

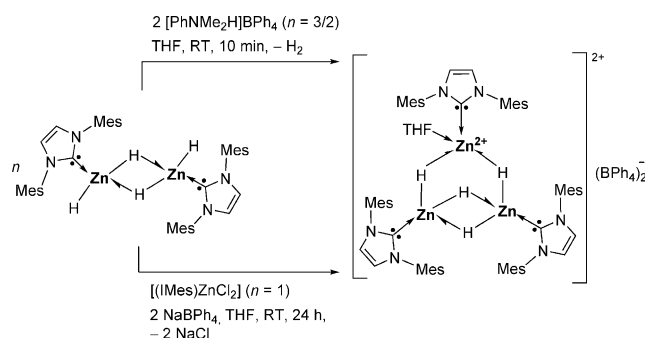
# A Cationic Zinc Hydride Cluster Stabilized by an N-Heterocyclic Carbene: Synthesis, Reactivity, and Hydrosilylation Catalysis\*\*

Arnab Rit, Alessandro Zanardi, Thomas P. Spaniol, Laurent Maron,\* and Jun Okuda\*

**Abstract:** The trinuclear cationic zinc hydride cluster  $[(\text{IMes})_3\text{Zn}_3\text{H}_4(\text{THF})(\text{BPh}_4)_2]$  (**1**) was obtained either by protonation of the neutral zinc dihydride  $[(\text{IMes})\text{ZnH}_2]_2$  with a Brønsted acid or by addition of the putative zinc dication  $[(\text{IMes})\text{Zn}(\text{THF})]^{2+}$ . A triply bridged thiophenolato complex **2** was formed upon oxidation of **1** with  $\text{PhS-SPh}$ . Protonolysis of **1** by methanol or water gave the corresponding trinuclear dicationic derivatives. At ambient temperature, **1** catalyzed the hydrosilylation of aldehydes, ketones, and nitriles. Carbon dioxide was also hydrosilylated under forcing conditions when using  $(\text{EtO})_3\text{SiH}$ , giving silylformate as the main product.

Since its discovery by Schlesinger et al. in 1947, zinc dihydride ( $\text{ZnH}_2$ )<sup>[1]</sup> has been used as hydride transfer reagent in organic synthesis.<sup>[2]</sup> Owing to its pronounced thermal sensitivity, the precise structure of zinc dihydride in the bulk<sup>[1,6]</sup> has remained unknown until this day. More recently, zinc dihydride was stabilized as thermally robust dimeric N-heterocyclic carbene (NHC) adducts,<sup>[3]</sup> following several reports on zinc monohydrides of the general formula  $(\text{LX})\text{ZnH}$  ( $\text{LX}$  = monoanionic ligand).<sup>[4]</sup> While anionic zinc hydrides<sup>[5]</sup> such as structurally characterized  $\text{Na}_2[\text{Zn}_2\text{Et}_4(\mu\text{-H})_2]$  and  $\text{Na}_3[\text{Zn}_2\text{iPr}_6(\mu\text{-H})]^{[5e]}$  had been known, a cationic zinc hydride  $[(\text{IPr})\text{ZnH}(\text{THF})](\text{OTf})$  ( $\text{IPr}$  = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) was reported only recently by Rivard et al.<sup>[5f]</sup> We describe here the synthesis, reactivity, and enhanced hydrosilylation activity of a trinuclear cationic zinc hydride cluster  $[(\text{IMes})_3\text{Zn}_3\text{H}_4(\text{THF})(\text{BPh}_4)_2]$  (**1**) ( $\text{IMes}$  = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) stabilized by an N-heterocyclic carbene.<sup>[6]</sup>

The cationic zinc hydride  $[(\text{IMes})_3\text{Zn}_3\text{H}_4(\text{THF})(\text{BPh}_4)_2]$  (**1**) was obtained by protonation of  $[(\text{IMes})\text{ZnH}_2]_2$ <sup>[3]</sup> with  $[\text{PhNMe}_2\text{H}]\text{BPh}_4$ , a Brønsted acid containing a weakly coordinating anion, under dihydrogen generation, and isolated in



**Scheme 1.** Preparation of a cationic zinc hydride cluster **1**.

86 % yield (Scheme 1). Alternatively, **1** was prepared in 82 % yield by treatment of  $[(\text{IMes})\text{ZnH}_2]_2$  with the putative zinc dication  $[(\text{IMes})\text{Zn}(\text{THF})]^{2+}$ , generated in situ by salt metathesis of  $[(\text{IMes})\text{ZnCl}_2]$ <sup>[7]</sup> with two equiv of  $\text{NaBPh}_4$  (Scheme 1). The zinc hydride cluster **1** is moderately soluble in THF and stable for over a week in THF solution. Isolated crystals of **1** are stable for months at  $-35^\circ\text{C}$  and decompose only at temperatures above  $165^\circ\text{C}$ .

