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## COMMUNICATION

## Monomeric Sn(II) and Ge(II) hydrides supported by a tridentate pincer-based ligand†‡

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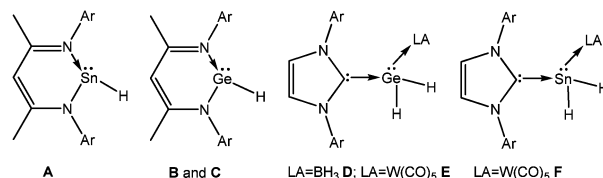
Herein we report the syntheses of terminal Sn(II) (**3**) and Ge(II) (**4**) hydrides from the corresponding chloride precursors  $[\{2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{NCMe}\}_2\text{C}_6\text{H}_3\text{MCl}]$  ( $\text{M} = \text{Sn}$  (**1**),  $\text{Ge}$  (**2**)) using  $[\text{K}\{\text{B}(\text{sec-Bu})_3\}\text{H}]$  as a hydrogenating agent. Combination of steric shielding and intramolecular  $\text{N} \rightarrow \text{M}$  interactions resulted in the protection of  $\text{M}(\text{II})\text{-H}$  bonds.

Main group metal hydrides are extremely important in chemical synthesis. They are notably used as precursors for the preparation of other metal hydrides, as reducing agents for a big variety of inorganic and organic substrates and function as potential feedstocks for hydrogen storage.<sup>1,2</sup> Hydrides are considered as promising candidates for the synthesis of new clusters and nanoparticles by controlled thermolysis.<sup>3</sup> By taking advantage of sterically bulky terphenyl ligands Power *et al.* isolated the first Sn(II) hydride  $[\{2,6\text{-Trip}_2\text{C}_6\text{H}_3\text{Sn}(\mu\text{-H})\}_2]$ , Trip = 2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>. However, this compound is dimeric with bridging hydrogen atoms.<sup>4</sup> The first dimeric structurally characterized Ge(II) hydride  $[\text{ArGeH}]_2$  (Ar = 2,6-Dipp<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Dipp = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) was reported by the same group.<sup>5</sup> Moreover in 2006, the first structurally characterized terminal Sn(II) and Ge(II) hydrides  $[\{\text{HC}(\text{CMeNAr})_2\}\text{MH}]$ , Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, M = Sn (**A**) and Ge (**B**)] were outlined, but compound **A** exhibited weak intermolecular Sn–H...Sn contacts.<sup>6</sup> In 2011, Jones *et al.* reported the synthesis of an analogous Ge(II) hydride  $[\{\text{HC}(\text{CMeNMe}_3)_2\}\text{GeH}]$ , (Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) (**C**) stabilized by a similar β-diketiminato backbone.<sup>7</sup> Further attempts to prepare the corresponding tin(II) hydride complex were not successful.<sup>7</sup> The instability of the tin analogue could

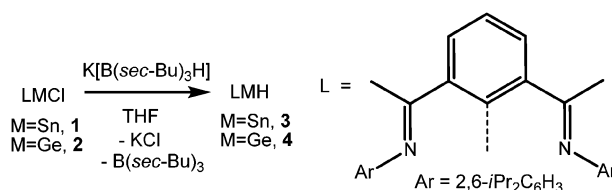
be due to the weaker nature of the Sn–H bond relative to the Ge–H bond.<sup>8</sup> Apart from these, Rivard *et al.* recently described the stabilization of the parent GeH<sub>2</sub> and SnH<sub>2</sub> complexes using a *N*-heterocyclic carbene (NHC) as a donor and a BH<sub>3</sub> or metal carbonyl complex as an acceptor (**D–F**).<sup>9</sup> These hydrides are coordinatively saturated because the lone pair of electrons at Ge and Sn effectively takes part in the coordination (Chart 1). However, in an insertion reaction of **F** with benzaldehyde, the C: → Sn bond readily cleaves indicating the lability of the NHC donor.<sup>9b</sup>

