Angewandte Chemie

Germanium Complexes Hot Paper

DOI: 10.1002/ange.201305689

Activation of H_2 by a Multiply Bonded Amido–Digermyne: Evidence for the Formation of a Hydrido–Germylene**

Terrance J. Hadlington, Markus Hermann, Jiaye Li, Gernot Frenking, and Cameron Jones**

Dedicated to Professor Werner Uhl on the occasion of his 60th birthday

The considerable advances that have been made in the field of low-oxidation-state *p*-block chemistry over the past two decades are exemplified by the development of the heavier group 14 element(I) alkyne analogues (or ditetrelynes), of the general formula REER (E = Si, Ge, Sn or Pb, R = bulky terphenyl, silyl or aryl).[1] Unlike their linear alkyne counterparts, these have *trans*-bent structures, and E−E bond orders that vary between one and close to three.[1,2] Within this compound class, Power et al. and others have investigated a range of digermynes ([RGeGeR]), and have found them all to possess Ge−Ge multiple bonds and apparent singlet biradicaloid character.[1,3] This character is thought to be one of the reasons behind the remarkable transition-metal-like reactivity that is emerging for digermynes and related compounds.[1,4] Perhaps most importantly, in 2005 Power et al. showed that H_2 can be activated by the terphenyl-substituted digermyne, [Ar′GeGeAr′] (Ar′ = 2,6-(2,6-iPr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$), at room temperature and atmospheric pressure.[5] This yielded mixtures of the mono-, di-, and tri-hydrogenation products, [Ar′(H)Ge=Ge(H)Ar′], [Ar′(H)$_2$GeGe(H)$_2$Ar′], and [Ar′GeH$_3$]. A recent in-depth theoretical study by Wang, Schleyer, et al. has found the mechanism of formation of the three hydrogenation products to be complex, and to involve the activation of H_2 by the digermyne [Ar′GeGeAr′], the hydrido–digermene [Ar′(H)Ge=Ge(H)Ar′], and its mixed-valence isomer, [Ar′GeGe(H)$_2$Ar′], respectively.[6]

To expand the field of digermyne chemistry, we have developed a new class of extremely bulky amide ligand (L), one example of which (L^1 = N(Ar^1)(SiMe$_3$); Ar^1 = 2,6-[C(H)Ph$_2$]$_2$-4-MeC$_6$H$_2$)[7] we have used to stabilize the first example of an amido–digermyne, [L^{1}GeGeL^1] (**1**),[8] as well as a range of other low-oxidation-state p- and d-block systems.[9] Unlike all previous aryl substituted digermynes, compound **1** has a very long (ca. 2.71 Å) Ge−Ge bond, which is thought to arise from significant overlap of the *p*-orbital lone pairs on the N atom of its ligands with the empty *p*-orbitals at its Ge centers, thereby discouraging Ge−Ge multiple bonding. Despite this, compound **1** readily activates H_2 at temperatures as low as −10 °C, both in solution and the solid state, to give the mixed-valence germanium hydride, [L^{1}GeGe(H)$_2$L^1] (**2**) in near quantitative yields.[8] Given the length of the Ge−Ge bond in **1**, we believed that incorporation of a significantly bulkier amide ligand at a Ge^{I} center might allow us access to an unprecedented example of a one-coordinate germanium radical ([LGe:]) related to our previously described two-coordinate germanium(I) radical, [($^{t\mathrm{Bu}}$Nacnac)Ge:]• ($^{t\mathrm{Bu}}$Nacnac = [{N(2,6-iPr$_2$C$_6$H$_3$)C(tBu)}$_2$CH]$^-$).[10] This was found not to be the case, and remarkably, we obtained an amido–digermyne with a Ge−Ge bond that is more than 0.35 Å shorter than that in **1**. This reacts cleanly with H_2 below 0 °C to give a hydrido–digermene (related to [Ar′(H)Ge=Ge(H)Ar′]), which spectroscopic evidence suggests dissociates by Ge−Ge bond cleavage in solution. Full details of this study are described herein.

