

# A Digermynes with a Ge–Ge Single Bond That Activates Dihydrogen in the Solid State

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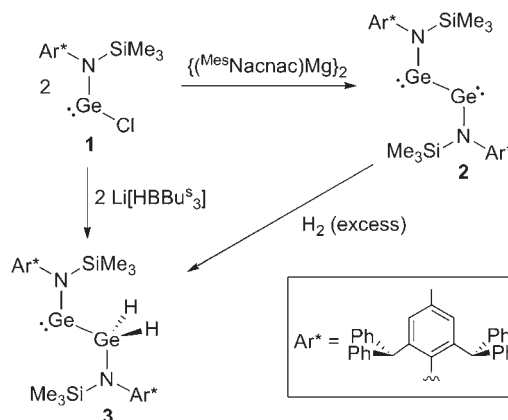
**S** Supporting Information

**ABSTRACT:** The reduction of the bulky amido-germanium(II) chloride complex, LGeCl (L = N(SiMe<sub>3</sub>)(Ar<sup>\*</sup>); Ar<sup>\*</sup> = C<sub>6</sub>H<sub>2</sub>Me{C(H)Ph<sub>2</sub>}<sub>2-4,2,6</sub>), with the magnesium(I) dimer, [{(Mes)<sup>Nacnac</sup>Mg]<sub>2</sub>} (Mes<sup>Nacnac</sup> = [(MesNCMe)<sub>2</sub>CH]<sup>-</sup>; Mes = mesityl), afforded LGeGeL, which represents the first example of a digermynes with a Ge–Ge single bond. Computational studies of the compound have highlighted significant electronic differences between it and multiply bonded digermynes. LGeGeL was shown to cleanly activate H<sub>2</sub> in solution or the solid state, at temperatures as low as –10 °C, to give the mixed valence compound, LGeGe(H)<sub>2</sub>L.

The past two decades have seen major fundamental advances in the chemistry of low oxidation state p-block compounds.<sup>1</sup> Perhaps the most archetypal of such systems are the heavier group 14 element(I) alkyne analogues (or ditetrelynes), REER (E = Si, Ge, Sn, or Pb; R = bulky terphenyl, silyl, or aryl), which unlike linear alkynes, have increasingly “*trans*-bent” REE fragments as the group is descended (RSiSi ~135° to RPbPb ~92°).<sup>2</sup> The results of many theoretical analyses of the bonding in ditetrelynes have shown that their E–E bond orders can range between three and one.<sup>3</sup> The most studied systems are the digermynes, RGeGeR, which invariably have short (ca. 2.2–2.3 Å) Ge–Ge multiple bonds, and can exhibit significant singlet biradicaloid character.<sup>2,4</sup> Their resultant high reactivity toward small molecules and unsaturated substrates has led to digermynes being described as main group mimics of transition metal complexes.<sup>1a,d</sup> This reactivity is epitomized by the landmark study of Power et al. who, in 2005, demonstrated for the first time that H<sub>2</sub> can be activated by a main group metal complex, Ar’GeGeAr’ (Ar’ = C<sub>6</sub>H<sub>3</sub>(C<sub>6</sub>H<sub>3</sub>Pr<sub>2-2,6</sub>)<sub>2-2,6</sub>), at room temperature and atmospheric pressure.<sup>5</sup> The hydrogenation of Ar’GeGeAr’ yielded mixtures of Ar’(H)GeGe(H)Ar’, Ar’(H)<sub>2</sub>GeGe(H)<sub>2</sub>Ar’, and Ar’GeH<sub>3</sub>, the compositions of which were shown to be dependent upon the reaction stoichiometry.<sup>5</sup> Since 2005, a variety of stable carbenes, main group based Frustrated Lewis Pairs, and other low oxidation p-block state systems have been shown to activate H<sub>2</sub> at or near ambient temperature.<sup>6</sup>

Although digermynes containing Ge–Ge single bonds are unknown,<sup>7</sup> they are attractive synthetic targets both for fundamental reasons, and because their reactivity could differ significantly to that of their well studied multiply bonded counterparts. We reasoned such systems could be accessed by incorporation of very bulky monodentate amide ligands,<sup>8</sup> which would not only provide kinetic protection, but could also circumvent Ge–Ge

