

Syntheses and structures of the first examples of zinc compounds with bridging fluorine and hydrogen atoms

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The first examples of zinc compounds with bridging fluorine and hydrogen atoms $[\{HC(CMeNAr)_2\}Zn(\mu-X)]_2$ ($Ar = 2,6-Me_2C_6H_3$, $X = F$, **8**; $X = H$, **9**) have been synthesised and structurally characterised.

Recent reports have shown increasing interest in the utilisation of zinc hydride complexes as reducing reagents¹ and as precursors for various transformations.² Generally, zinc hydride complexes are synthesised from ZnH_2 .³ However, the impurity, thermal mobility and the inertness of ZnH_2 compared to its group 13 analogues often resulted in impure products.^{4,5} In addition, hydrogen is believed to play a bridging role between two zinc atoms in many zinc hydride complexes as presumed in ZnH_2 , resulting in polymeric or oligomeric species that are difficult to crystallise and characterise.⁵ Therefore, zinc hydride complexes are less well known and have been less thoroughly investigated than the group 13 analogues and other zinc reagents. Before this work started, only three zinc hydride complexes had been structurally characterised, namely $[Me_2N(CH_2)_2N(Me)ZnH]_2$ **1**,⁶ $[\{\eta^3-HB(3-RC_3N_2H_2)_3\}ZnH]$ ($R = Bu^t$) **2**⁷ and $[(Me_3PN)ZnH]_4 \cdot 4THF$ **3**.⁷ In these three compounds, all hydrogen atoms are terminally arranged. The bridging role of hydrogen atoms in zinc hydride complexes remains crystallographically unveiled. Kläui *et al.*⁸ had successfully synthesised $[\{\eta^3-HB(3-R-5-MeC_3N_2H_2)_3\}ZnH]$ ($R = p-Tol$) **4** from the metathesis reaction of Et_3SiH with the first structurally characterised zinc fluoride compound $[\{\eta^3-HB(3-R-5-MeC_3N_2H_2)_3\}ZnF]$ ($R = p-Tol$) **5**.⁸ However, Kläui's fluorination method is not applicable for most of the other zinc precursors due to their moisture sensitivity.

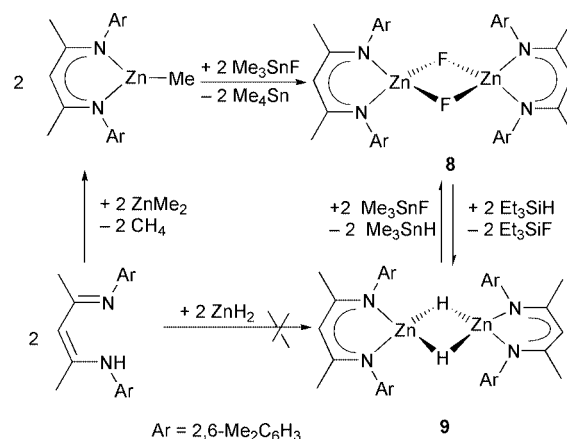
Recently, we trapped 'molecular' ZnF_2 and $MeZnF$ by using organotitanium fluorides as matrices to yield $[(Cp^*TiF_3)_8(ZnF_2)_3]$ **6** and $[(Cp^*TiF_3)_4(MeZnF)_2]$ **7**, respectively.⁹ Compound **7** is an intermediate for the formation of **6**, the methyl groups in **7** can be easily exchanged by Me_3SnF to afford **6**. This implies that zinc fluorides can be made by fluorination of the corresponding alkyl derivatives with Me_3SnF ¹⁰ if suitable supporting ligands are chosen. Herein, we describe the preparation and structural characterisation of $[\{HC(CMeNAr)_2\}Zn(\mu-X)]_2$ ($Ar = 2,6-Me_2C_6H_3$, $X = F$, **8**; $X = H$, **9**).

The reaction of $[\{HC(CMeNAr)_2\}ZnR]$ ($R = Me, Et$)¹¹ with 1 equiv. of Me_3SnF in toluene at 100 °C for 8 h resulted in the disappearance of solid Me_3SnF . After removal of all volatiles *in vacuo*, the residue was recrystallised from hot toluene affording **8** as colourless crystals suitable for X-ray single crystal determination in high yield (80%). EI-MS shows the molecular ion peak of the dimeric **8**, in agreement with the structure established by X-ray analysis. Having observed several cases of the same bridging fashion of fluorine and hydrogen,¹² we inferred that the corresponding hydride should similarly contain bridging hydrogen atoms with a composition of $[\{HC(CMeNAr)_2\}Zn(\mu-H)]_2$ **9**. The electron deficient three-centre-two-electron intermolecular $Zn-H-Zn$ bonds are more favoured in **9** due to the bulky substituents at N of the diketiminato ligand that prevent the condensation through N atoms as seen in **1** and **3**.

