Zinc Hydride Cations

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# Accessing Zinc Monohydride Cations through Coordinative Interactions**

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**Abstract:** *We present isolable examples of formal zinc hydride cations supported by N-heterocyclic carbene (NHC) donors, and investigate the dual electrophilic and nucleophilic (hydridic) character of the encapsulated $[ZnH]^+$ units by computational methods and preliminary hydrosilylation catalysis.*

While zinc dihydride has been known since 1947,[1] this parent species is pyrophoric, insoluble in most solvents and decomposes over time at room temperature, thus counteracting the potential utility of this species as a reducing agent.[2] With a judicious choice of anionic co-ligand, soluble and more thermally stable examples of zinc(II) hydride complexes $[LZnH]_x$ ($x \geq 1$) have been prepared with varying degrees of nuclearity depending on the steric bulk and denticity of the ligand present (Figure 1).[3] Moreover, the use of the hydridic ($H^{\delta-}$) character within Zn–H residues to activate substrates, such as $CO_2$ and imines, represents a promising low-toxicity approach for chemical synthesis.[4,5] One possible way to increase the reactivity of Zn hydrides is to open coordination sites for substrate binding/activation by the synthesis of complexes featuring formally cationic $[ZnH]^+$ moieties, while concurrently retaining the requisite hydridic character. To this end, we now report a mild procedure to access stable complexes of $[ZnH]^+$ each supported by an N-heterocyclic carbene (NHC) donor.[6] This work builds upon our prior investigations of NHC Group 12 element complexes[7] and parent inorganic hydride adducts of $EH_2$ and $H_2EEH_2$ (E = Si, Ge and/or Sn).[8]

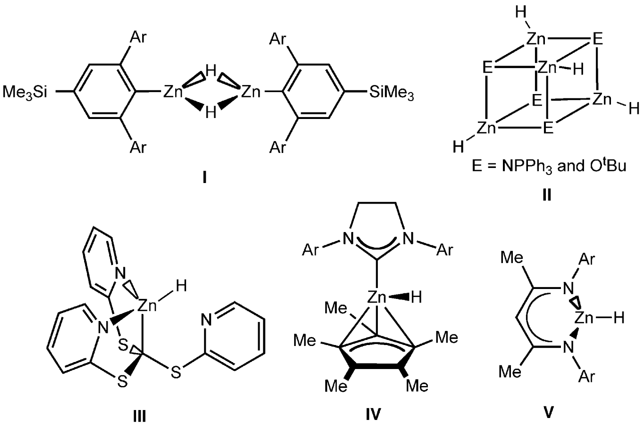
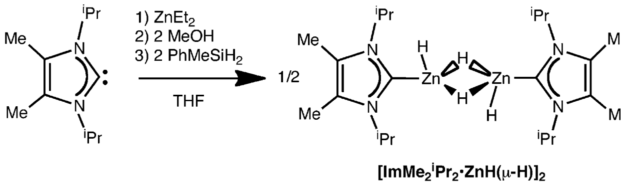


**Figure 1.** Selected zinc(II) hydride complexes; Ar = hindered aryl groups.

At the onset of this study, it appeared that the most direct route to form a zinc hydride cation, $[ZnH]^+$, would be to begin with an isolable $ZnH_2$ complex and perform hydride abstraction chemistry. Fortunately, Okuda and co-workers recently prepared the first examples of such species with the assistance of NHC donors.[5] For example, the metastable dimer $[IPr{\cdot}ZnH(\mu\text{-}H)]_2$ (**1**) (IPr = $[(HCNDipp)_2C{:}]$; Dipp = 2,6-$^iPr_2C_6H_3$)[9] was shown to be active in the catalytic methanolysis of silanes, as well as being reactive towards $CO_2$.[5] Okuda's original synthesis involved the use of pyrophoric $ZnEt_2$ as a reagent, therefore in our laboratory we prepare **1** in a ca. 95% yield from the direct reaction of the readily available adduct $IPr{\cdot}ZnI_2{\cdot}THF$[7] with two equivalents of $K[HB^sBu_3]$ (Scheme 1).[10] Attempts to generate **1** from the reaction of $IPr{\cdot}ZnI_2{\cdot}THF$ with $Li[HBEt_3]$ as a hydride source affords $IPr{\cdot}BEt_3$, $IPrH_2$[8b] and zinc metal as involatile products.[7] In addition, we prepared the less hindered $Zn^{II}$ dihydride adduct $[ImMe_2{}^iPr_2{\cdot}ZnH(\mu\text{-}H)]_2$ (**2**) in a one-pot procedure [Eq. (1)].[5,11] Compound **2** is a colorless solid (Mp = 131–134 °C) that adopts a similar centrosymmetric dimer arrangement as **1** with both terminal and bridging Zn–H units present (Figure S6 in the Supporting Information).[11] Slightly elongated $Zn{-}C_{IPr}$ bonds [2.0737(10) Å] and Zn···Zn separation [2.5150(2) Å] are present in **2** in relation to the corresponding values in the IPr analogue **1**. While distinct $^1H$ NMR resonances are noted for the terminal and bridging hydrides within $[IPr{\cdot}ZnH(\mu\text{-}H)]_2$ (**1**), a single broad resonance