Reaction of the extremely bulky lithium amide, Li(L^2) (L^2 = N(Ar^2)(SiiPr$_3$), Ar^2 = 2,6-[C(H)Ph$_2$]$_2$-4-iPrC$_6$H$_2$),[11] with GeCl$_2$·dioxane afforded a high yield of the monomeric germylene, L^{2}GeCl (see the Supporting Information). Reduction of this with the magnesium(I) dimer, [{($^{\mathrm{Mes}}$Nacnac)Mg}$_2$] ($^{\mathrm{Mes}}$Nacnac = [(MesNCMe)$_2$CH]$^-$; Mes = mesityl),[12] gave a good yield of the amido–digermyne, [L^{2}GeGeL^2] (**3**), as a dark-orange crystalline solid (Scheme 1). It is of note that attempts to prepare the amido–distannyne analogue of **3** by reduction of L^{2}SnCl, instead led to deposition of tin metal and the generation of L^{2}H. The NMR spectroscopic data for **3** are consistent with its proposed formulation, and show the compound to be diamagnetic in solution. Its UV/Vis spectrum exhibits two absorption bands ($\lambda_{\max}$ = 399 nm (ε = 3,920 L mol^{-1} cm^{-1}) and 472 nm (650 L mol^{-1} cm^{-1})) at similar wavelengths, and of comparable intensities, to the $\pi \rightarrow \pi^*$ and $n_- \rightarrow n_+$ transitions reported for multiply bonded digermynes.[1,3] This gave a first indication that, in contrast to **1**, compound **3** may be a multiply bonded amido–digermyne.

Compound **3** was crystallographically characterized, and its molecular structure (Figure 1) revealed it to be a *trans*-bent molecule with a Ge–Ge bond (2.3568(3) Å) that is shorter

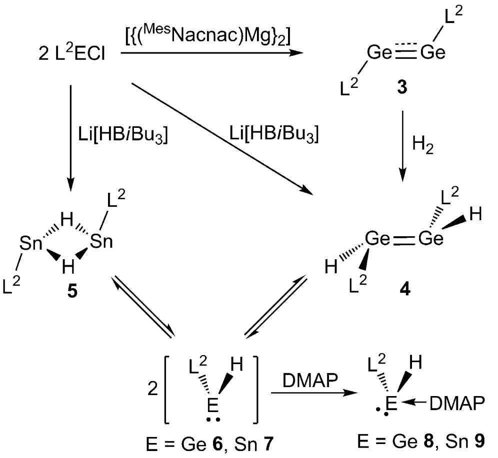
---

[*] T. J. Hadlington, J. Li, Prof. C. Jones
School of Chemistry, Monash University
P.O. Box 23, Melbourne, VIC, 3800 (Australia)
E-mail: cameron.jones@monash.edu
Homepage: http://monash.edu/science/jonesgroup

M. Hermann, Prof. Dr. G. Frenking
Fachbereich Chemie, Philipps-Universität Marburg
35032 Marburg (Germany)
E-mail: frenking@chemie.uni-marburg.de

[**] We thank the Australian Research Council (C.J.), The U.S. Air Force Asian Office of Aerospace Research and Development (FA2386-11-1-4110, to C.J.), and the Deutsche Forschungsgemeinschaft. The EPSRC is also thanked for access to the UK National Mass Spectrometry Facility. Part of this research was undertaken on the MX1 beamline at the Australian Synchrotron, Victoria, Australia.

Supporting information for this article, including full synthetic, spectroscopic, and crystallographic details for new compounds, as well as full details and references for the DFT calculations, is available on the WWW under http://dx.doi.org/10.1002/anie.201305689.



Scheme 1. Synthesis of compounds **3**–**9** (by-products omitted).

