

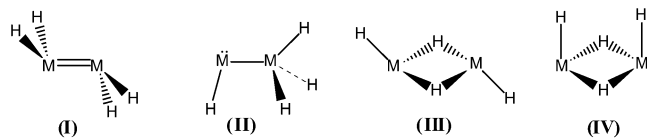
Isomeric Forms of Divalent Heavier Group 14 Element Hydrides:  
Characterization of  $\text{Ar}'(\text{H})\text{GeGe}(\text{H})\text{Ar}'$  and  $\text{Ar}'(\text{H})_2\text{GeGeAr}'\cdot\text{PMe}_3$   
( $\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6-Dipp}_2$ ;  $\text{Dipp} = \text{C}_6\text{H}_3\text{-2,6-Pr}^i_2$ )

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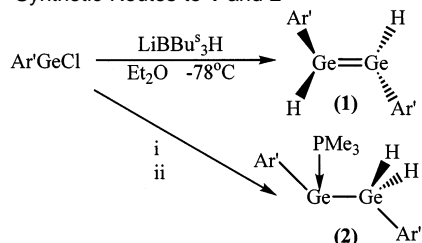
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Tetravalent hydrides of the heavier group 14 elements have been studied extensively because of their widespread uses in organic synthesis,<sup>1</sup> and as precursors for high-purity elements or related alloys, which are of importance in electronics.<sup>2</sup> In contrast, divalent hydrides of these elements remained unknown until 2000 when it was shown that large co-ligands such as the aryl  $\text{Ar}^*$  ( $\text{C}_6\text{H}_3\text{-2,6-Trip}_2$ ;  $\text{Trip} = \text{C}_6\text{H}_2\text{-2,4,6-Pr}^i_3$ ) or the  $\beta$ -diketiminato ligand  $\text{HC}(\text{CMeNDipp})_2$  (i.e.,  $\text{Dipp}_2\text{N}^{\wedge}\text{N}$ ,  $\text{Dipp} = \text{C}_6\text{H}_3\text{-2,6-Pr}^i_2$ ) could stabilize divalent hydrides as exemplified by the formulas  $\{\text{Ar}^*\text{Sn}(\mu\text{-H})\}_2$ <sup>3</sup> and  $\text{Dipp}_2\text{N}^{\wedge}\text{NGeH}$ .<sup>4</sup> The Sn compound had a hydrogen-bridged dimeric structure,<sup>3</sup> whereas the Ge derivative was a monomer in which the Ge was three-coordinate.<sup>3</sup> In addition to their possible synthetic applications the divalent hydrides are of fundamental interest because theoretical studies on model species have predicted that they exist in a number of isomeric forms separated by relatively low energies. For example, a computational study by Trinquier<sup>5</sup> has shown that the simplest divalent hydrides, i.e.,  $\text{MH}_2$  ( $\text{M} = \text{Si}$  through  $\text{Pb}$ ) can exist as dimers that have several different structures of various stabilities, which are represented by I–IV.



The trans-pyramidal **I** was calculated to be the most stable for Si and Ge, whereas the trans-bridged **III** is the most stable for Sn and Pb. The mixed valence isomer **II** lies between these and is also a minimum on the potential surfaces. Of the four isomers listed, only a tin derivative of **III** has been isolated as a stable compound.<sup>3</sup> We now report the isolation and characterization of a germanium (II) hydride,  $\text{Ar}'(\text{H})\text{GeGe}(\text{H})\text{Ar}'$  **1** ( $\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6-Dipp}_2$ ), that corresponds to **I**, and  $\text{Ar}'(\text{H})_2\text{GeGeAr}'\cdot\text{PMe}_3$ , corresponding to base-stabilized **II**, which were synthesized as in Scheme 1.

Scheme 1. Synthetic Routes to **1** and **2**<sup>a</sup>



<sup>a</sup> Conditions: i) 1 equiv L-selectride in toluene,  $-78^\circ\text{C}$ , ii) 2.0 equiv  $\text{PMe}_3$ , extract with hexane.