(1)

$[ImMe_2{}^iPr_2{\cdot}ZnH(\mu\text{-}H)]_2$

**2**

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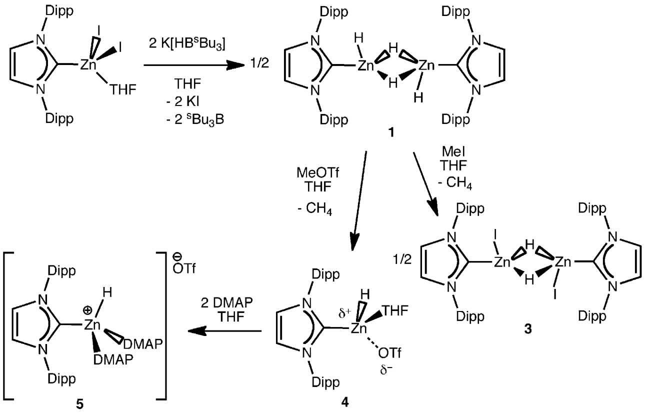


***Scheme 1.*** Alternate synthesis of $[\mathrm{IPr{\cdot}ZnH(\mu\text{-}H)}]_2$ (**1**), preparation of the iodo analogue $[\mathrm{IPr{\cdot}ZnI(\mu\text{-}H)}]_2$ (**3**) and the formal $[\mathrm{ZnH}]^+$ complexes **4** and **5**.

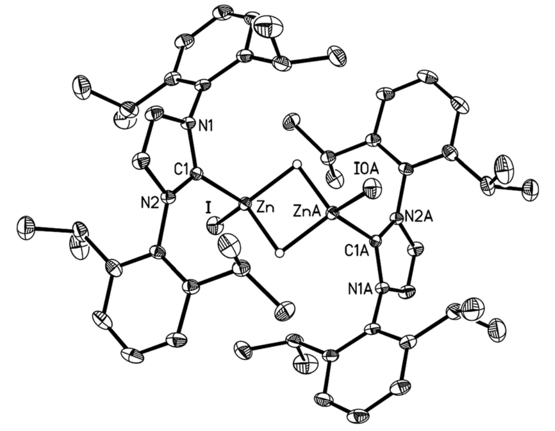
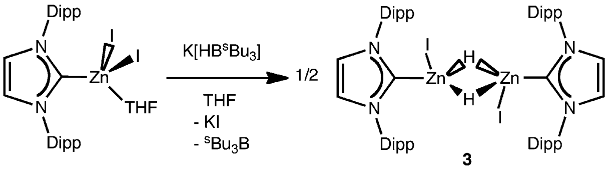


***Figure 2.*** Molecular structure of $[\mathrm{IPr{\cdot}ZnI(\mu\text{-}H)}]_2$ (**3**) with thermal ellipsoids at the 30% probability level; a crystallographic inversion center is present in the molecule. All carbon bound hydrogen atoms and THF solvate have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn–C(1) 2.018(2), Zn–H(1) 1.77(2), Zn–H(1A) 1.79(2), Zn–I 2.5681(3), Zn⋯Zn 2.4683(5); C(1)-Zn-H(1) 111.8(8), C(1)-Zn-H(1A) 106.2(8), C(1)-Zn-I 118.66(6), I-Zn-H(1) 110.6(8), I-Zn-H(1A) 114.0(8), H(1)-Zn-H(1A) 92.5(11).