Formation of a new hydrido complex was revealed by a hydride signal at  $\delta = 1.79$  ppm (showing no correlation in the  $^{13}\text{C}\text{-}^1\text{H}$  HSQC NMR spectrum) in the  $^1\text{H}$  NMR spectrum in  $[\text{D}_8]\text{THF}$ . One set of signals was observed for both the  $\text{IMes}$  and  $(\text{BPh}_4)^-$  anions. Variable temperature ( $-80$  to  $50^\circ\text{C}$ )  $^1\text{H}$  NMR spectra in  $[\text{D}_8]\text{THF}$  did not lead to decoalescence of the hydride signals, which is most likely due to fast exchange among the hydrido ligands. The coordinated THF in **1** was detected as broad signals at  $\delta = 1.61$  and  $3.16$  ppm in  $\text{CD}_2\text{Cl}_2$ . In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum, the zinc-coordinated NHC signal was detected at  $\delta = 169.25$  ppm in  $[\text{D}_8]\text{THF}$ , in the range of other zinc(II)–NHC complexes.<sup>[3,7]</sup>

The structure analysis of crystals grown from THF/hexane solution of **1** shows a trinuclear zinc dicationic core connected by four hydrides (Figure 1). Hydride **1** can be regarded as the  $[(\text{IMes})\text{Zn}(\text{THF})]^{2+}$  dication bonded to the neutral  $[(\text{IMes})\text{ZnH}_2]_2$  through two terminal hydrides. To the best of our knowledge, **1** is the first example of a hydride-bridged cationic molecular zinc cluster.

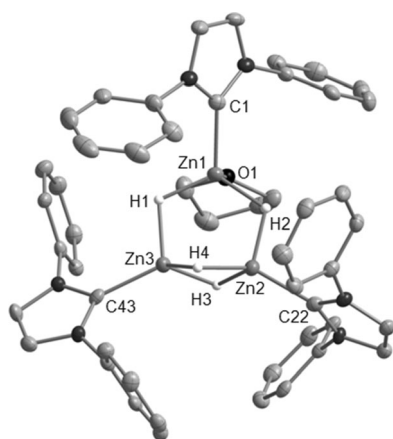
All three zinc centers in **1** are tetrahedrally coordinated. As expected for a cationic compound, the  $\text{Zn}\text{-}\mu\text{-H}$  ( $1.65(3)\text{--}1.75(4)$  Å) and  $\text{Zn}\text{-C}_{\text{NHC}}$  bonds ( $1.974(4)\text{--}1.995(4)$  Å) are shorter than those in the neutral parent complex  $[(\text{IMes})\text{ZnH}_2]_2$ <sup>[3]</sup> ( $\text{Zn}\text{-}\mu\text{-H}$   $1.71(4)\text{--}1.81(3)$  Å and  $\text{Zn}\text{-C}_{\text{NHC}}$   $2.052(3)\text{--}2.054(3)$  Å), reflecting the higher Lewis acidity of the zinc atoms in **1**. Three zinc atoms form a triangle with two hydrides bridging the short  $\text{Zn}_2\cdots\text{Zn}_3$  distance ( $2.4137(7)$  Å,

[\*] Dr. A. Rit, Dr. A. Zanardi, Dr. T. P. Spaniol, Prof. Dr. J. Okuda  
Institute of Inorganic Chemistry, RWTH Aachen University  
Landoltweg 1, 52056 Aachen (Germany)  
E-mail: jun.okuda@ac.rwth-aachen.de

Prof. Dr. L. Maron  
Université de Toulouse et CNRS, INSA, UPS, CNRS; UMR 5215  
LPCNO  
135 avenue de Rangouli, F-31077 Toulouse (France)  
E-mail: laurent.maron@irsamc.ups-tlse.fr

[\*\*] We thank the Deutsche Forschungsgemeinschaft for financial support through the International Research Training Group "Selectivity in Chemo- and Biocatalysis" (GRK 1628). L.M. is a fellow of the Alexander von Humboldt Foundation. We thank Toni Gossen for assistance with the NMR spectroscopy.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201408346>.