**Scheme 1. Syntheses of Compounds 2 and 3 (Byproducts Omitted)**



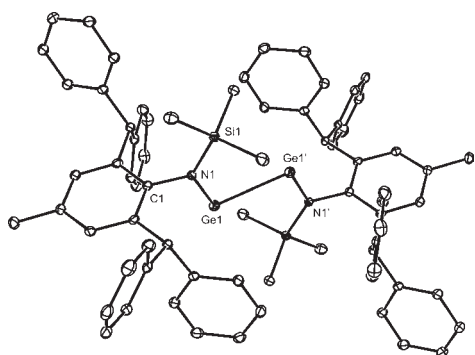
multiple bonding by offering the possibility of N lone pair → Ge  $\pi$ -interactions in the complex. Here, we report the synthesis, characterization, and bonding analysis of the first amido-substituted digermynes, which possesses a Ge–Ge single bond, and which cleanly activates H<sub>2</sub> in solution or the solid state at atmospheric pressure and temperatures as low as –10 °C.

The reduction of the bulky monomeric amido-germanium(II) chloride, LGeCl **1** (L = N(SiMe<sub>3</sub>)(Ar<sup>\*</sup>); Ar<sup>\*</sup> = C<sub>6</sub>H<sub>2</sub>Me{C(H)Ph<sub>2</sub>}<sub>2-4,2,6</sub>),<sup>9</sup> with half an equivalent of the magnesium(I) dimer, [{(Mes)<sup>Nacnac</sup>Mg]<sub>2</sub>} (Mes<sup>Nacnac</sup> = [(MesNCMe)<sub>2</sub>CH]<sup>-</sup>; Mes = mesityl),<sup>10</sup> afforded a moderate isolated yield (55%) of **2** as an extremely air sensitive pink-orange solid after recrystallization from diethyl ether (Scheme 1). It is of note that attempts to prepare **2** via the reduction of **1** with alkali metals, KC<sub>8</sub>, or sodium naphthalide, gave, at best, only low yields of **2**, and generally led to the deposition of elemental germanium. Solutions of **2** in aromatic solvents are red-purple in color (toluene:  $\lambda_{\text{max}}$  [nm] ( $\epsilon$  [L mol<sup>-1</sup> cm<sup>-1</sup>): 531 (588), 383 (3235)) and exhibit NMR spectra consistent with the proposed formulation of the compound.

The molecular structure of **2** (Figure 1) reveals the compound to be a *trans*-bent dimer with N–Ge–Ge angles (100.09(6)°) that are markedly more acute than the C–Ge–Ge angles in all previously reported digermynes (range: 123.6–138.7°).<sup>2</sup>

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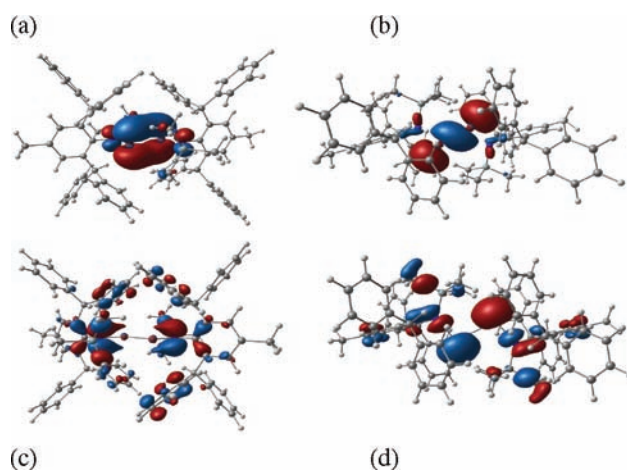
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**Figure 1.** Thermal ellipsoid plot (20% probability surface) of the molecular structure of [LGeGeL] (**2**); hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)–N(1) 1.872(2), Ge(1)–Ge(1') 2.7093(7), Si(1)–N(1) 1.762(2), N(1)–C(1) 1.445(3), N(1)–Ge(1)–Ge(1') 100.09(6), C(1)–N(1)–Si(1) 118.50(16), C(1)–N(1)–Ge(1) 110.12(15), Si(1)–N(1)–Ge(1) 131.38(11). Symmetry operation:  $' -x + 1/2, -y + 1, -z + 1$ .

