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Terminal Hydridozinc Cation

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A thermally stable terminal hydridozinc cation has been isolated. The nucleophilicity of the hydride ligand is demonstrated by inserting carbon dioxide, carbodiimide and benzophenone across the Zn-H bond in a facile manner. Preliminary studies on catalytic hydrosilylation using $PhSiH_3$ indicate that the hydridozinc cation in the presence of BPh_3 can selectively reduce CO_2 to $PhSi(OCHO)_3$.

The chemistry of organozinc and organomagnesium compounds has flourished simultaneously after the seminal works of Frankland[1] and Grignard.[2] At the molecular level, there are significant similarities in the coordination geometries of zinc and magnesium.[3] However, the isostructural compounds derived from these two elements differ fundamentally in their Lewis acidity, zinc being soft and magnesium being hard.[4] Zn—C bonds are significantly less polar than Mg—C bonds due to the difference in electronegativity. Several examples of addition of Zn—C and Mg—C across unsaturated organic substrates have demonstrated this concept.[5] Due to low polarity, Zn—C bonds are more tolerant towards functional groups in organic molecules and hence they are more chemoselective and stereospecific as compared to organomagnesium reagents.[6] Cationic compounds of zinc and magnesium have attracted the attention of chemists in the activation of electrophiles.[7] Our interest in this area led us to prepare a butylmagnesium cation, $[(Me_6tren)Mg(n\text{-}Bu)]^+$ (Me_6tren = tris[2(dimethylamino)ethyl]-amine) possessing a disguised hydride on the β-carbon of the butyl group.[8] While the applicability of this β-hydride was restricted to the reduction of benzophenone,[8] attempts to prepare a hydridomagnesium cation, which can effect a variety of reductions, have so far remained unsuccessful. The possibility of an increased stability of Zn—H bond [9] prompted us to explore the hydridozinc cation. Hydridozinc cations are scarcely found in the literature (Fig. 1A and B) and their reactivity is not well explored. In this communication, we present the synthesis and reactivity of a thermally stable terminal hydridozinc cation $[(Me_6tren)ZnH]^+$ (Fig. 1C).

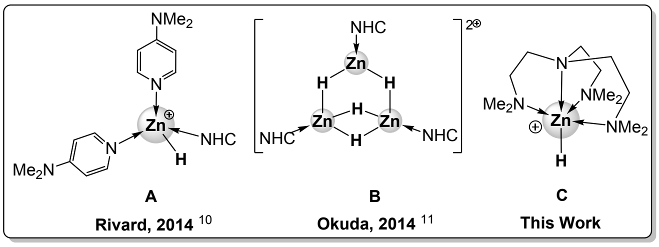
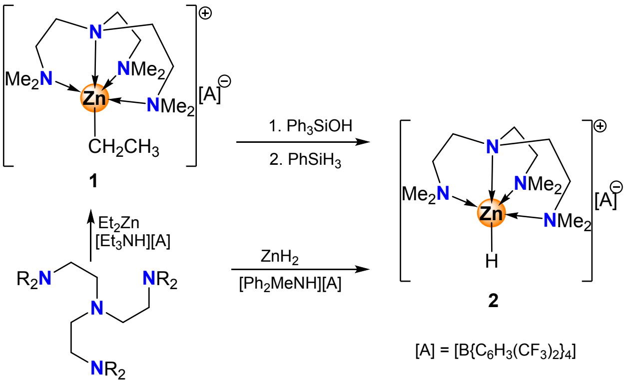


Fig 1 Structurally characterised hydridozinc cations.

To isolate hydridozinc cation, we considered employing the tripodal tetradentate nitrogen donor Me_6tren, a ligand extensively used in s-block chemistry.[12] Diethylzinc was treated with Me_6tren and the Brønsted acid $[Et_3NH][B\{C_6H_3(CF_3)_2\}_4]$ to obtain the ethylzinc cation, $[(Me_6tren)ZnEt][B\{C_6H_3(CF_3)_2\}_4]$ (**1**, Scheme 1).



Scheme 1 Synthetic methods to prepare the hydridozinc cation **2**.