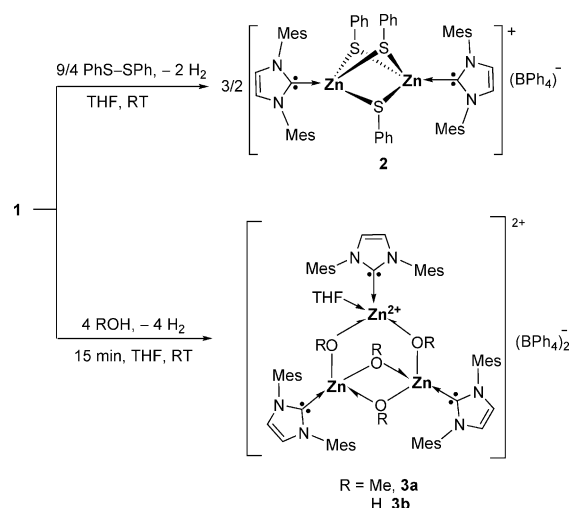
**Figure 1.** Molecular structure of the dication  $[(\text{IMes})_3\text{Zn}_3\text{H}_4(\text{THF})]^{2+}$  in 1:2 THF (the hydrogen atoms except those connected to zinc, co-crystallized THF molecules,  $\text{BPh}_4^-$  anions, and the methyl groups of the mesityl moieties are omitted for clarity).

as found in  $\text{RZn}(\mu\text{-H})\text{ZnR}$ <sup>[8]</sup> and one hydride bridging each of the two long  $\text{Zn}\cdots\text{Zn}$  separations ( $\text{Zn1}\cdots\text{Zn2}$  2.8116(7) Å,  $\text{Zn1}\cdots\text{Zn3}$  2.8008(7) Å). The  $(\text{BPh}_4)^-$  anions do not show significant interactions with the cationic part.

The hydrido ligands in **1** did not exchange with  $\text{D}_2$  (1 bar) in  $[\text{D}_8]\text{THF}$  over a week at 25 °C;  $[(\text{IMes})\text{ZnH}_2]_2$  was also found to be inert.<sup>[3]</sup> The concentration dependence of the  $^1\text{H}$  NMR chemical shifts of the IMes together with the hydrido ligands and the observation of free THF in  $[\text{D}_8]\text{THF}$  solution indicate that the coordinated THF is labile. When **1** was reacted with 1 equiv of  $\text{PMe}_3$  in  $\text{CD}_2\text{Cl}_2$ , the coordinated THF was completely replaced, as revealed by the  $^1\text{H}$  NMR spectrum, and the coordination of  $\text{PMe}_3$  to the zinc center is indicated by a signal at  $\delta = -46.96$  ppm in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum.<sup>[9]</sup> No  $\nu_{\text{Zn-H}}$  stretching frequencies for **1** could be assigned, as they overlap with the aromatic vibrations of the IMes ligand.<sup>[3,8]</sup>

Bonding analysis of **1** at the DFT level (see the Supporting Information) gave geometric parameters close to the experimental values. The computed  $\text{Zn-H}$  bond lengths (1.69–1.76 Å) agree with the experimental values (1.65(3)–1.75(4) Å). Similarly, the  $\text{Zn}\cdots\text{Zn}$  distances are reproduced: the short  $\text{Zn2}\cdots\text{Zn3}$  distance (2.43 Å vs 2.4139(7) Å) as well as the two long  $\text{Zn1}\cdots\text{Zn2}/\text{Zn3}$  distances (2.86–2.88 Å vs. 2.8008(7)–2.8116(6) Å). The NBO analysis indicates that the charge at Zn1 is almost twice of that at Zn2 and Zn3 (+0.92 vs. +0.50), in line with a formal +2 charge located at Zn1. While the Wiberg index of 0.33 for the  $\text{Zn2}\cdots\text{Zn3}$  distance indicates a partial bonding interaction, the Wiberg bond indexes of 0.14 calculated for  $\text{Zn1}\cdots\text{Zn2}$  and  $\text{Zn1}\cdots\text{Zn3}$  point to weaker interactions.

With 2.25 equiv of  $\text{PhS-SPh}$ , the hydrido ligands in **1** were readily oxidized to dihydrogen with concomitant reduction of  $\text{PhS-SPh}$  to  $(\text{PhS})^-$  to give the dinuclear thiophenolato complex  $[(\text{IMes})_2\text{Zn}_2(\text{SPh})_3](\text{BPh}_4)$  (**2**) as colorless crystals in 69 % yield (Scheme 2). Dihydrogen formation was observed by  $^1\text{H}$  NMR spectroscopy. Complex **2** is formed by one-electron oxidation of one of the  $(\text{BPh}_4)^-$  anions under release of  $\text{BPh}_3$  (detected by  $^{11}\text{B}$  NMR spectroscopy;  $\delta = 67$  ppm in