In addition, the Ge–Ge separation (2.7093(7) Å) in the compound is consistent with a very long single bond (sum of two Ge covalent radii = 2.44 Å),<sup>4</sup> which is more than 0.4 Å longer than those of other multiply bonded digermynes.<sup>2</sup> It is noteworthy that terphenyl substituted, singly bonded distannynes and diplymbynes related to **2** have been reported.<sup>11</sup> The differences between **2** and other digermynes could result from the fact that its NSiCGe and Ge<sub>2</sub>N<sub>2</sub> least-squares planes are essentially coplanar (dihedral angle: 5.2°), thereby potentially allowing N → Ge  $\pi$ -interactions,<sup>12</sup> which in turn would discourage Ge–Ge multiple bond formation. In this respect, compound **2** could be viewed as an unprecedented two-coordinate 1,2-bis-(germylene), that is, a heavier analogue of as yet unknown 1,2-dicarbene. There are no significant aryl–Ge contacts (closest: 3.34 Å, cf. 3.03 Å in LGeCl<sup>9</sup>) in the compound.

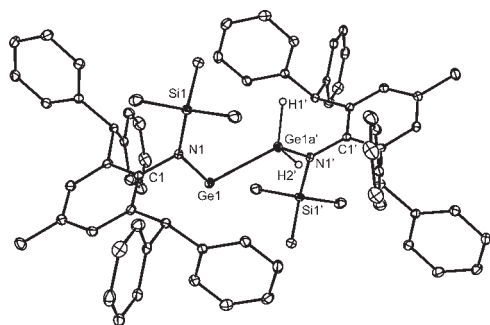
To shed light on the electronic structure of **2**, DFT calculations were carried out on the full molecule in the gas phase (RI-BP86/def2-SVP). Its optimized geometry is very similar to that in the crystal structure of the compound, but with slightly overestimated Ge–Ge (2.764 Å) and N–Ge (1.909 Å; N–Ge–Ge angle: 100.1°) bonds (see Supporting Information for full details). An analysis of the frontier orbitals of the molecule (see Figure 2) revealed that the Ge–Ge single bond is associated with the HOMO, and is of very high *p*-character (92.8%). This is likely a significant factor behind the length of this bond<sup>13</sup> (cf. the Ge–Ge distance in H<sub>3</sub>GeGeH<sub>3</sub>: 2.403 Å<sup>14</sup>). The LUMO has considerable Ge–Ge  $\pi$ -bonding character, while the highest energy orbital with significant Ge lone pair character is the HOMO-23, which lies some 3.06 eV below the HOMO (N.B. the HOMO–LUMO gap is very narrow at 0.62 eV, cf. 2.10 eV for MeGeGeMe<sup>1a</sup>). As expected, several MOs (e.g., HOMO-6) exhibit significant N–Ge  $\pi$ -bonding character which is seemingly the basis of the electronic differences between **2** and the aforementioned multiply bonded aryl substituted digermynes. It is of note that a previous theoretical study on the parent digermine, HGeGeH, has shown that its singly bonded form (Ge–Ge 2.720 Å, H–Ge–Ge 90.6°) is 15.3 kcal/mol higher in energy than the multiply bonded isomer (Ge–Ge 2.211 Å, H–Ge–Ge 124.0°).<sup>3b</sup> In contrast, in the current study, the multiply bonded isomer of **2**, viz., **2a** (Ge–Ge 2.393 Å, N–Ge–Ge 119.4°), was calculated to lie  $\Delta G = 10.0$  kcal/mol higher in energy than **2**.