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^1H NMR spectrum of **1** recorded in CD_2Cl_2 indicates the κ^4 coordination of Me_6tren to the zinc centre (see SI). The methylene protons on the ethyl group bound to the zinc centre exhibit a chemical shift of δ 0.20 ppm. Solid state structure of **1**, elucidated by single crystal X-ray diffraction studies, confirms κ^4 coordination of Me_6tren to the zinc centre (Fig. 2) contrary to the κ^2 coordination of Me_6tren in the neutral [(Me_6tren)Zn(tBu)$_2$] reported by Mulvey and Robertson.[13] The zinc atom in **1** has a trigonal bi-pyramidal arrangement of the donor atoms similar to [(Me_6tren)Mg(n-Bu)]$^+$. The Zn—N distances are observed in a range from 2.258 to 2.289 Å. The Zn—C distance is found to be 2.007 Å similar to those observed in other cationic alkylzinc compounds.[7a-i]

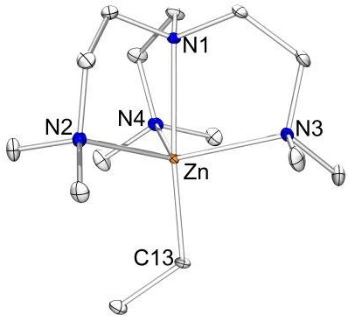


Fig 2 Solid state structure of cationic part of **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C13—Zn1 2.007(5), N1—Zn1 2.288(4), N2—Zn1 2.257(4), N3—Zn1 2.290(4), N4—Zn1 2.265(4), C13—Zn1—N2 105.5(2), C13—Zn1—N4 104.2(2), N2—Zn1—N4 115.47(15), C13—Zn1—N1 175.13(19), N2—Zn1—N3 115.22(17), N4—Zn1—N3 115.26(17), N1—Zn1—N3 76.96(14).

Having obtained the ethylzinc cation, **1**, we probed the reactivity of β-CH towards organic electrophiles. **1** did not react with Ph_2CO unlike in the case of [(Me_6tren)Mg(n-Bu)]$^+$ where, reduction of Ph_2CO was observed. We concluded that the Zn—C bond in **1** is less polar than the Mg—C bond in [(Me_6tren)Mg(n-Bu)]$^+$ and hence β-CH in **1** is inactive.

We then set out to prepare the hydridozinc cation, [(Me_6tren)ZnH]$^+$. Molecular zinc hydrides have been earlier prepared from zinc alkyls. In this route, zinc alkyls are treated with triphenylsilanol (Ph_3SiOH) to generate zinc siloxide species followed by the reaction with phenylsilane to obtain the zinc hydrides.[14] Accordingly, **1** was treated with Ph_3SiOH to obtain [(Me_6tren)ZnOSiPh$_3$][B{$C_6H_3(CF_3)_2$}$_4$] in quantitative yield (See SI). [(Me_6tren)ZnOSiPh$_3$][B{$C_6H_3(CF_3)_2$}$_4$] was reacted with a 2.2 fold excess of $PhSiH_3$ to obtain the hydridozinc cation [(Me_6tren)ZnH][B{$C_6H_3(CF_3)_2$}$_4$] (**2**) in 93% yield (Scheme 1). The purity of **2** was confirmed by elemental analysis and NMR spectroscopy (see SI). [(Me_6tren)ZnH]$^+$ was alternatively prepared from polymeric [ZnH_2] and Me_6tren in the presence of one equivalent of the Brønsted acid [Et_3NH][B{$C_6H_3(CF_3)_2$}$_4$]. Compound **2** is well soluble and stable in CH_2Cl_2, THF and MeCN. A solution of **2** in MeCN was found to be stable at 90 °C for more than 200 hours under air-and moisture-free conditions.