for **2** is present in $C_6D_6$ at room temperature, suggesting that exchange between terminal and bridging positions occurs in solution. Consistent with this observation, our accompanying computational studies[11] show that the dimerization of $\mathrm{ImMe_2{}^iPr_2{\cdot}ZnH_2}$ to give **2** in the gas phase (through formation of Zn-H-Zn bridges) is less thermodynamically favorable than for the IPr analogue (Scheme S1). Variable temperature (VT) NMR analysis (Figure S2 and S3) showed a coalescence of the Zn-H resonances in **2** at ca. 0 °C, with the appearance of two distinct peaks upon cooling below this temperature. DOSY NMR experiments[11,12] suggest that this fluxional process does not involve the formation of large quantities of monomeric $\mathrm{ImMe_2{}^iPr_2{\cdot}ZnH_2}$, but rather that scrambling of the hydrides occurs within dimetallic species with retention of some Zn-H-Zn bridges; a similar observation has been noted previously for $[\mathrm{IMes{\cdot}Zn(\mu\text{-}H)H}]_2$ [IMes = $[(\mathrm{HCNMes})_2\mathrm{C}\!:]$; Mes = 2,4,6-$\mathrm{Me_3C_6H_2}$)].[5] The hydrodynamic radii for **2** in both [$D_8$]toluene and [$D_8$]-THF (as derived from DOSY) were of similar value (ca. 5.4 Å), and match fairly well with the solid state structure of **2** which shows an overall molecular end-to-end distance of ca. 12.3 Å.[11,12] $[\mathrm{ImMe_2{}^iPr_2{\cdot}ZnH(\mu\text{-}H)}]_2$ (**2**) does not interact with the Lewis bases THF, $\mathrm{Cy_3P}$, DMAP (4-dimethylaminopyridine), nor the nucleophilic carbon-based donors $\mathrm{Ph_3PCMe_2}$,[13] $\mathrm{IPrCH_2}$[14] and $\mathrm{:C(N^iPr_2)_2}$.[15]

Attempts to convert the known Group 12 element halide adducts $[\mathrm{IPr{\cdot}CdI(\mu\text{-}I)}]_2$[16] and $\mathrm{IPr{\cdot}HgI_2}$[17] to the corresponding metal dihydride complexes, $\mathrm{IPr{\cdot}CdH_2}$ and $\mathrm{IPr{\cdot}HgH_2}$, using $\mathrm{K[HB^sBu_3]}$as a hydride source resulted in the immediate formation of metallic precipitates, and the isolation of free IPr and the aminal $\mathrm{IPrH_2}$[8b] from solution in both cases (presumably due to the highly reactive nature of Cd–H and Hg–H bonds).[18]

Complementary computational studies were undertaken on the $\mathrm{ZnH_2}$ adducts **1** and **2** at the M06-2X/cc-pVTZ level of theory, with corresponding NBO and AIM analyses, to further understand the bonding and potential reactivity of these species.[11] These studies indicate the presence of significant hydridic character on each zinc-bound hydrogen atom (−0.435/−0.646 to −0.470/−0.738 in **1**/**2**; NBO charge analysis). Thus it appeared that hydride removal from either complex was a feasible synthetic endeavor.[19] Accordingly we achieved hydride removal in an efficient manner with the use of methylating agents. For example, MeI interacted with $[\mathrm{IPr{\cdot}ZnH(\mu\text{-}H)}]_2$ (**1**) to yield the hydrido-iodo product $[\mathrm{IPr{\cdot}ZnI(\mu\text{-}H)}]_2$ (**3**) in a high yield of 76% with concomitant loss of methane (Scheme 1; Figure 2); compound **3** could also be prepared by the treatment of $\mathrm{IPr{\cdot}ZnI_2{\cdot}THF}$ with one equiv of $\mathrm{K[HB^sBu_3]}$ as shown in Equation (2).



(2)

$[\mathrm{IPr{\cdot}ZnI(\mu\text{-}H)}]_2$ (**3**) adopts a dimeric arrangement in the solid state (Figure 2) with bridging Zn-H-Zn arrays at its core; the metrical parameters are similar to those observed for $[\mathrm{IPr{\cdot}ZnH(\mu\text{-}H)}]_2$ (**1**).[5]