**Figure 2.** (a) LUMO (−2.934 eV), (b) HOMO (−3.557 eV), (c) HOMO-6 (−5.844 eV), and (d) HOMO-23 (−6.623 eV) of **2**.

Given the emerging “transition metal-like” reactivity of multiply bonded digermynes,<sup>1a,d</sup> reactions of **2** with dihydrogen were examined. When toluene or *d*<sub>6</sub>-benzene solutions of the compound were exposed to an excess of H<sub>2</sub> at 1 atm and 20 °C, the orange monohydrogenation product, **3**, was formed in essentially quantitative yield in less than 20 min (Scheme 1). Similar reactions carried out at 0 and −10 °C were complete after 1 and 2 h, respectively. Remarkably, when finely ground crystalline samples of **2** were placed under 1 atm of H<sub>2</sub> at 20 °C, compound **3** was also formed in yields of >95% after 1 h. Similar solid-state reactions carried out at −10 °C led to formation of **3** in yields of ca. 60% after 1 h. In contrast to Ar'(H)GeGe(H)Ar', solutions of compound **3** do not react with further equivalents of H<sub>2</sub> up to 100 °C.<sup>15</sup> It is of note, however, that mixtures of the formal double hydrogenation product, L(H)<sub>2</sub>GeGe(H)<sub>2</sub> **4**, and **3** were obtained from the reactions of LGeCl with either Li[HBBu<sup>s</sup><sub>3</sub>] or K[HBt<sub>3</sub>].<sup>16</sup> Considering the thermal stability and reluctance to hydrogenation of **3**, the germanium(III) hydride, **4**, probably results from the disproportionation of an unstable monomeric intermediate, LGe<sup>III</sup>H, in these reactions. The other product, **3**, can easily be envisaged as ultimately resulting from the dimerization of LGe<sup>III</sup>H (vide infra).

Both compounds **3** and **4** display two Ge–H stretching bands in their infrared spectra (**3**:  $\nu$  1990, 2031 cm<sup>−1</sup>; **4**:  $\nu$  2030, 2076 cm<sup>−1</sup>), which lie in the expected region for terminal tetravalent germanium hydrides.<sup>17</sup> In their <sup>1</sup>H NMR spectra, hydride resonances appear at  $\delta$  6.13 ppm (**3**) and  $\delta$  4.91 ppm (**4**); however, that for **3** is very broad at 20 °C, as are the silyl and methine resonances for the compound. Upon warming a *d*<sub>8</sub>-THF solution of **3** to 70 °C, these resonances sharpen, yielding a spectrum consistent with a compound having chemically equivalent amide ligands. In contrast, cooling the same solution to −50 °C produced a resolved spectrum with one hydride resonance and two sets of amide resonances. It appears that a fluxional process is occurring at higher temperatures which is rapid on the NMR time scale. This could involve an equilibrium between the mixed valence compound, **3**, and its symmetrical germanium(II) isomer, L(H)GeGe(H)L **5**, which interconvert via intramolecular hydride migration. A similar equilibrium has been proposed between Ar'(H)GeGe(H)Ar' and Ar'(H)<sub>2</sub>GeGeAr',<sup>1a</sup> evidence for which comes from the addition of PMe<sub>3</sub> to a solution of Ar'(H)GeGe(H)Ar', which leads to the base stabilized mixed valence compound, Ar'(H)<sub>2</sub>GeGeAr' · PMe<sub>3</sub>.<sup>18</sup>



**Figure 3.** Thermal ellipsoid plot (20% probability surface) of the molecular structure of  $[LGeGe(H)_2L]$  (**3**); hydrogen atoms (except hydrides) are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Ge(1)–Ge(1A)′ 2.5507(8), Ge(1)–N(1) 1.8802(16), Ge(1A)′–N(1)′ 1.8748(16), Ge(1A)′–H(1)′ 1.515(19), Ge(1A)′–H(2)′ 1.482(18), N(1)–Ge(1)–Ge(1A)′ 101.04(5), N(1)′–Ge(1A)′–Ge(1) 114.71(5), H(1)′–Ge(1A)′–H(2)′ 101(2). Symmetry operation:  $' -x + 1/2, -y + 3/2, -z + 1$ .

The crystal structure of **3** is isomorphic with that of **2** (Figure 3, see Supporting Information for the structure of **4**), and confirms that the compound exists in the solid state in its  $Ge^I/Ge^{III}$  mixed valence isomeric form. This is supported by the fact that both hydride ligands were located from difference maps and refined isotropically. Moreover, the Ge–Ge distance (2.5507(8) Å) in the compound is considerably shorter than that in **2**, comparable with the Ge–Ge single bond length in  $Ar'(H)_2GeGeAr' \cdot PMe_3$  (2.5304(7) Å),<sup>18</sup> yet significantly longer than the double bond in  $Ar'(H)GeGe(H)Ar'$  (2.3026(3) Å).<sup>5</sup> The differing geometries about the Ge(1) and Ge(2) centers of **3** are also fully consistent with its mixed valence formulation.