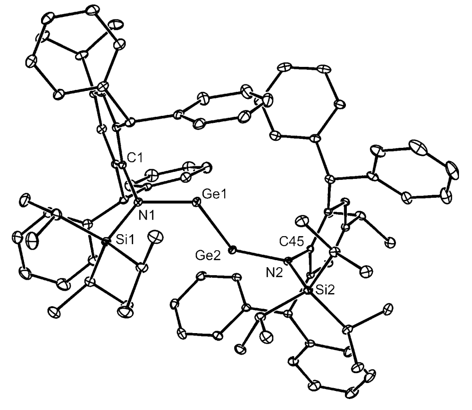


Figure 1. Molecular structure of **3** (25 % ellipsoids; hydrogen atoms omitted). Relevant bond lengths (Å) and angles (°) (Calculated values at BP86 + D3/def2-TZVPP in square brackets): Ge1–Ge2 2.3568(3) [2.362], Ge1–N1 1.8601(14) [1.886], Ge2–N2 1.8631(14) [1.886], N1-Ge1-Ge2 120.39(4) [116.86], N2-Ge2-Ge1 121.03(4) [116.91], C1-N1-Si1 125.22(11) [121.91], C45-N2-Si2 126.44(11) [121.90].

than the single bond in **1** (2.7093(7) Å) by more than 0.35 Å. This is despite the significantly bulkier amido ligands in **3**, and strongly suggests multiple-bond character for the compound. Indeed, the Ge–Ge bond in **3** is only marginally longer than those in known terphenyl digermynes (for example, 2.2850(8) Å for [Ar′GeGeAr′])[3c], whereas its N-Ge-Ge angles (120.7° mean, vs. 100.09(6)° for **1**)[8] are slightly more acute than digermyne C-Ge-Ge angles (for example, 128.67(8)° in [Ar′GeGeAr′]).[3c] The reason for the counter-intuitive Ge–Ge bond shortening in **3**, relative to **1**, most likely lies with the increased ligand bulk in the former. This, apparently, prevents planarization of its Ge$_2$NSiC fragments, thereby disallowing N→Ge π-bonding, as is present in **1**.[13] A comparison of the dihedral angles between the GeNSiC and Ge$_2$N$_2$ least-squares planes in the two compounds (**3**: 73.0°, **1**: 5.2°) supports this view. Another intriguing feature of the structure of **3** is the fact that its Si*i*Pr$_3$ groups take up *cis* positions relative to the Ge$_2$N$_2$ plane, presumably to minimize steric repulsion within the compound.

So as to compare the electronic structure of **3** with that reported for **1** in the gas phase,[8] DFT calculations were carried out on **3**. The calculated and experimental geometries of the compound agree very well (Figure 1), although the slight deviations between the experimental and calculated bond angles might arise from intermolecular interactions for the former in the solid state. An analysis of the frontier orbitals of **3** (Figure 2) reveals its electronic structure to be similar to those previously reported for multiply bonded digermynes. That is, its HOMO largely comprises a π-bond orthogonal to the Ge$_2$N$_2$ fragment, whereas the HOMO-1 is comparable to the essentially non-bonding, or “slipped”, π orbital that lies in the Ge$_2$C$_2$ plane of the organo–digermynes, and is thought to give rise to their singlet biradicaloid character. The LUMO + 1 and LUMO represent the antibonding counterparts of these two orbitals, and no MO exhibits any N→Ge π bonding. Taken as a whole, these results suggest that **3** possesses a