^1H NMR spectrum of **2** in THF[D_8] exhibits the hydride signal at δ 3.47 ppm, a much shielded value compared to other terminal zinc hydrides reported in the literature (δ 5.60- 4.39 ppm)[12a,b,15] except in the two coordinate {(R_3Si)(Ar)N}ZnH (δ 1.87-1.85 ppm) reported by Jones and co-workers.[16] ^1H NMR spectrum of **2** also confirms the κ^4 coordination of Me_6tren to the zinc centre. **2** was crystallized from THF/pentane at -30 °C and the solid state structure was analysed by single crystal X-ray diffraction studies (Fig. 3). The Zn—H distance in **2** is found to be 1.59 Å consistent with other neutral terminal zinc hydrides known in the literature.[12a,b,15] The axial Zn—N bond *trans* to the Zn—H bond is slightly elongated (2.311 Å) as compared to the equatorial Zn—N distances (av. 2.200 Å).

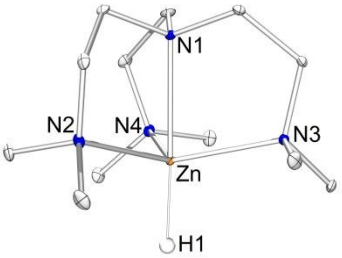
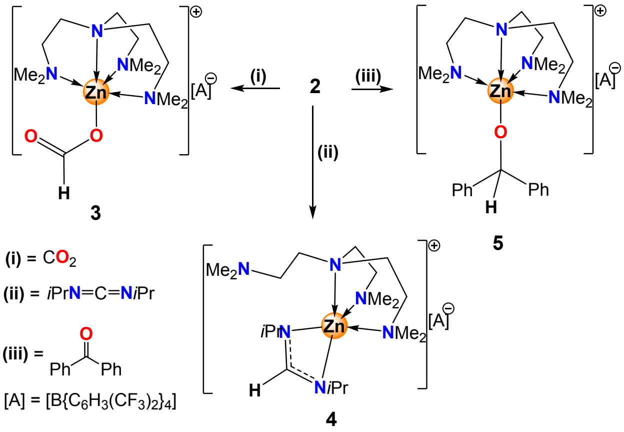


Fig 3 Solid state structure of cationic part of **2**. Hydrogen atoms except H1 are omitted for clarity. Selected bond lengths [Å] and angles [°]:Zn1—H1 1.59(3), N1—Zn1 2.311(2), N2—Zn1 2.225(2), N3—Zn1 2.195(2), N4—Zn1 2.182(2), N4—Zn1—N3 114.78(9), N4—Zn1—N2 117.18(9), N3—Zn1—N2 116.41(8), N4—Zn1—N1 78.97(8), N3—Zn1—N1 78.53(8), N2—Zn1—N1 78.01(9), N4—Zn1—H1 99.3(10), N3—Zn1—H1 103.8(10), N2—Zn1—H1 101.3(10), N1—Zn1—H1 177.6(10).

Following the facile isolation of the hydridozinc cation, **2**, we probed its reactivity with CO_2, *N,N'*-diisopropylcarbodiimide (iPrN=C=NiPr) and benzophenone (Scheme 1). We observed that **2** instantaneously reduces CO_2 at ambient temperature resulting in the formate complex, **3**. Reduction of iPrN=C=NiPr by **2** was successfully carried out to obtain cationic amidinate complex, **4**. Ph_2CO was quantitatively reduced to result in the alkoxyzinc complex, **5**.



Scheme 2 Reactivity of the hydridozinc cation **2** at ambient temprature.

The inserted hydride in **3**-**5** was confirmed by ^1H NMR spectroscopy (see SI). Additionally the solid state structures of **3**-**5** were established in single crystal X-ray diffraction studies (Fig. 4). **3**, **4** and **5** constitute the first examples of zinc cations bearing formate, amidinate and alkoxide ligands respectively.

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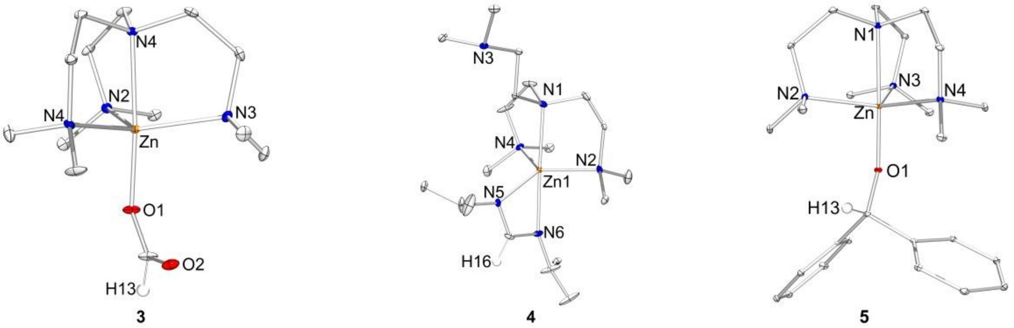

Fig 4 Solid state structures of cationic parts of **3**, **4** and **5**.