It is intriguing that **2** appears to be considerably more reactive toward monohydrogenation than  $Ar'(H)GeGeAr'$ , yet unlike that compound, its second hydrogenation does not proceed (N.B.  $Ar'(H)GeGe(H)Ar'$  readily reacts with  $H_2$  at ambient temperature<sup>5</sup>). To assess if there is a thermodynamic reason behind these differences, the first and second hydrogenation energies for **2** were calculated (RI-BP86/def2-SVP). The first hydrogenation was found to be exothermic to give either **3** ( $\Delta H = -18.7$  kcal/mol,  $\Delta G = -9.6$  kcal/mol) or **5** ( $\Delta H = -15.9$  kcal/mol,  $\Delta G = -8.6$  kcal/mol), and revealed that the mixed valence system, **3**, is favored over the germanium(II) hydride, **5** by only 1.1 kcal/mol. This is in line with the apparent equilibrium between these isomers in solution (vide supra). The second hydrogenation to give **4** (from **3**) is also exothermic ( $\Delta H = -16.6$  kcal/mol,  $\Delta G = -6.5$  kcal/mol) which suggests that there is a significant kinetic barrier to this hydrogenation in practice.

At present we can only speculate on the mechanism of hydrogenation of **2**, though this clearly must be different to that proposed for multiply bonded  $Ar'(H)GeGeAr'$ , which involves interaction of its frontier  $\pi$ -bonding HOMO and nonbonding LUMO ( $n+$  combination) with the  $H_2$   $\sigma^*$ - and  $\sigma$ -orbitals, respectively.<sup>1d</sup> Instead, it could be similar to the mechanism proposed for the hydrogenation of the germylene,  $Ar'_2Ge$ : ( $Ar'_2 = C_6H_3(C_6H_2Me_3-2,4,6)_2-2,6$ ), which proceeds only at 65  $^\circ C$  to give  $Ar'_2GeH_2$ . This mechanism is thought to entail an initial interaction of the  $H_2$   $\sigma$ -orbital with the empty 4p orbital at Ge, with concomitant back-donation from the Ge lone pair into the  $H_2$   $\sigma^*$ -orbital.<sup>19</sup> Nevertheless, the relatively low lying Ge-lone pairs calculated for **2**, in combination with its very high reactivity

toward  $H_2$ , could well count against this proposal. We are currently employing experimental and computational techniques to explore the mechanism, kinetics, and potential reversibility of the hydrogenation of **2**. In addition, studies of the use of this reactive molecule for the “transition metal-like” activation of other small molecules are in hand. These investigations will form the basis of future publications.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Details of the synthesis and characterizing data for **2–4**. Full details and references for the crystallographic and computational studies. Crystallographic data in CIF format, ORTEP diagrams for **4**,  $[L(H)_2GeGe(H)(OH)L]$  and  $[L(H)_2GeGe(H)\{K(OEt)_2\}_2L]$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## ■ REFERENCES

- (1) Selected recent reviews: (a) Power, P. P. *Acc. Chem. Res.* **2011**, *44*, 627. (b) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354. (c) Yao, S.; Xiong, Y.; Driess, M. *Organometallics* **2011**, *30*, 1748. (d) Power, P. P. *Nature* **2010**, *463*, 171. (e) Fischer, R. C.; Power, P. P. *Chem. Rev.* **2010**, *110*, 3877. (f) Schnöckel, H. *Chem. Rev.* **2010**, *110*, 4125. (g) Lee, V. Y.; Sekiguchi, A. *Organometallic Compounds of Low-Coordinate Si, Ge, Sn and Pb*; Wiley: Chichester, 2010.
- (2) Recent reviews on ditetrelene chemistry: (a) Sekiguchi, A. *Pure Appl. Chem.* **2008**, *80*, 447. (b) Power, P. P. *Organometallics* **2007**, *26*, 4362. (c) Rivard, E.; Power, P. P. *Inorg. Chem.* **2007**, *46*, 10047.
- (3) See for example (a) Takagi, N.; Nagase, S. *Organometallics* **2007**, *26*, 3627. (b) Lein, M.; Krapp, A.; Frenking, G. *J. Am. Chem. Soc.* **2005**, *127*, 6290. (c) Bridgeman, A. J.; Ireland, L. R. *Polyhedron* **2001**, *20*, 2841. (d) Chen, Y.; Hartmann, M.; Diedenhofen, M.; Frenking, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2052. See, also, relevant theoretical studies cited in ref 2.
- (4) The first report of a stable digermene appeared in 2002: Stender, M.; Phillips, A. D.; Wright, R. J.; Power, P. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 1785.
- (5) Spikes, G. H.; Fetting, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 12232.
- (6) See for example: (a) Martin, D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2011**, *2*, 389. (b) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 46. (c) Ref 1a.
- (7) A handful of dimers containing three-coordinate  $Ge^I-Ge^I$  bonds have been reported. See for example: (a) Jones, C.; Bonyhady, S. J.;