The use of MeOTf as an electrophile resulted in clean conversion of **1** in THF into the carbene-ligated zinc hydridotriflate, $\mathrm{IPr{\cdot}ZnH(OTf){\cdot}THF}$ (**4**) in high yield (88%; Scheme 1; Figure 3) as a moisture-sensitive, yet thermally stable (up to 260 °C) colorless solid. Notably, the NHC–$\mathrm{ZnH_2}$ adducts **1** and **2** do not interact with THF, while the zinc monohydride unit in **4** coordinates one equivalent of THF as indicated by both NMR spectroscopy and X-ray crystallography (Figure 3).[11] This suggests the presence of increased positive charge at the zinc center in $\mathrm{IPr{\cdot}ZnH(OTf){\cdot}THF}$ (**4**) in relation to its dihydride progenitor **1**; our computations reveal that hydride removal (conversion of **1** into **4**) is accompanied by an increase in charge at Zn from +0.65 to +1.08

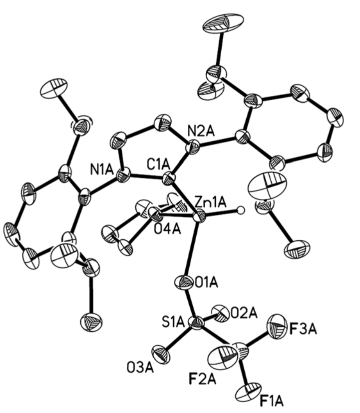


***Figure 3.*** Molecular structure of IPr·ZnH(OTf)·THF (**4**) with thermal ellipsoids at the 30% probability level. All carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] with values belonging to a second molecule in the asymmetric unit listed in square brackets: Zn(1)–O(1) 2.068(3) [2.078(3)], Zn(1)–O(4) 2.156(3) [2.124(3)], Zn(1)–H(1) 1.38(3) [1.36(3)], Zn(1)–C(1) 2.031(3) [2.041(3)]; C(1)-Zn(1)-O(1) 103.43(13) [101.78(12)], C(1)-Zn(1)-O(4) 106.69(12) [107.93(13)], O(1)-Zn(1)-O(4) 94.31(12) [93.93(12)].

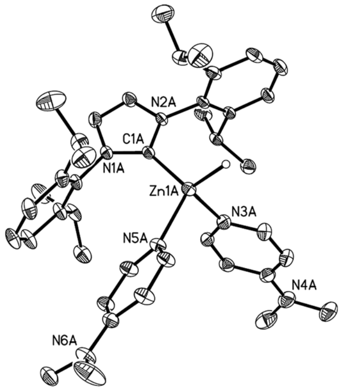


***Figure 4.*** Molecular structure of [IPr·ZnH(DMAP)$_2$]OTf (**5**) with thermal ellipsoids at the 30% probabilty level; all carbon-bound hydrogen atoms and the OTf$^-$ anion have been omitted for clarity. Selected bond lengths [Å] and angles [°] with values due to a second molecule of **5** in the asymmetric unit in square brackets: Zn(1A)–H(1A) 1.92(3) [1.93(3)], Zn(1A)–C(1A) 2.071(4) [2.074(4)], Zn(1A)–N(3A) 2.074(5) [2.135(4)], Zn(1A)–N(5A) 2.097(3) [2.059(4)]; C(1A)-Zn(1A)-N(3A) 104.92(14) [112.18(15)], C(1A)-Zn(1A)-N(5A) 112.84(14) [110.86(14)], C(1A)-Zn(1A)-H(1A) 122.0(12) [117.2(13)].

(Figure S3).[11] A lack of dimerization of **4** might be attributed to mutual repulsion between two [ZnH]$^+$ units (overall charge for each [ZnH]$^+$ unit in **4** is $+0.545$ by NBO analysis).[11] Steric effects could also be responsible for promoting the monomeric nature of **4** in the solid state as this species now contains added bulk (relative to **1** and **3**) in the form of a bound OTf$^-$ group; however, $^{19}$F NMR spectroscopy indicates that the OTf$^-$ unit in **4** is only weakly bound in [D$_8$]-THF ($\delta = -78.5$ ppm). A terminal Zn–H stretching band was located in the IR spectrum of **4** at 1766 cm$^{-1}$ which is shifted to higher frequency in relation to the terminal Zn$^{II}$ hydride vibrations in the ZnH$_2$ adducts **1** and **2** (1625 and 1635 cm$^{-1}$, respectively). The computed IR spectrum for **4** also contains a prominent Zn–H stretching band at 1765 cm$^{-1}$ which supports our initial structural assignment (Figure S7).[11]