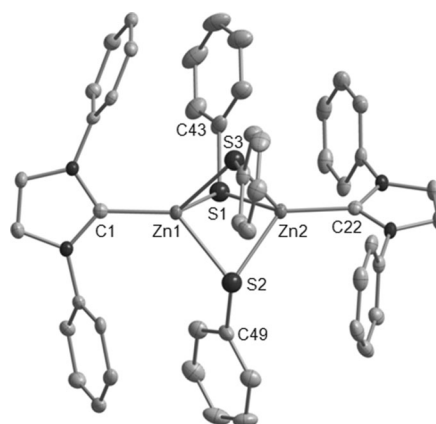


**Scheme 2.** Reactivity studies of **1**.

$\text{C}_6\text{D}_6$ ) and biphenyl (detected by GC-MS analysis). Similar oxidation of  $(\text{BPh}_4)^-$  has also been observed with other metal complexes.<sup>[10]</sup> Complex **2** is readily soluble in dichloromethane, but sparingly soluble in THF. The  $^1\text{H}$  NMR spectrum of **2** in  $\text{CD}_2\text{Cl}_2$  shows one set of signals for each of the IMes and thiophenolato ligands and  $(\text{BPh}_4)^-$  anions in 2:3:1 ratio, in agreement with the formulation of **2** as  $[(\text{IMes})_2\text{Zn}_2(\text{SPh})_3]-(\text{BPh}_4)$ .

Single crystals of **2** suitable for X-ray diffraction were grown from a saturated THF solution. The molecular structure contains a non-crystallographic  $\text{C}_3$ -symmetric  $\text{Zn}_2\text{S}_3$  core with three sulfur atoms forming an almost equilateral triangle connected to a zinc atom on each side of the plane (Figure 2). The  $\text{Zn1}\cdots\text{Zn2}$  distance of 2.791(6) Å is close to the  $\text{Zn}\cdots\text{Zn}$  separations in **1** that are bridged by one hydrido ligand.

Zinc hydride cation **1** reacted readily with four equivalents of methanol or water at room temperature under immediate evolution of dihydrogen to give the methoxy



**Figure 2.** Molecular structure of the monocation  $[(\text{IMes})_2\text{Zn}_2(\text{SPh})_3]^+$  in 2-THF (hydrogen atoms, co-crystallized THF molecules,  $\text{BPh}_4^-$  anions, and the methyl groups of the mesityl moieties are omitted for clarity).

[(IMes)<sub>3</sub>Zn<sub>3</sub>(OMe)<sub>4</sub>(THF)](BPh<sub>4</sub>)<sub>2</sub> (**3a**) and hydroxy [(IMes)<sub>3</sub>Zn<sub>3</sub>(OH)<sub>4</sub>(THF)](BPh<sub>4</sub>)<sub>2</sub> (**3b**) complexes in 83 and 80% yield, respectively (Scheme 2). All of the hydrido ligands in **1** reacted within 15 min; no protonation of the IMes ligands was observed under these conditions. Complexes **3a,b** are readily soluble in THF and dichloromethane and are stable at –35 °C as solids.

The methoxy unit in **3a** is characterized by one singlet at  $\delta = 2.20$  ppm in the <sup>1</sup>H NMR spectrum and by one signal at  $\delta = 55.62$  ppm in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum ([D<sub>8</sub>]THF). The hydroxy unit in **3b** was detected as singlet at  $\delta = -1.36$  ppm in the <sup>1</sup>H NMR spectrum ([D<sub>8</sub>]THF) and at 3648 cm<sup>-1</sup> in the IR spectrum, which are in the same regions of those of other hydroxide bridged zinc complexes.<sup>[11]</sup> <sup>1</sup>H NMR patterns similar to those of **1** were observed for both the IMes and BPh<sub>4</sub> counterions in **3a,b** and the integration ratios of methoxy/hydroxy units: IMes ligands: (BPh<sub>4</sub>)<sup>-</sup> anion of 4:3:2 confirmed the retention of the trinuclear structures as for **1**. The molecular structure of **3b**, confirmed by single crystal X-ray diffraction, showed a trinuclear structure similar to that of **1**, with zinc centers bridged by  $\mu_2$ -hydroxide ligands (see the Supporting Information). As observed for **1**, the THF ligands in **3a,b** are also labile in [D<sub>8</sub>]THF. IMes coordination to zinc was revealed by signals at  $\delta = 170.14$  (**3a**) and 171.83 (**3b**) ppm in the <sup>13</sup>C{<sup>1</sup>H} NMR spectra in [D<sub>8</sub>]THF. <sup>1</sup>H NMR spectroscopic monitoring showed that **3a** react with silanes PhSiH<sub>3</sub>, PhMeSiH<sub>2</sub>, or (EtO)<sub>3</sub>SiH at room temperature to generate **1** quantitatively.