Holzmann, N.; Frenking, G.; Stasch, A. *Inorg. Chem.* [Online early access]. DOI: 10.1021/ic200682p. (b) Wang, W.; Inoue, S.; Yao, S.; Driess, M. *Chem. Commun.* **2009**, 2661. (c) Leung, W.-P.; Chiu, W.-K.; Chong, K.-H.; Mak, C. W. *Chem. Commun.* **2009**, 6822. (d) Nagendran, S.; Sen, S. S.; Roesky, H. W.; Koley, D.; Grubmüller, H.; Pal, A.; Herbst-Irmer, R. *Organometallics* **2008**, *27*, 5459. (e) Green, S. P.; Jones, C.; Junk, P. C.; Lippert, K.-A.; Stasch, A. *Chem. Commun.* **2006**, 3978.

(8) Lappert, M. F.; Power, P. P.; Protchenko, A. V.; Seeber, A. L. *Metal Amide Chemistry*; Wiley-VCH: Weinheim, 2009.

(9) Li, J.; Stasch, A.; Schenk, C.; Jones, C. *Dalton Trans.* **2011**, *40*, 10448.

(10) Magnesium(I) dimers are emerging as selective reducing agents in inorganic synthesis: (a) Woodul, W. D.; Carter, E.; Müller, R.; Richards, A. F.; Stasch, A.; Kaupp, M.; Murphy, D. M.; Driess, M.; Jones, C. *J. Am. Chem. Soc.* **2011**, *133*, 10074. (b) Stasch, A.; Jones, C. *Dalton Trans.* **2011**, *40*, 5659. (c) Bonyhady, S. J.; Jones, C.; Nembenna, S.; Stasch, A.; Edwards, A. J.; McIntyre, G. J. *Chem.—Eur. J.* **2010**, *16*, 938.

(11) See for example Peng, Y.; Fischer, R. C.; Merrill, W. A.; Fischer, J.; Pu, L.; Ellis, B. D.; Fettingner, J. C.; Herber, R. H.; Power, P. P. *Chem. Sci.* **2010**, *1*, 461.

(12) Similar stabilizing interactions have been proposed for N-heterocyclic germylenes. See Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479.

(13) The lone-pair orbitals at the Ge atoms accumulate high s-character which was calculated to be 86.9%. This leaves little percentage s-contribution for the Ge—Ge bonding orbital. It is well known that heavier main-group elements are much less prone to s/p hybridization than elements of the first octal row. This comes from the poor overlap between the valence s and p orbitals of the former atoms: Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

(14) Beagley, B.; Monaghan, J. J. *Trans. Faraday Soc.* **1970**, *66*, 2745.

(15) A very bulky distannylene has been reported to react with excess H<sub>2</sub> to give the related mixed valence compound, [Ar''SnSn(H)<sub>2</sub>Ar''] (Ar'' = C<sub>6</sub>HPr<sup>1</sup><sub>2</sub>(C<sub>6</sub>H<sub>2</sub>Pr<sup>3</sup>-2,4,6)<sub>2</sub>-3,5,2,6). Peng, Y.; Brynda, M.; Ellis, B. D.; Fettingner, J. C.; Rivard, E.; Power, P. P. *Chem. Commun.* **2008**, 6042.

(16) Two other very low yielding byproduct were obtained from reactions with K[HBEt<sub>3</sub>], viz., [L(H)<sub>2</sub>GeGe(H)(OH)L] and [L(H)<sub>2</sub>-GeGe(H){K(OEt)<sub>2</sub>}L]. Their formation and X-ray crystal structures are discussed in the Supporting Information.

(17) Rivard, E.; Power, P. P. *Dalton Trans.* **2008**, 4336.

(18) Richards, A. F.; Phillips, A. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 3204.

(19) Peng, Y.; Guo, J.-D.; Ellis, B. D.; Zhu, Z.; Fettingner, J. C.; Nagase, S.; Power, P. P. *J. Am. Chem. Soc.* **2009**, *131*, 16272.