Consequently, we treated **8** with an excess amount of Et_3SiH (5–10 equiv.) in benzene under refluxing conditions for 16 h. After the removal of all volatiles, the residue was recrystallised from hot benzene resulting in colourless crystals of **9** in high yield (75%). The dimeric nature of the compounds is indicated by EI-MS and confirmed by X-ray crystallography. Unlike **1** and **2**, compound **9** cannot be obtained from the reaction of ZnH_2 with $[ArN=C(Me)CH=C(Me)NHAr]$. However, upon treatment of **9** with Me_3SnF in benzene under reflux for 6 h, compound **9** can be readily converted back to **8** (Scheme 1). Satisfactory microanalyses of **8** and **9** have been obtained.† The ¹H NMR spectrum reveals a singlet for the bridging hydrogens of **9** (δ 4.59), while the ¹⁹F NMR of compound **1** shows a singlet for $\mu-F$ at δ -61.6.

The structures of **8** and **9** have been determined by X-ray single crystal analysis and are shown in Figs. 1 and 2, respectively.‡ Both molecular structures are dimeric with an inversion centre in the centroid of the four-membered Zn_2X_2 ($X = F, H$) ring. The two zinc atoms in **8** and **9** are bridged by fluorine and hydrogen atoms, respectively, forming the three-centre-four electron $Zn-F-Zn$ and the three-centre-two-electron $Zn-H-Zn$ bonds.

The average $Zn-N$ bond length in **8** (1.955 Å) is quite close to that in **9** (1.967 Å), but the six-membered ring in **9** formed by Zn and the ligand backbone is essentially planar (mean deviation 0.0149 Å). There is a C_2 axis passing through C(2), Zn(1), Zn(1A) and C(2A) atoms in **9**. However, in compound **8**, the ligand backbone is slightly folded. The $(\mu-F)-Zn$ bond lengths in **8** [F(1)-Zn(1) 2.0034(11), F(1)-Zn(1A) 1.9473(12), av. 1.975 Å] are close to the sum of the covalent radii, and ca. 0.126 Å longer than the terminal $F-Zn$ bond length found in **5** [1.849(4) Å]; they are also comparable to those in **6** and **7**. The $(\mu-H)-Zn$ bond lengths (1.766 Å) from the refinement of X-ray diffraction data are slightly shorter than those in the ionic $MeZnBH_4$ (av. 1.82 Å).¹³ The distances are longer than the terminal $H-Zn$ bond lengths found in **1** (1.62 Å) and **3** (1.50 Å), respectively.



Scheme 1

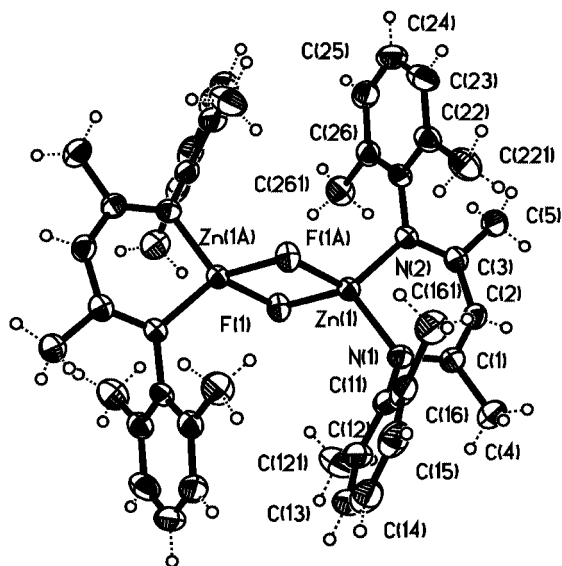


Fig. 1 The molecular structure of **8** in the crystal (with 50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Zn(1)–N(2) 1.951(2), Zn(1)–N(1) 1.9588(14), Zn(1)–F(1) 2.0034(11), Zn(1)–Zn(1A) 2.9754(6), F(1)–Zn(1A) 1.9473(12), F(1A)–Zn(1)–F(1) 82.28(5), Zn(1A)–F(1)–Zn(1) 97.72(5).

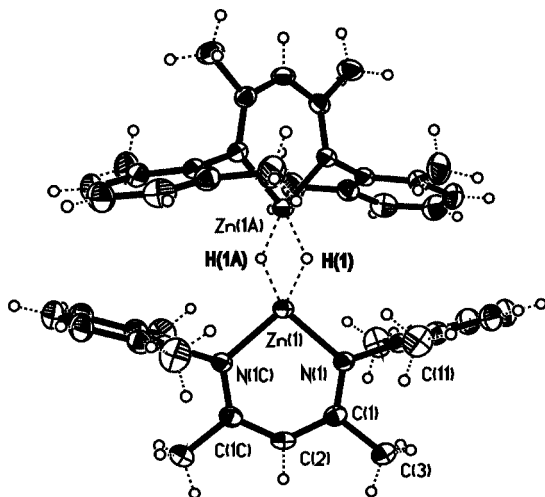


Fig. 2 The molecular structure of **9** in the crystal (with 50% probability ellipsoids). Lattice solvents are omitted. Selected bond lengths or distances (Å) and angles (°): Zn(1)–H(1) 1.766, Zn(1)–N(1) 1.9672(17), Zn(1)–N(1A) 1.9673(17), Zn(1)–Zn(1A) 2.4513(9), Zn(1)–H(1)–Zn(1A) 87.9, H(1)–Zn(1)–H(1A) 92.1.

