(5), Zn1–H3 1.76(4), Zn1–H4 1.79(5), Zn2–H1 1.85(5), Zn2–H5 1.76(5), Zn3–H2 1.81(5), Zn3–H5 1.75(5), Zn4–H3 1.79(5), Zn4–H6 1.74(5), Zn5–H4 1.80(5), Zn5–H6 1.76(4); H1-Zn1-H2 114(2), H1-Zn1-H3 95(2), H1-Zn1-H4 120(2), H2-Zn1-H3 120(2), H2-Zn1-H4 97(2), H3-Zn1-H4 112(2).

elimination of $[Ph_2Zn(tmeda)]$.[28] A similar reaction leading to **6** is considered unlikely in the present case because $\{ZnR_2\}$ would be too crowded. Attempts to synthesize the dialkyl from two equivalents of RLi and $ZnBr_2$[29] have given only the mono-alkyl complex **5**.

Experimental Section

5: Methyllithium (1.6 M solution in Et_2O, 3.4 mL, 5.4 mmol) was added slowly to a solution of $HC(SiMe_3)_2(SiMe_2hpp)$ (1.91 g, 5.4 mmol) in THF (35 mL) at room temperature. The resultant solution was stirred for 6 h, then added dropwise to a stirred suspension of $ZnBr_2$ (1.22 g, 5.4 mmol) in THF (20 mL) at −110 °C. The mixture was allowed to warm to room temperature, the volatiles were removed under reduced pressure from the pale yellow solution, and the residue was extracted with toluene (3 × 25 mL). Following removal of solids by filtration, the extract was reduced in volume (to 10 mL) and stored overnight at 0 °C to give **5** as colorless crystals (2.19 g, 81 %); m.p. 189–190 °C; ^{1}H NMR (400 MHz, [D$_6$]benzene): $\delta = 3.32$ (m, 2H, hpp-CH_2), 2.60 (m, 2H, hpp-CH_2), 2.21–2.14 (m, 4H, hpp-CH_2), 1.23 (m, 2H, hpp-CH_2), 1.05 (m, 2H, hpp-CH_2), 0.43 (s, 18H, $SiMe_3$), 0.31 ppm (s, 6H, $SiMe_2$); ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]benzene): $\delta = 159.4$ (CN_3), 48.5, 47.9, 43.1, 41.7, 23.7, 22.7 (hpp-CH_2), 5.8 (^1J(Si,C) = 51 Hz, $SiMe_3$), 5.1 ppm ($SiMe_2$).[30] ^{29}Si{^{1}H} NMR (119 MHz, [D$_6$]benzene): $\delta = 7.9$ ($SiMe_2$), −6.7 ppm ($SiMe_3$). MS (EI, values given are for ^{79}Br and ^{66}Zn): *m*/*z* (%): 499 (2) [M^+], 484 (40) [M^+−Me], 324 (100) [$Me_2Si{=}C(SiMe_2hpp)SiMe_2$], 201 (15), 155 (50). Elemental analysis calcd (%) for $C_{16}H_{36}BrN_3Si_3Zn$: C 38.43, H 7.26, N 8.40; found: C 38.35, H 7.16, N 8.29.

6:A mixture of **5** (0.50 g, 1.0 mmol) and NaH (1.5 equiv, 0.036 g, 1.5 mmol) was taken up in THF (30 mL) and the resultant grey slurry was stirred at room temperature for 3 days. The volatiles were removed under reduced pressure and the residue was extracted with pentane (2 × 20 mL). Following removal of solids by filtration, the extract was reduced in volume (to 5 mL) and stored for two days at −30 °C to give **6** as colorless crystals (0.23 g, two crops, 65 % based on **5**); m.p. 145–147 °C; ^{1}H NMR (500 MHz, [D$_6$]benzene): $\delta = 5.10$ (br s, 6H, Zn(μ-H)), 3.33, 2.73, 2.37, 2.29, 1.35, 1.17 (m, 8H, hpp-CH_2), 0.44 (s, 72H, $SiMe_3$), 0.39 ppm (s, 24H, $SiMe_2$). ^{13}C{^{1}H} NMR (125 MHz, [D$_6$]benzene): $\delta = 158.3$ (CN_3), 48.3, 48.1, 45.9, 41.6, 23.9, 23.1 (hpp-CH_2), 6.0 (^1J(Si,C) = 50 Hz, $SiMe_3$), 5.4 ppm ($SiMe_2$).[30] ^{29}Si{^{1}H} NMR (119 MHz, [D$_6$]benzene): $\delta = 6.2$ ($SiMe_2$), −5.9 ppm ($SiMe_3$). MS (EI): *m*/*z* (%) 862 (2) and 842 (1) containing Zn_3, 786 (1), 768 (2) [R_2Zn_2H-$SiMe_3$], 422 (60, two overlapping peaks at 418 and 422) [RZn] and [$RZnH_4$], 346 (60) [$RZnH{-}SiMe_3$], 324 (100) [$Me_2Si{=}C(SiMe_2hpp)SiMe_2$], 138 (65) [hpp], 73 (40) [$SiMe_3$]. Elemental analysis calcd (%) for $C_{64}H_{150}N_{12}Si_{12}Zn_5$: C 43.88, H 8.63, N 9.59; found: C 44.14, H 8.71, N 9.56.

Crystal data: **5**: triclinic; space group $P\bar{1}$, $a = 9.2263(2)$, $b = 10.7777(2)$, $c = 11.9010(3)$ Å; $\alpha = 103.930(2)$, $\beta = 96.849(1)$, $\gamma = 93.504(2)°$; $V = 1135.45(4)$ Å^3; $Z = 1$; $\rho_{calcd} = 1.46$ Mg m^{-3}; $R1 = 0.035$ [$I > 2\sigma(I)$]; $wR2 = 0.078$ (all data); GOF = 1.202. **6**: monoclinic; space group $P2_1/n$, $a = 17.3310(2)$, $b = 13.7533(2)$, $c = 43.8478(6)$ Å; $\beta = 101.087(1)°$; $V = 10256.4(2)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.23$ Mg m^{-3}; $R1 = 0.060$ [$I > 2\sigma(I)$]; $wR2 = 0.141$ (all data); GOF = 1.026.

CCDC 699752 and 699753 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

Received: August 26, 2008
Revised: October 16, 2008
Published online: November 19, 2008

Keywords: cluster compounds · hydride ligands · organometallic compounds · spiro compounds · zinc

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