New monomeric Sn(II) hydride could be achieved by increasing the coordination around the Sn(II) center. Very recently, we have reported a pincer supported bis-stannylene ( $[\{2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{NCMe}\}_2\text{C}_6\text{H}_3\text{Sn}]_2$ ) with a Sn(II)–Sn(II) bond by reducing  $[\{2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{NCMe}\}_2\text{C}_6\text{H}_3\text{SnCl}]$  (**1**) with KC<sub>8</sub>.<sup>10</sup> So *et al.* reported the analogous bis-germylene compound using a comparable ligand.<sup>11</sup> Moreover, Jurkschat *et al.* outlined the synthesis of  $[\{2,6\text{-}(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{Sn}(\text{H})\text{W}(\text{CO})_5]$ , a pincer based Sn(II) hydride stabilized in the coordination sphere of W(CO)<sub>5</sub>.<sup>12</sup> This encouraged us to prepare the hitherto elusive terminal Sn(II) hydride.

Treatment of compounds **1** and **2**, respectively, with  $[\text{K}\{\text{B}(\text{sec-Bu})_3\}\text{H}]$  in THF at 0 °C followed by recrystallization in toluene afforded dark reddish-orange colored crystals of **3** and **4**

Ar=2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> for **A**, **B**, **D–F**; Ar=2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> for **C**

**Chart 1** Monomeric Lewis base coordinate Sn(II) and Ge(II) hydrides **A–C**; Lewis acid and Lewis base coordinate Sn(II) and Ge(II) hydrides **D–F**.



**Scheme 1** Syntheses of **3** and **4**.

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† This paper is dedicated to Professor Anton Meller on the occasion of his 80th birthday.

‡ Electronic supplementary information (ESI) available: Full synthetic, spectroscopic, X-ray crystallographic and theoretical details for **3** and **4**. CCDC 863378 (**3**) and 863377 (**4**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc31214j

(Scheme 1). Conclusive evidence for the formation of the monomeric hydrides **3** and **4** was obtained by X-ray crystallography (Fig. 1), NMR and IR spectroscopy, and theoretical calculations. The stabilization of **3** and **4** may be occurring by increasing the electron density at the empty p orbital of the metal centre from the adjacent nitrogen donors. The most noticeable feature of **3** is the absence of any kind of intermolecular interactions (Sn–Sn or Sn–H) in the crystal packing confirming an exclusively monomeric nature of Sn(II) hydride. However, the position of the MH (M = Sn and Ge) hydrogen atom cannot be determined reliably. Therefore, the corresponding bond distance and angle are not discussed herein. In both cases the MH moiety is disordered over two positions resulting in a superposition of the electron density of the M–H bond and the Ge and Sn lone pairs, respectively (for more details see ESI†).

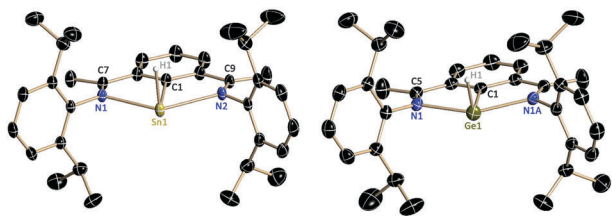
Compound **3** crystallizes in the monoclinic space group *Pc*.<sup>13</sup> The molecular structure of **3** reveals that the Sn atom is four-coordinated and exhibits a distorted seesaw geometry considering the lone pair of electrons. The flanking aromatic rings are nearly perpendicular to the central ring of the ligand. The two nitrogen atoms are coordinated intra-molecularly to the Sn atom with bond lengths of 2.4538(13) and 2.4664(14) Å, respectively, which are consistent with those for intra-molecularly coordinated Sn–N bonds.<sup>14</sup> Similarly, the Sn–C bond length of **3** (2.1665(16) Å) is in good accordance with the Sn–C bond distances in  $[\{2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{NCMe}\}_2\text{C}_6\text{H}_3\text{Sn}]_2$  (2.1575(18) and 2.1880(19) Å)<sup>10</sup> and  $[\{2,6\text{-}(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{Sn}]_2$  (2.180(11) and 2.193(10) Å).<sup>15</sup> Compound **4** crystallizes in the monoclinic space group *C2/c* and adopts an isostructural motif as its Sn–H congener **3**. The two intra-molecularly coordinated Ge–N bond lengths in **4** (2.2722(15) and 2.2746(15) Å) are in line with that of  $[\{2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{NC(H)}\}_2\text{C}_6\text{H}_3\text{GeCl}]$  (2.247(3) Å).<sup>11</sup> The Ge1–C1 bond length (1.9483(18) Å) is shorter compared to that of  $[\{2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{NC(H)}\}_2\text{C}_6\text{H}_3\text{GeCl}]$  (2.028(3) Å).<sup>11</sup>