Initial work on the synthesis of **1** followed a synthetic route similar to that described for the divalent tin hydride.<sup>3</sup> However, it

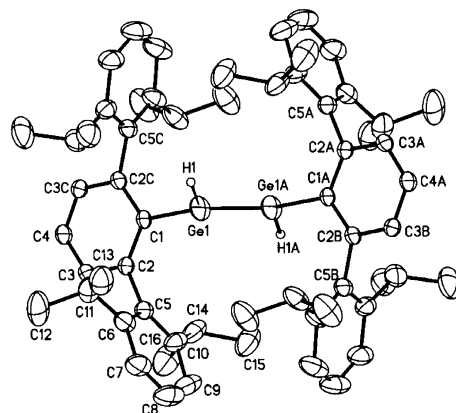
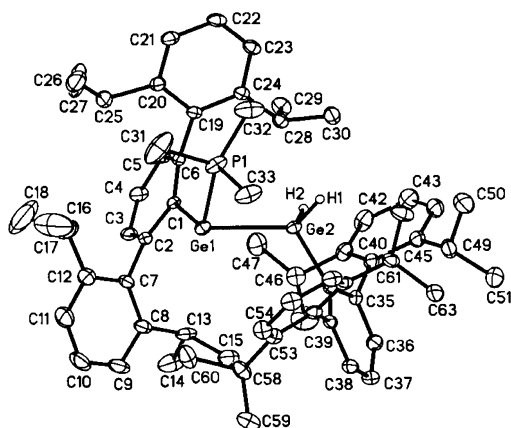


Figure 1. Thermal ellipsoid (35%) drawing of **1**. Selected bond distances (Å) and angles (deg):  $\text{Ge}(1)\text{--Ge}(1a) = 2.3723(11)$ ,  $\text{Ge}(1)\text{--C}(1) = 2.021(3)$ ,  $\text{C}(1)\text{--Ge}(1)\text{--Ge}(1a) = 108.78(9)$ ,  $\text{C}(1)\text{--Ge}(1)\text{--H}(1) = 119.07(3)$ ,  $\text{H}(1)\text{--Ge}(1)\text{--Ge}(1a) = 127.07(5)$ .

was found that use of DIBAL (di-isobutyl aluminum hydride), or reducing agents such as  $\text{LiAlH}_4$ ,  $\text{LiH}$ , or  $\text{NaH}$ , gave, upon reaction with  $\text{Ar}'\text{GeCl}$ , colorless solutions from which crystals of  $\text{Ar}'\text{GeH}_3$  were isolated. A milder reducing agent in the form of  $\text{Li}\{\text{BBu}^s_3\text{H}\}$ , (L-selectride), was therefore used. It was also anticipated that use of a bulkier reductant would not allow coordination of the  $\text{BBu}_3$  to the Ge center as in the case of the reduction of  $\text{Dipp}_2\text{N}^{\wedge}\text{NGeCl}$  by  $\text{NaBH}_4$ .<sup>4</sup>