Having observed the reduction of CO_2 to formate, we investigated the hydrosilylation of CO_2 using $PhSiH_3$. While catalytic hydrosilylation of CO_2 using $(EtO)_3SiH$ is well explored, reactions involving $PhSiH_3$ usually result in a mixture of products namely silylformates, silylacetals, methoxysilanes and methane.[17] Selective reduction to $PhH_2Si(O_2CH)$ has been recently observed using BPh_3 [18] and to CH_4 using a combination of [κ^3-Tism^{PriBenz}]ZnH and $B(C_6F_5)_3$.[15b] When a constant pressure of 1.5 bar of CO_2 was maintained in a reaction mixture comprising of $PhSiH_3$ (324 µmol), **2** (16.2 µmol) and BPh_3 (16.2 µmol) in acetonitrile[D_3] at 50 °C for 2 h, the silylformate, $PhSi(O_2CH)_3$, was the only product observed in 98% yield with a turn over frequency of 29.1 h^{-1}. Our finding assumes importance since all the Si—H in $PhSiH_3$ are quantitatively consumed resulting in the selective formation of $PhSi(OCHO)_3$ (Fig 5). However, the mechanism needs to be explored both by experiments and computations.

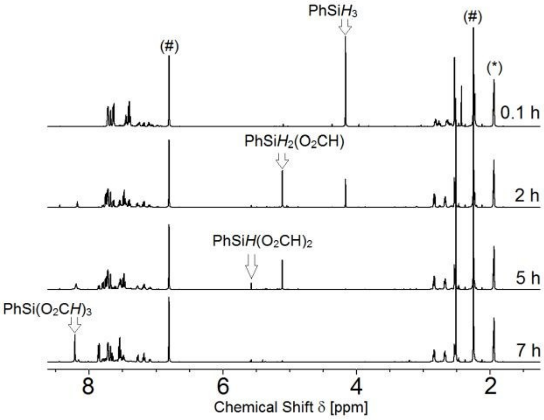

Fig 5 Stacked ^1H NMR spectra monitoring the progress of hydrosilylation of CO_2 (1.5 bar) using $PhSiH_3$ (70.0 µmol), **2** (10.5 µmol) and BPh_3 (5.25 µmol) in acetonitrile[D_3] (*) at 50 °C. The reaction was internally referenced with mesitylene (#).

We further found that **2** (5 mol%) alone catalyses the hydrosilylation of Ph_2CO at 60 °C in 6 h by inserting Ph_2CO across all three Si—H bonds in $PhSiH_3$ to give $PhSi(OCHPh_2)_3$ (see SI). During all the hydrosilylation experiments, **2** was quantitatively recovered reflecting its stability.

Contrary to the reactivity of the disguised hydride in the butylmagnesium cation, [(Me$_6$tren)Mg(*n*-Bu)]$^+$,[8] we have demonstrated that the thermally stable terminal hydridozinc cation, [(Me$_6$tren)ZnH]$^+$, can efficiently reduce the electrophiles CO_2, PH_2CO and *i*PrN=C=N*i*Pr. Selective conversion of CO_2 to $PhSi(OCHO)_3$ has been successfully demonstrated. The presence of a single reactive site in [(Me$_6$tren)ZnH]$^+$ makes it a unique species to probe into further catalytic reactions and their mechanisms.

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Conflicts of interest

There are no conflicts to declare.

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Thermally stable hydridozinc cation catalytically converts CO_2 to $PhSi(OCHO)_3$ using $PhSiH_3$ in the presence of a mild Lewis acid BPh_3.