The constitutions of **3** and **4** derived from single crystal X-ray diffraction studies were further confirmed by spectrochemical analyses. In **3** a sharp singlet appears at  $\delta$  10.59 ppm with  $^1J(^{119}\text{Sn}^{-1}\text{H}) = 112$  Hz which is shifted to the high field relative to that of **A** ( $\delta$  13.96 ppm) but to low field relative to that of  $[\{2,6\text{-Trip}_2\text{C}_6\text{H}_3\text{Sn}(\mu\text{-H})\}_2]$  ( $\delta$  7.87 ppm).<sup>4</sup> The corresponding resonance for **4** appears at  $\delta$  6.69 ppm for the hydrogen attached to germanium (Ge–H) which is at lower field than those reported for  $[\text{ArGeH}]_2$  (Ar = 2,6-Dipp<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Dipp = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) ( $\delta$  3.48 ppm) and  $\text{Ar}(\text{H})_2\text{GeGeAr}\cdot\text{PMe}_3$  (Ar = 2,6-Dipp<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Dipp = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) ( $\delta$  3.81 ppm)<sup>5</sup> but shifted to higher field than that reported for **B** ( $\delta$  8.08 ppm).<sup>6a</sup> The low field chemical

shift of **3** compared to that of **4** is similar to those found in **A** and **B** and presumably due to the less electron transfer from the nitrogen atoms to the Sn–H bond than that within the Ge–H bond.<sup>6a</sup> The <sup>119</sup>Sn NMR spectrum of **3** exhibits a singlet ( $\delta$  –114.27 ppm) with a coupling constant of  $^1J_{\text{Sn-H}} = 112.9$  Hz. The chemical shift is high field shifted when compared with **A** ( $\delta$  –4.45 ppm) and the precursor **4** ( $\delta$  –20 ppm). The Sn–H coupling constant is in line with that of **A** ( $^1J_{\text{Sn-H}} = 45$  Hz) and with several dimeric tin(II) hydrides ( $^1J_{\text{Sn-H}} = 87\text{--}95$  Hz) reported previously.<sup>16</sup> In all the cases, Sn centres carry a lone pair of electrons. However the value of the coupling constant is significantly smaller than that of **F** ( $^1J_{\text{Sn-H}} = 1158$  Hz) and  $[\{2,6\text{-}(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{Sn}(\text{H})\text{W}(\text{CO})_5]$  (1302 Hz)<sup>12</sup> where the lone pair at the Sn centre coordinates to a Lewis acid. This indicates that the coupling constant is strongly influenced by the nature of surrounding ligands at the Sn centre. The solid-state CPMAS NMR of **3** (See ESI†, Fig. S6), which shows a single <sup>119</sup>Sn resonance at –119.4 ppm, supports the assignment of a monomeric structure for **3** both in solution and in the solid state. In the IR spectra of **3** and **4**, strong absorptions were observed at 1826 cm<sup>–1</sup> and 1985 cm<sup>–1</sup> which are tentatively assigned to the Sn–H and Ge–H stretching frequencies, respectively. The corresponding deuterated complex LGeD (**5**) was prepared by reacting **2** with LiAlD<sub>4</sub> and yielded the isotopically shifted Ge–D (1462 cm<sup>–1</sup>) IR band and thereby supported the initially assigned Ge–H stretching vibration of **4**. The wave numbers match well with those of respective four-coordinate M–H species by Rivard *et al.* (**D–F**),<sup>9</sup> Power *et al.*,<sup>17</sup> and our results<sup>18</sup> but more than those reported for **A** (1733 cm<sup>–1</sup>),<sup>6a</sup> **B** (1849 cm<sup>–1</sup>),<sup>6a</sup> and **C** (1722 cm<sup>–1</sup>).<sup>7</sup> In the EI-MS spectra of **3** and **4**, each molecular ion was observed as the most abundant peak with highest relative intensity at *m/z* 599 and 553, respectively. The corresponding *m/z* for **5** was found at 555.