Preliminary studies showed fast insertion of PhCHO into the Zn–H bonds in **1**, even though a single product could not be isolated from the reaction with 4 equiv of benzaldehyde. This observation along with the conversion of the alkoxy complex **3a** into **1** when reacted with silanes prompted us to probe the suitability of **1** as catalyst for hydrosilylation reaction. Recently, zinc hydride species have proved to be an alternative to precious-metal-based catalysts for various organic transformations.<sup>[12]</sup> Hydrosilylation of carbonyl and nitrile substrates results in reduction to form silyl ethers and silyl imines, respectively.<sup>[13,14]</sup>

Employing 0.5 mol % of **1**, quantitative hydrosilylation of PhCHO with primary silane PhSiH<sub>3</sub> (Table 1) to give 95 % of PhSiH(OCH<sub>2</sub>Ph)<sub>2</sub> was observed within 10 min at room temperature. PhCHO can also be inserted into all three Si–H bonds of PhSiH<sub>3</sub> to give PhSi(OCH<sub>2</sub>Ph)<sub>3</sub>, an alternative synthetic approach towards PhSi(OR)<sub>3</sub> derivatives.<sup>[12a]</sup> Secondary silane PhMeSiH<sub>2</sub> works also efficiently (entries 2 and 7). While the tertiary silane PhMe<sub>2</sub>SiH was less reactive, comparatively inexpensive (EtO)<sub>3</sub>SiH shows high activity.<sup>[15]</sup> PhCHO is hydrosilylated with (EtO)<sub>3</sub>SiH to the corresponding silyl ether within 1 h (entry 3). Notably, this catalytic system tolerates different substituents on aldehydes, such as nitro, cyano, halide, and alkoxy groups (see the Supporting Information). While an electron-withdrawing group marginally increases the reaction rates (entries 4–5), an electron-donating group (OMe) slows down the rate (entry 6). Beside aromatic aldehydes, alkyl aldehyde *n*BuCHO (entry 8) as well as ketones (entries 9 and 10) were also efficiently hydrosilylated at room temperature. Complex [(IPr)ZnH(THF)](OTf) was found to catalyze the hydrosilylation of Ph<sub>2</sub>CO

**Table 1:** Hydrosilylation of aldehydes and ketones catalyzed by **1**.

$\text{R}^1\text{C}(=\text{O})\text{R}^2 + \text{R}_3\text{SiH} \xrightarrow[\text{[D}_8\text{]THF, 25 }^\circ\text{C}]{\text{catalyst 1}} \text{R}_3\text{Si}-\text{O}-\text{CH}(\text{R}^1)\text{R}^2$					
Entry	R <sup>1</sup> , R <sup>2</sup>	Silane	Time [min]	Catalyst loading [mol %]	Conv. [%] <sup>[a]</sup>
1	Ph, H	PhSiH <sub>3</sub>	10	0.5	> 98
2	Ph, H	PhMeSiH <sub>2</sub>	15	2.2	> 98
3	Ph, H	(EtO) <sub>3</sub> SiH	60	2.2	> 98
4	4-F-C <sub>6</sub> H <sub>4</sub> , H	(EtO) <sub>3</sub> SiH	45	2.2	> 98
5	4-Br-C <sub>6</sub> H <sub>4</sub> , H	(EtO) <sub>3</sub> SiH	50	2.2	> 98
6	4-OMe-C <sub>6</sub> H <sub>4</sub> , H	(EtO) <sub>3</sub> SiH	120	2.2	> 98
7	4-OMe-C <sub>6</sub> H <sub>4</sub> , H	PhMeSiH <sub>2</sub>	30	2.2	> 98
8	<i>n</i> Bu, H	(EtO) <sub>3</sub> SiH	180	2.7	97
9	Ph, Ph	(EtO) <sub>3</sub> SiH	180	3.3	95
10	Ph, Me	PhMeSiH <sub>2</sub>	60	3.3	87

[a] determined by <sup>1</sup>H NMR spectroscopy.

**Table 2:** Hydrosilylation of nitriles catalyzed by **1**.<sup>[a]</sup>

$\text{R}^1\text{C}\equiv\text{N} + \text{R}_3\text{SiH} \xrightarrow[\text{[D}_8\text{]THF, 25 }^\circ\text{C}]{\text{catalyst 1}} \text{R}^1\text{C}(\text{H})=\text{N}-\text{SiR}_3$				
Entry	R <sup>1</sup>	Silane	Time [h]	Conv. [%] <sup>[b]</sup>
1	Ph	(EtO) <sub>3</sub> SiH	9	> 98
2	Ph	PhMeSiH <sub>2</sub>	7	> 98
3	3-Br-C <sub>6</sub> H <sub>4</sub>	(EtO) <sub>3</sub> SiH	4	90
4	4-OMe-C <sub>6</sub> H <sub>4</sub>	(EtO) <sub>3</sub> SiH	8	94
5	2-naphthyl	(EtO) <sub>3</sub> SiH	6	> 98
6	<i>t</i> Bu	(EtO) <sub>3</sub> SiH	48	92
7	4-pyridyl	(EtO) <sub>3</sub> SiH	24	41 <sup>[c]</sup>