The shorter (μ -H)–Zn distance compared to the (μ -F)–Zn bond length correlates well with a smaller Zn(1)–H(1)–Zn(1A) angle (87.9°) and a wider Zn(1)–F(1)–Zn(1A) angle (97.72°). Consequently, a wider H(1)–Zn(1)–H(1A) angle (92.1°) results compared to the F(1)–Zn(1)–F(1A) angle (82.28°), which leads to a significantly shorter Zn–Zn distance [2.4513(9) Å] in **9** (by 0.522 Å) than that in **8** [2.9754(6) Å]. This short Zn–Zn distance is in the range of the sum of the covalent radii (2.50 Å), but a Zn–Zn interaction is unlikely.

In summary, we have developed an efficient route to zinc fluorides that are key precursors for the corresponding hydrides. We have also established the first examples of zinc compounds

with bridging fluorine and bridging hydrogen atoms. Further studies with **2** are in progress.

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Notes and references

† For **8**: mp 278–281 °C. EI-MS: m/z (%) 778 (M^+ , 100). ^1H NMR (C_6D_6 , 200.131 MHz): δ 6.80–6.95 (m, 12 H, Ar H), 4.68 (s, 2H, γ -CH), 1.99 (s, 24 H, Ar-Me), 1.35 (s, 12 H, β -CMe). ^{19}F NMR (C_6D_6 , 188.28 MHz): δ –61.62. Anal. Calc. (found) for $\text{C}_{42}\text{H}_{50}\text{F}_2\text{N}_4\text{Zn}_2$: C, 64.70 (64.76); H, 6.46 (6.49); N, 7.19 (7.16)%.

For **9**: mp 215–217 °C. EI-MS: m/z 743 [$M - \text{H}$] $^+$. ^1H NMR (C_6D_6 , 200.131 MHz): δ 6.92 (s, 12 H, Ar H), 4.82 (s, 2 H, γ -CH), 4.59 [s, 2 H, Zn-(μ -H)], 2.03 (s, 24 H, Ar-Me), 1.44 (s, 12 H, β -CMe). Anal. Calc. (Found) for $\text{C}_{48}\text{H}_{58}\text{N}_4\text{Zn}_2$ (incl. one molecule C_6H_6): C, 70.16 (69.97); H, 7.11 (7.03); N, 6.82 (7.15)%.

‡ *Crystallography*: the data were collected on a Stoe-Siemens four-circle diffractometer by using Mo-K α ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods (SHELXS-97) and refined against F^2 using SHELXL-97.¹⁴ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the refinement in geometrically ideal positions.

Crystal data for **8**: $\text{C}_{42}\text{H}_{50}\text{F}_2\text{N}_4\text{Zn}_2$, $M = 779.60$, monoclinic, space group $P2_1/n$, $a = 13.02.6(2)$, $b = 8.8051(12)$, $c = 17.309(2)$ Å, $\beta = 105.240(11)^\circ$, $U = 1915.5$ Å 3 , $Z = 2$, $D_c = 1.352$ g cm $^{-3}$, $F(000) = 2514$, $T = 203(2)$ K, $\mu(\text{Mo-K}\alpha) = 1.296$ mm $^{-1}$, $7.02 \leq 2\theta \leq 50.04^\circ$, 6762 reflections measured, 3381 unique ($R_{\text{int}} = 0.0650$) were used in all calculations. $R1 = 0.0273$ [$I > 2\sigma(I)$] and $wR2 = 0.0723$ (all data); max./min. residual electron density: 0.380 / –0.233 e Å $^{-3}$. CCDC 155083.

For **9**: $\text{C}_{48}\text{H}_{58}\text{N}_4\text{Zn}_2$ (incl. one molecule benzene), $M = 821.72$ orthorhombic, space group $Fddd$, $a = 1.6941(5)$, $b = 2.0576(3)$, $c = 2.4918(4)$ Å, $U = 8686(3)$ Å 3 , $Z = 8$, $D_c = 1.257$ g cm $^{-3}$, $F(000) = 3472$, $T = 200(2)$ K, $\mu(\text{Mo-K}\alpha) = 1.141$ mm $^{-1}$, $7.04 \leq 2\theta \leq 50.06^\circ$; 3065 reflections measured, 1915 unique ($R_{\text{int}} = 0.0279$) which were used in all calculations. $R1 = 0.0309$ [$I > 2\sigma(I)$] and $wR2 = 0.0831$ (all data); max./min. residual electron density: 0.286 / –0.579 e Å $^{-3}$. CCDC 155084.

See <http://www.rsc.org/suppdata/cc/b1/b102275j/> for crystallographic data in CIF or other electronic format.

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