In order to draw a clearer picture on the Sn–H and Ge–H bonds, quantum chemical calculations were carried out on **3** and **4**. Their structures were optimized at the BP86/def2-SVP (with effective core potentials for the Sn and Ge atoms) level of theory.<sup>19</sup> Frequency calculations were used to confirm the structures as true minima. Taking into account the bulkiness of both compounds, one could expect that dispersion interactions play a significant role in their structures. Therefore, we have also carried out optimizations with the same functional and basis set, but including dispersion corrections, as proposed by Grimme (BP86-D/def2-SVP).<sup>20</sup> Both sets of calculations agree closely in the local geometry of the M–H (M = Sn and Ge) bond. The M–H distances are 1.792 and 1.787 Å for M = Sn, using BP86 and BP86-D, respectively. However, the computed stretching frequencies (1621/1646 cm<sup>–1</sup>) are somewhat lower than the experimentally measured value of 1826 cm<sup>–1</sup>. In the case of Ge, the distances are 1.588 (BP86) and 1.583 Å (BP86-D) with a stretching frequency of 1882/1918 cm<sup>–1</sup>.

The most significant difference between the DFT results with and without dispersion corrections is the conformation of the isopropyl groups. In the case of BP86-D/def2-SVP, for both **3** and **4**, one of these groups has a methyl moiety pointing towards the metal bonded hydrogen atom. The experimentally derived structures, as well as the computed BP86/def2-SVP geometries, show the less steric hydrogen in this position. This is somewhat unexpected since there should be little energy gain



**Fig. 1** Molecular structures of **3** and **4**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms except the ones attached to Sn1 and Ge1, lattice toluene molecules and the disordered Sn–H and Ge–H moieties are not shown for clarity. The Sn1–H1 and Ge1–H1 distances were set to the theoretical data.

in such an interaction. Instead, one would expect all methyl groups to point outward, conserving the symmetry and avoiding steric contacts. In order to better understand this occurrence, DF-MP2/cc-pVTZ (cc-pVTZ-PP in the case of Sn and Ge)<sup>21</sup> single points were computed on the DFT optimized geometries. The results show that, in fact, the BP86-D optimized structures are higher in energy. The BP86/def2-SVP structures are 2.9 and 0.2 kcal mol<sup>-1</sup> lower in energy for structures **3** and **4**, respectively, than the BP86-D analogues. The torsion of the isopropyl group seems, therefore, to be an artifact of the dispersion correction terms.

We have also performed a NBO analysis of the two compounds at the BP86/def2-SVP level of theory.<sup>22</sup> The Sn–H bond is built from a Sn hybrid orbital with 89.3% p-character. This value is close to the one reported for compound **A** (87.7%) and higher than that of **F** (65.1%), which again relates to the small  $J_{\text{Sn-H}}$  coupling constant measured. The p-character of the hybrid is similar for Ge–H in compound **4** (85.8%). The lone pair of Sn and Ge is predominantly of s-character (79.4% (Sn) 70.9% (Ge)). In the dominant Lewis structures, the metals are only covalently bound to the hydrogen and the ring carbon. However, the second-order perturbation energy analysis of the NBOs shows a significant donation from each N lone pair to a p-orbital of the metal. The values are about 50 kcal mol<sup>-1</sup> for Ge (per Ge–N contact) and 35 kcal mol<sup>-1</sup> for Sn.

While Dostál *et al.* exploited the pincer-based NCN ligand to isolate the first monomeric stibinidene and bismuthinidene derivatives,<sup>23</sup> we have shown that such a ligand is also useful to isolate monomeric Sn(II) and Ge(II) hydrides. This is the first example of a Sn(II) hydride where no Sn–H intermolecular interaction is present. The monomeric structures of **3** and **4** are mainly stabilized by donating electron density to the empty p orbital of the central metal atoms as supported by theoretical calculations. The chemistry of these new hydrides will be explored and published in due course.

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