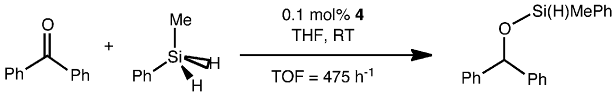
X-ray crystallography confirmed the presence of a monomeric zinc hydride adduct IPr·ZnH(OTf)·THF (**4**) with elongated Zn–O bonds involving the THF and OTf$^-$ units [2.140(4) and 2.073(4) Å, respectively; average of the two molecules in the asymmetric unit]. For comparison, IMes·Zn(OTf)$_2$·THF[20] displays significantly shorter Zn–O(Tf) distances of 1.966(2) and 1.973(2) Å. The zinc-bound hydride unit could be located in the electron difference map, however restraints were applied during the refinement thus preventing a detailed discussion of its metrical parameters. The adjacent Zn–C$_{IPr}$ bond length in **4** [2.036(4) Å avg.] is similar to the corresponding distance in the four-coordinate Zn adduct, IPr·ZnI$_2$·THF [2.0419(19) Å].[7]

We also attempted the one-electron reduction of IPr·ZnH(OTf)·THF (**4**) with Na, KC$_8$ and sodium naphthalenide in ethereal solvents, and in each case obtained free carbene IPr and Zn metal in place of the target Zn$^I$ complex IPr·Zn(H)-Zn(H)·IPr.[21]

In order to further probe the electrophilicity of the zinc center in IPr·ZnH(OTf)·THF (**4**), this species was treated with the strong donor 4-dimethylaminopyridine (DMAP). In the presence of two equivalents of DMAP, we were able to displace both THF and OTf$^-$ from the coordination sphere of zinc and generate the formal [ZnH]$^+$ complex [IPr·ZnH(DMAP)$_2$]OTf (**5**) (Scheme 1; Figure 4).[11] Compound **5** contains a tetrahedrally coordinated Zn$^{II}$ center with a slightly elongated C$_{IPr}$–Zn bond [2.073(5) Å avg.] in relation to the triflato precursor **4** [2.036(4) Å avg.]. The zinc-bound hydride could be located in the electron difference map but again, restraints were applied in the refinement of this residue. The Zn···OTf distances in **5** are $>8.0$ Å and thus lie well outside the sum of the van der Waals radii for Zn and O. $^{19}$F NMR spectroscopy also supported the presence of an outer-sphere OTf$^-$ ion in solution as a shielded resonance for this anion at $-78.7$ ppm was noted in [D$_8$]-THF.

There has been recent literature precedence for the use of either isolable or transiently generated zinc hydrides to catalyze the hydrosilylation of activated unsaturated compounds.[2b,5,22] Following the notion that the dual electrophilic and hydridic character within the [ZnH]$^+$ unit in **4** along with the facile access to an open coordination site would encourage substrate binding and hydride transfer from Zn, we decided to investigate the catalytic hydrosilylation of benzophenone. This portion of the study was buoyed by our computational studies which clearly show the retention of hydridic character at the zinc-bound H atom in **4** (NBO charge $-0.534$; Figure 5).[11]

When benzophenone was combined with a stoichiometric equivalent of MePhSiH$_2$ in the presence of 0.1 mol% of **4** in THF, the rapid and quantitative formation of the reduced product Ph$_2$C(H)OSi(H)MePh, Equation (3), was noted



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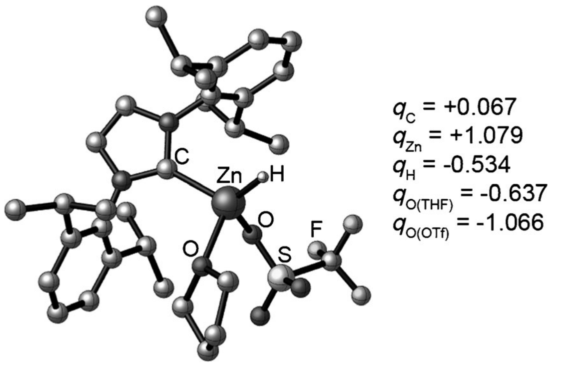

**Figure 5.** Selected NBO atomic charges for IPr·ZnH(OTf)·THF (4) at the M06-2X/cc-pVTZ level of theory. The corresponding molecular electrostatic potential (MEP) is available in Figure S9.[11]