Addition of 1 equiv of L-selectride to an orange  $\text{Et}_2\text{O}$  solution of  $\text{Ar}'\text{GeCl}$  at ca.  $-78^\circ\text{C}$  furnished a deep-red solution upon warming to ambient temperature.<sup>7</sup> Stirring was maintained for 6 h whereupon the reaction mixture was concentrated, filtered, and stored at ca.  $-5^\circ\text{C}$  for 12 h to yield orange crystals of **1**. Their composition was established by X-ray crystallography<sup>8</sup> and NMR and IR spectroscopies.<sup>7</sup> The structure of **1** is illustrated in Figure 1. The molecule has crystallographic  $2/m$  symmetry in which the  $\text{C}\text{--Ge}\text{--Ge}\text{--C}$  array is incorporated in the mirror plane. It features a trans-pyramidal, “dimetallene” core arrangement with a  $\text{Ge}\text{--Ge}$  distance of 2.3723(11) Å. This distance lies in the upper half of the currently known range for digermenes, probably as a result of the steric effects of the  $\text{Ar}'$  ligands.<sup>9</sup> The presence of lone pair character at Ge is indicated by an out-of-plane angle of  $20.5^\circ$ . Spectroscopic studies corroborated the X-ray structure, and a chemical shift at 3.48 ppm in the  $^1\text{H}$  NMR spectrum was assigned to  $\text{Ge}\text{--H}$ . This shift is comparable to the 4–6 ppm range in  $\text{Ge}(\text{IV})$  hydrides.<sup>10</sup> The IR absorption for  $\text{Ge}\text{--H}$  was observed at  $1785\text{ cm}^{-1}$  (cf  $1726\text{ cm}^{-1}$  for  $\text{Dipp}_2\text{N}^{\wedge}\text{NGeH}$ ),<sup>4</sup> and is lower than those in  $\text{Ge}(\text{IV})$  hydrides, which are generally observed in the region of  $1900\text{--}2000\text{ cm}^{-1}$ .<sup>10</sup> This may be due to a lower ionic component in the  $\text{Ge}(\text{II})\text{--H}$  bond which reduces its strength. The structure of **1**, which is the only stable heavier group 14 dimetallene hydride



**Figure 2.** Thermal ellipsoid (50%) drawing of **2**. Selected bond distances (Å) and angles (deg): Ge(1)–Ge(2) = 2.5304(7), Ge(1)–C(1) = 2.070(3), Ge(2)–C(34) = 1.991(3), Ge(2)–H(1) = 1.40(3), Ge(2)–H(2) = 1.44(3), Ge(1)–P(1) = 2.4041(9), C(1)–Ge(1)–P(1) = 110.34(7), Ge(2)–Ge(1)–P(1) = 88.98(3), Ge(2)–Ge(1)–C(1) = 101.59(7).

derivative, may be contrasted with that of the bridged tin hydride  $\{\text{Ar}^*\text{Sn}(\mu\text{-H})\}_2^3$ .

Use of L-selectride resulted in the formation of  $\text{BBu}_3$  as an involatile side product, which could complicate reactivity studies. We attempted to avoid this through addition of  $\text{PMe}_3$  to form the adduct  $\text{Bu}_3\text{B}\cdot\text{PMe}_3$ . To this end, a toluene solution of  $\text{Ar}^*\text{GeCl}$  was treated with 1 equiv of L-selectride at  $-78^\circ\text{C}$ .<sup>7</sup> The orange solution became reddish green immediately, with concomitant precipitate formation. Following filtration, 2 equiv of neat  $\text{PMe}_3$  was added dropwise with constant stirring. Removal of the toluene under vacuum and extraction with hexane permitted separation of  $\text{Bu}_3\text{B}\cdot\text{PMe}_3$  as a white solid. The yellow supernatant liquid was separated and stored at ca.  $-5^\circ\text{C}$  for 48 h to give **2** as yellow crystals in 14% yield. The structure<sup>8</sup> (Figure 2) displayed a Ge–Ge distance of 2.5304(7) Å, which is at the longer end of the Ge–Ge single-bond range (cf. covalent radius of Ge = 1.22 Å). The Ge hydrogens were located using a difference map and refined with restrained lengths of 1.44(4) Å. The IR spectrum of **2** had a Ge–H absorption at  $1905\text{ cm}^{-1}$ , and the  $^1\text{H}$  NMR spectrum displayed a signal at 3.81 ppm due to Ge–H. A feature of **2** is the presence of Ge in two formal oxidation states: Ge(I) (divalent) and Ge(III) (tetravalent). Prior examples are limited to a few compounds,<sup>11,12</sup> e.g. (2,6-Mes<sub>2</sub>H<sub>3</sub>C<sub>6</sub>)GeGe(Bu<sup>t</sup>)<sub>3</sub> (Mes = C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>) which has a similar Ge–Ge distance of 2.5439(7) Å.<sup>12</sup> The Ge(1)–C(1) bond to divalent Ge (2.070(3) Å) is longer than that of tetravalent Ge(2)–C(34), 1.991(3) Å. This may be due to the smaller ionic contribution to the Ge(1)–C(1) bond strength as a result of the increased electron density at phosphine complexed Ge(1). Two structurally characterized examples of phosphine adducts to Ge exist,<sup>13,14</sup> namely,  $\text{GeCl}_2(\text{PPh}_3)$  and  $\text{GeI}_2(\text{PPh}_3)$ . They have an average Ge–P distance of 2.51 Å, which is slightly longer than the 2.4041(9) Å Ge(1)–P(1) distance in **2**. Future work will involve exploration of the reactivity of **1**.