[a] 3.3 mol % catalyst loading. [b] Determined by <sup>1</sup>H NMR spectroscopy. [c] Catalyst deactivation.

only with PhMeSiH<sub>2</sub>, no catalysis was observed with tertiary silanes.<sup>[5f]</sup> Complex **1** shows comparatively better catalytic activity than some transition-metal systems, which requires either higher temperature or longer reaction time.<sup>[16]</sup>

Nitriles can also be catalytically hydrosilylated by **1** to give monoreduced *N*-silyl imines at room temperature (Table 2). This is a rare example where such a process is catalyzed by a non-transition-metal catalyst.<sup>[12d]</sup> Benzonitrile was hydrosilylated with both PhMeSiH<sub>2</sub> and (EtO)<sub>3</sub>SiH (entries 1–2). Electron-withdrawing/releasing substituents on the phenyl ring are tolerated and facile hydrosilylation was observed (entry 3–4). 2-Naphthonitrile was hydrosilylated faster than benzonitrile (entry 5). Alkyl nitrile *t*BuCN was reduced slowly (entry 6). For 4-pyridinecarbonitrile, only 41 % conversion was observed within 1 d before the catalyst was deactivated (entry 7). Complex **1** shows catalytic activity comparable with that reported for [(Dipp-nacnac)ZnH] (Dipp-nacnac = CH[(CMe)<sub>2</sub>(2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N))<sub>2</sub>).<sup>[12d]</sup>

Competitive hydrosilylation experiment with 1:1 mixture of benzaldehyde and benzonitrile when using PhMeSiH<sub>2</sub> (2.2 mol % **1**, 25 °C) showed that only benzaldehyde was quantitatively reduced to PhSiHMe(OCH<sub>2</sub>Ph) within 15 min

at room temperature, leaving benzonitrile unchanged (see the Supporting Information).

Based on the observations that **1** readily inserts benzaldehyde and the resulting alkoxy compound (not isolated) as well as **3a** regenerates **1** when reacted with silanes (see the Supporting Information), the following catalytic cycle is proposed. Insertion of carbonyl functions into the Zn–H bonds is followed by the reaction of the resulting alkoxy intermediates with silanes to regenerate **1** along with the release of silyl ethers. This proposal is supported by NMR experiments. When the deuterium isotopomer **1-D<sub>4</sub>** was reacted with 4 equiv of PhCHO followed by addition of the silane PhSiH<sub>3</sub>, PhMeSiH<sub>2</sub>, or (EtO)<sub>3</sub>SiH, quantitative formation of **1-H<sub>4</sub>** was observed. On the other hand, when **1-H<sub>4</sub>** was treated with 4 equiv of PhCHO followed by PhSiD<sub>3</sub>, the deuterium isotopomer **1-D<sub>4</sub>** was obtained quantitatively (see the Supporting Information). A similar mechanism has been postulated for the hydrosilylation catalyzed by a [(NHC)Cu<sup>+</sup>H]<sup>[17]</sup> and a [[2,6-(iPr<sub>2</sub>PO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]NiH] catalyst.<sup>[16b]</sup> Alternatively, coordination of Si–H  $\sigma$ -bond or oxidative addition of silanes to a zinc center,<sup>[18]</sup> proposed for other systems, is quite unlikely to operate here, as **1** did not react with PhMeSiH<sub>2</sub> or (EtO)<sub>3</sub>SiH over one day at room temperature in [D<sub>8</sub>]THF.

Compound **1** was also found to catalyze the hydrosilylation of more challenging substrate CO<sub>2</sub> (40 bar, THF, 60 °C). Complete conversion was achieved after 64 h when (EtO)<sub>3</sub>SiH and 1 mol % of **1** were used. Triethoxysilylformate (<sup>1</sup>H NMR: 8.01 ppm (CHO); <sup>13</sup>C NMR: 157.9 ppm (CHO); <sup>29</sup>Si NMR: –86.4 ppm) was identified as the major product (>80 %) along with bis(triethoxysiloxy) methane (<20 %).<sup>[12a]</sup>

In conclusion, we have isolated a cationic zinc hydride cluster<sup>[19]</sup> that retains hydridic character and shows versatile hydrosilylation activity toward electrophiles such as carbonyl compounds, nitriles, and importantly more challenging substrate carbon dioxide. Detailed mechanistic studies including the nature of the active species are underway.