(room temperature; TOF = turnover frequency = 475 h$^{-1}$). A likely mechanism of this transformation involves first the binding of ketone to form [IPr·Zn(H)OCPh$_2$]$^+$, followed by hydride transfer to the ketonic carbon to yield an alkoxide intermediate [IPr·Zn(OCPh$_2$)]$^+$ that is later converted into **4** and silylether by known silane-mediated metathesis.[3,23] The presence of strongly donating DMAP groups about Zn in **5** appears to shut down the activity of this species as no catalytic reduction of benzophenone was observed, thus lending support to the abovementioned mechanism. [IPr·ZnH(μ-H)]$_2$ (**1**) was also found to be active in the hydrosilylation of Ph$_2$CO under similar conditions albeit with slightly lower activity (TOF = 190 h$^{-1}$) relative to **4**. This is consistent with the increased reactivity of **4** due to the labile nature of the THF and OTf$^-$ that encourage substrate (ketone) binding/activation. Somewhat to our surprise, the less hindered ZnH$_2$ adduct [ImMe$_2{}^i$Pr$_2$·ZnH(μ-H)]$_2$ (**2**) was also quite active as a hydrosilylation catalyst and mediated the reduction of Ph$_2$CO with a TOF of ca. 600 h$^{-1}$. The high activity of **2** could be due to the presence of trace quantities of coordinatively unsaturated ImMe$_2{}^i$Pr$_2$·ZnH$_2$ monomer in solution, yet the VT and DOSY NMR studies described already suggest a predominance of the dimeric form in solution. For added comparison, the three-coordinate zinc(II) hydride [HC-(MeCNDipp)$_2$ZnH] (c.f. **V** in Scheme 1) catalyzes the hydrosilylation of Ph$_2$CO with an approximate TOF 0.6 h$^{-1}$. Thus our results portent well for the future use of [ZnH]$^+$ in abundant-metal catalysis.[22] Despite reacting quite rapidly with PhMeSiH$_2$, attempts to instigate hydrosilylation (from **4**) using tertiary silanes such as Et$_3$SiH or (EtO)$_3$SiH did not yield any catalysis; thus we are currently exploring analogous [ZnH]$^+$ complexes as **4** but with less-hindered carbene donors. Of added note, **4** was able to effect the hydroboration of benzophenone using the widely used reagent HBPin [Bpin = B(OCMe$_2$)$_2$] with a TOF of 1100 h$^{-1}$ at 25 °C. It should also be mentioned that the formal [ZnH]$^+$ complex IPr·ZnH(OTF)·THF (**4**) is significantly more thermally stable than the Zn$^{II}$ dihydride–carbene adducts **1** and **2**. Specifically, compounds **1** and **2** both degrade quantitatively to free carbene and zinc metal upon heating THF solutions to 60 °C for 4 h, while compound **4** remains unchanged upon heating to 60 °C in THF for two days. Furthermore, compounds **4** and **5** can be stored at ambient temperature in the solid state with no decomposition noted over multiple months of storage;[9] thus IPr·ZnH(OTF)·THF (**4**) represents an easy to handle base-metal hydrosilylation and hydroboration catalyst.

To summarize, we have prepared stable examples of donor-stabilized [ZnH]$^+$ cations supported by N-heterocyclic donors and demonstrate that the triflato-analogue IPr·ZnH-(OTf)·THF (**4**) is an active, yet thermally stable, catalyst for the hydrosilylation and hydroboration of ketones under mild conditions. Future work will expand upon these promising early studies to include a wider range of substrates and catalytic transformations (including the reduction of CO$_2$) whereby an electrophilic late metal center and an adjacent hydride unit act in concert to mediate bond activation.

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[9] In our hands, compound **1** shows signs of decomposition into Zn metal over time in the solid state (including upon storage at −35 °C under nitrogen in the absence of light).

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[11] For full synthetic, crystallographic and computational details see the Supporting Information. CCDC 997530 (**2**), 997531 (**3**), 997532 (**4**), and 997533 (**5**) 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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[21] We have investigated the structure of the intended $Zn^I$ hydride product, $ImMe_2{}^iPr_2{\cdot}Zn(H){-}Zn(H){\cdot}ImMe_2{}^iPr_2$ (and its isomers) by computational methods. It was found that the direct dehydrogenation of **2** to yield $ImMe_2{}^iPr_2{\cdot}Zn(H){-}Zn(H){\cdot}ImMe_2{}^iPr_2$ is endergonic ($\Delta G_{dehydro} = +18.4\ kcal\,mol^{-1}$; see Scheme S3).

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