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**Supporting Information Available:** CIF data for **1** and **2** are available at <http://pubs.acs.org>. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) Under anaerobic and anhydrous conditions, 1 equiv of  $\text{LiBu}_3\text{BH}$  (1.0 M solution in THF) was added dropwise at  $-78^\circ\text{C}$  to an ethereal solution of  $\text{Ar}^*\text{GeCl}$  (1 mmol). The reaction mixture was warmed slowly to ambient temperature, to furnish a deep-red solution which was filtered, concentrated and stored at  $-5^\circ\text{C}$  overnight, affording **1** in 41% yield: mp  $123^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 399.7 MHz,  $25^\circ\text{C}$ )  $\delta$  1.041 (d,  $^3J_{\text{H,H}} = 6.8$  Hz, 24H;  $o\text{-CH}(\text{CH}_3)_2$ ), 1.38 (d,  $^3J_{\text{H,H}} = 6.8$  Hz, 24H;  $o\text{-CH}(\text{CH}_3)_2$ ), 2.78 (sept,  $^3J_{\text{H,H}} = 6.8$  Hz, 8H;  $o\text{-CH}(\text{CH}_3)_2$ ), 3.48 (s, GeH, 2H), 6.93 (d,  $^3J_{\text{H,H}} = 8.0$  Hz, 4H;  $m\text{-C}_6\text{H}_3$ ), 7.10 (d,  $^3J_{\text{H,H}} = 8.0$  Hz, 8H;  $m\text{-Dipp}$ ), 7.15 (t,  $^3J_{\text{H,H}} = 8.0$  Hz, 2H;  $p\text{-C}_6\text{H}_3$ ), 7.22 (t,  $^3J_{\text{H,H}} = 8.0$  Hz, 4H;  $p\text{-Dipp}$ ),  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 100.59 MHz,  $25^\circ\text{C}$ )  $\delta$  = 25.65 ( $o\text{-CH}(\text{CH}_3)_2$ ), 26.15 ( $o\text{-CH}(\text{CH}_3)_2$ ), 30.81, ( $o\text{-CH}(\text{CH}_3)_2$ ), 122.73 ( $m\text{-Dipp}$ ), 128.18 ( $p\text{-C}_6\text{H}_3$ ), 129.31 ( $m\text{-C}_6\text{H}_3$ ), 140.86 ( $p\text{-Dipp}$ ), 146.61 ( $i\text{-Dipp}$ ), 146.69 ( $o\text{-Dipp}$ ), 147.43 ( $o\text{-C}_6\text{H}_3$ ) ( $i\text{-C}_6\text{H}_3$  carbon was not observed). IR (Nujol, KBr plates):  $\nu$  ( $\text{cm}^{-1}$ ) = 1785 (m, GeH), 1570 (m), 1500 (m), 1170 (s), 930 (s), 590 (m), 460 (m), 400 (s); **2**: A PhMe solution of  $\text{Ar}^*\text{GeCl}$  (1 mmol) was treated with L-selectride (1 mmol of a 1.0 M soln in THF) at  $-78^\circ\text{C}$ . The deeply colored solution was warmed to room temperature with constant stirring. After 6 h, the mixture was filtered and 2 equiv of  $\text{PMe}_3$  was added dropwise. Extraction into hexane afforded compound **2** as yellow blocks in 14% yield: mp =  $91^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 399.7 MHz,  $25^\circ\text{C}$ )  $\delta$  = 0.990 (d,  $^3J_{\text{H,H}} = 6.8$  Hz, 24H;  $o\text{-CH}(\text{CH}_3)_2$ ), 1.0–1.1 ( $(\text{PCH}_3)_3$ ), 1.26, (d,  $^3J_{\text{H,H}} = 6.8$  Hz, 24H;  $o\text{-CH}(\text{CH}_3)_2$ ), 2.62, (sept,  $^3J_{\text{H,H}} = 6.8$  Hz, 8H;  $o\text{-CH}(\text{CH}_3)_2$ ), 3.81 (s, 2H, GeH), 6.85, (d,  $^3J_{\text{H,H}} = 8.0$  Hz, 4H;  $m\text{-C}_6\text{H}_3$ ), 7.0 (d,  $^3J_{\text{H,H}} = 8.0$  Hz, 8H;  $m\text{-Dipp}$ ), 7.20 (t,  $^3J_{\text{H,H}} = 8.0$  Hz, 2H;  $p\text{-C}_6\text{H}_3$ ), 7.24 (t,  $^3J_{\text{H,H}} = 8.0$  Hz, 4H;  $p\text{-Dipp}$ ),  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 100.59 MHz,  $25^\circ\text{C}$ )  $\delta$  = 14.67 ( $(\text{PCH}_3)_3$ ), 25.68 ( $o\text{-CH}(\text{CH}_3)_2$ ), 26.03 ( $o\text{-CH}(\text{CH}_3)_2$ ), 31.79 ( $o\text{-CH}(\text{CH}_3)_2$ ), 124.62 ( $m\text{-Dipp}$ ), 127.59 ( $p\text{-C}_6\text{H}_3$ ), 131.03 ( $m\text{-C}_6\text{H}_3$ ), 140.91 ( $p\text{-Dipp}$ ), 146.58 ( $i\text{-Dipp}$ ), 146.68 ( $i\text{-C}_6\text{H}_3$ ), 147.43 ( $o\text{-Dipp}$ ), 159.1 ( $o\text{-C}_6\text{H}_3$ );  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ )  $\delta$  =  $-14$  (broad) IR (Nujol, NaCl plates):  $\mu$  ( $\text{cm}^{-1}$ ) = 1905 (GeH), 1275 (s), 1012 (s), 1100 (s), 870 (m), 760 (w), 740 (w), 710 (m)  $\text{cm}^{-1}$ .
- (8) (a) The hydrogen was located from a difference map and found to be disordered with respect to the mirror plane. It was refined with 50% occupancy, keeping the isotropic  $U = 1.5 \times U_{\text{Ge}}$ , but with no other restraints. However, a region of highly disordered solvent was refined using the crystallography program "SQUEEZE", van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194. (b) Crystal data for **1** and **2** at 90 K with Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation; **1**, monoclinic,  $C2/m$ , orange,  $a = 18.3776(17)$  Å,  $b = 17.7496(17)$  Å,  $c = 13.0929(12)$  Å,  $\beta = 117.432(2)^\circ$ ,  $V = 3790.6(6)$  Å<sup>3</sup>,  $Z = 2$ , R1 (obs data) = 0.0498, wR2 (all data) = 0.1373, GOF = 1.08. **2**:  $C_{66}H_{80}Ge_2P$ , monoclinic,  $P2_1/c$ , yellow,  $a = 13.114(4)$  Å,  $b = 37.253(11)$  Å,  $c = 12.614(4)$  Å,  $\beta = 107.251(5)^\circ$ ,  $V = 5885(3)$  Å<sup>3</sup>,  $Z = 4$ , R1 (obs data) = 0.0595, wR2 (all data) = 0.1434, GOF = 1.12.
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