Received: August 18, 2014

Published online: September 24, 2014

**Keywords:** carbon dioxide · homogeneous catalysis · hydrides · N-heterocyclic carbenes · zinc

- [1] a) A. E. Finholt, A. C. Bond, Jr., H. I. Schlesinger, *J. Am. Chem. Soc.* **1947**, *69*, 1199–1203; b) J. J. Watkins, E. C. Ashby, *Inorg. Chem.* **1974**, *13*, 2350–2354; c) E. C. Ashby, J. J. Watkins, D. Greig, D. F. Shriver, *Inorg. Synth.* **1977**, *17*, 6–8; d) A. J. De Koning, J. Boersma, G. J. M. Van Der Kerk, *J. Organomet. Chem.* **1980**, *186*, 159–172; e) E. C. Ashby, A. B. Goel, *J. Organomet. Chem.* **1981**, *204*, 139–145; f) For gas phase structure, see: A. Shayesteh, D. R. T. Appadoo, I. E. Gordon, P. F. Bernath, *J. Am. Chem. Soc.* **2004**, *126*, 14356–14357; g) For noble gas matrix isolation study, see: T. M. Greene, W. Brown, L. Andrews, A. J. Downs, G. V. Chertihin, N. Rueneberg, P. Pyykkö, *J. Phys. Chem.* **1995**, *99*, 7925–7934.
- [2] a) Y. Gao, H. Urabe, F. Sato, *J. Org. Chem.* **1994**, *59*, 5521–5523; b) Y. Gao, K. Harada, T. Hata, H. Urabe, F. Sato, *J. Org. Chem.* **1995**, *60*, 290–291.
- [3] A. Rit, T. P. Spaniol, L. Maron, J. Okuda, *Angew. Chem. Int. Ed.* **2013**, *52*, 4664–4667; *Angew. Chem.* **2013**, *125*, 4762–4765.
- [4] For selected references, see: a) A. Looney, R. Han, I. B. Gorrell, M. Cornebise, K. Yoon, G. Parkin, A. L. Rheingold, *Organometallics* **1995**, *14*, 274–278; b) H. Hao, C. Cui, H. W. Roesky, G. Bai, H.-G. Schmidt, M. Noltemeyer, *Chem. Commun.* **2001**, 1118–1119; c) M. P. Coles, S. M. El-Hamrni, J. D. Smith, P. B. Hitchcock, *Angew. Chem. Int. Ed.* **2008**, *47*, 10147–10150; *Angew. Chem.* **2008**, *120*, 10301–10304; d) J. Spielmann, D. Piesik, B. Wittkamp, G. Jansen, S. Harder, *Chem. Commun.* **2009**, 3455–3456; e) B. Gutschank, S. Schulz, D. Bläser, R. Boese, C. Wölper, *Organometallics* **2010**, *29*, 6133–6136; f) D. Mukherjee, A. Ellern, A. D. Sadow, *J. Am. Chem. Soc.* **2010**, *132*, 7582–7583; g) W. Sattler, G. Parkin, *J. Am. Chem. Soc.* **2011**, *133*, 9708–9711; h) N. J. Brown, J. E. Harris, X. Yin, I. Silverwood, A. J. P. White, S. G. Kazarian, K. Hellgardt, M. S. P. Shaffer, C. K. Williams, *Organometallics* **2014**, *33*, 1112–1119; i) P. Jochmann, D. W. Stephan, *Chem. Commun.* **2014**, *50*, 8395–8397.
- [5] a) G. J. Kubas, D. F. Shriver, *J. Am. Chem. Soc.* **1970**, *92*, 1949–1954; b) D. F. Shriver, G. J. Kubas, J. A. Marshall, *J. Am. Chem. Soc.* **1971**, *93*, 5076–5079; c) E. C. Ashby, R. G. Beach, *Inorg. Chem.* **1971**, *10*, 2486–2488; d) E. C. Ashby, J. J. Watkins, *Inorg. Chem.* **1973**, *12*, 2493–2503; e) A. Lennartson, M. Håkansson, S. Jagner, *Angew. Chem. Int. Ed.* **2007**, *46*, 6678–6680; *Angew. Chem.* **2007**, *119*, 6798–6800; f) P. A. Lummis, M. R. Momeni, M. W. Lui, R. McDonald, M. J. Ferguson, M. Miskolcic, A. Brown, E. Rivard, *Angew. Chem. Int. Ed.* **2014**, *53*, 9347–9351; *Angew. Chem.* **2014**, *126*, 9501–9505.
- [6] For reviews on N-heterocyclic carbenes, see: a) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; *Angew. Chem.* **2008**, *120*, 3166–3216; b) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 8810–8849; *Angew. Chem.* **2010**, *122*, 8992–9032.
- [7] D. Wang, K. Wurst, M. R. Buchmeiser, *J. Organomet. Chem.* **2004**, *689*, 2123–2130.
- [8] a) Z. Zhu, R. J. Wright, M. M. Olmstead, E. Rivard, M. Brynda, P. P. Power, *Angew. Chem. Int. Ed.* **2006**, *45*, 5807–5810; *Angew. Chem.* **2006**, *118*, 5939–5942; b) Z. Zhu, M. Brynda, R. J. Wright, R. C. Fischer, W. A. Merrill, E. Rivard, R. Wolf, J. C. Fetting, M. A. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2007**, *129*, 10847–10857.
- [9] a) F. A. Cotton, G. Schmid, *Polyhedron* **1996**, *15*, 4053–4059; b) D. J. Darensbourg, M. S. Zimmer, P. Rainey, D. L. Larkins, *Inorg. Chem.* **2000**, *39*, 1578–1585.
- [10] W. J. Evans, S. A. Kozimer, J. W. Zeller, *Chem. Commun.* **2005**, 4681–4683.
- [11] a) D. L. Reger, A. E. Pascui, P. J. Pellechia, M. D. Smith, *Inorg. Chem.* **2013**, *52*, 11638–11649; b) G. Anantharaman, K. Elango, *Organometallics* **2007**, *26*, 1089–1092.
- [12] a) W. Sattler, G. Parkin, *J. Am. Chem. Soc.* **2012**, *134*, 17462–17465; b) D. Mukherjee, R. R. Thompson, A. Ellern, A. D. Sadow, *ACS Catal.* **2011**, *1*, 698–702; c) P. Jochmann, D. W. Stephan, *Angew. Chem. Int. Ed.* **2013**, *52*, 9831–9835; *Angew. Chem.* **2013**, *125*, 10014–10018; d) C. Boone, I. Korobkov, G. I. Nikonov, *ACS Catal.* **2013**, *3*, 2336–2340; e) A. Rit, T. P. Spaniol, J. Okuda, *Chem. Asian J.* **2014**, *9*, 612–619.
- [13] *The Chemistry of Organic Silicon Compounds*, Vol. 3 (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **2001**.
- [14] For reviews on hydrosilylation, see: a) *Hydrosilylation: A Comprehensive Review on Recent Advances* (Ed.: B. Marciniec), Springer, Heidelberg, **2009**; b) O. Riant, N. Mostefaï, J. Courmarcel, *Synthesis* **2004**, 2943–2958.
- [15] Hydrosilylation of aldehydes with (EtO)<sub>3</sub>SiH gave a mixture of silyl ethers (R<sub>1</sub>CH<sub>2</sub>O)<sub>x</sub>Si(OEt)<sub>4-x</sub> (x = 0–3) by redistribution of alkoxide ligands, which has also been observed previously;<sup>[12d,16a]</sup> this is presumably catalyzed by a metal hydride species.



- [16] Selected references: a) E. Peterson, A. Y. Khalimon, R. Simionescu, L. G. Kuzmina, J. A. K. Howard, G. I. Nikonov, *J. Am. Chem. Soc.* **2009**, *131*, 908–909; b) S. Chakraborty, J. A. Krause, H. Guan, *Organometallics* **2009**, *28*, 582–586.
- [17] a) H. Kaur, F. K. Zinn, E. D. Stevens, S. P. Nolan, *Organometallics* **2004**, *23*, 1157–1160; b) S. Díez-González, N. M. Scott, S. P. Nolan, *Organometallics* **2006**, *25*, 2355–2358; c) S. Díez-González, E. D. Stevens, N. M. Scott, J. L. Petersen, S. P. Nolan, *Chem. Eur. J.* **2008**, *14*, 158–168.
- [18] a) I. Ojima, T. Kogure, M. Kumagai, S. Horiuchi, T. Sato, *J. Organomet. Chem.* **1976**, *122*, 83–97; b) G. Du, P. E. Fanwick, M. M. Abu-Omar, *J. Am. Chem. Soc.* **2004**, *126*, 8072–8073; c) T. Steinke, C. Gemel, M. Cokoja, M. Winter, R. A. Fischer, *Angew. Chem. Int. Ed.* **2004**, *43*, 2299–2302; *Angew. Chem.* **2004**, *116*, 2349–2352.
- [19] CCDC 1014080 (**1**), 1014081 (**2**), and 1014082 (**3b**) 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](http://www.ccdc.cam.ac.uk/data_request/cif).
-