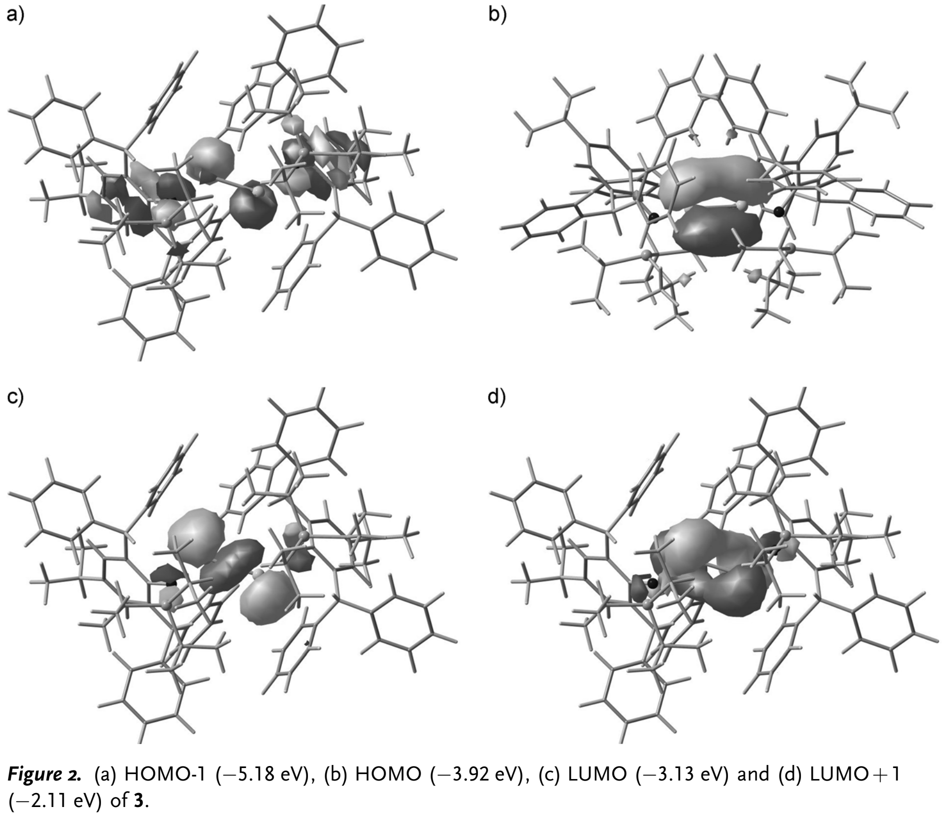


Figure 2. (a) HOMO-1 (−5.18 eV), (b) HOMO (−3.92 eV), (c) LUMO (−3.13 eV) and (d) LUMO + 1 (−2.11 eV) of **3**.

Ge−Ge interaction that is close to a double bond, a view consistent with the Wiberg bond index (WBI) of 1.75. In contrast to **3**, the Ge–Ge σ bond of singly bonded **1** (WBI = 0.94) is associated with its HOMO, whereas its LUMO encompasses an empty Ge–Ge π bond orthogonal to the Ge_2N_2 plane. Despite the significant electronic differences between **3** and **1**, the HOMO–LUMO gaps of both are very narrow (**3**: 0.79 eV, **1**: 0.72 eV), which indicates that **3** might be similarly effective for the activation of dihydrogen as **1**, and [Ar′GeGeAr′].

This proposal was tested by reacting a toluene solution of **3** with excess H_2, which generated an essentially quantitative yield of the orange hydrido–digermene, $[L^2(H)Ge{=}Ge(H)L^2]$ (**4**), within 20 min at 20 °C. The reaction is slower at lower temperatures, but proceeds within 1 hr at temperatures as low as −10 °C. The formation of **4** contrasts with the hydrogenation of **1**, which yielded the mixed-valence species, $[L^1GeGe(H)_2L^1]$ (**2**). However, as was the case with **1**, there was no evidence for the formation of di- or tri-hydrogenation products, even when the reaction with excess H_2 was carried out at elevated temperature. Furthermore, treating **3** with D_2 gave only the deuteride complex, $[L^2(D)Ge{=}Ge(D)L^2]$ (**4-D**). Attempts to reverse the addition of H_2 to **3** by placing a solid sample of **4** under vacuum at 100 °C for 1 h were not successful, but placing a toluene solution of **4-D** under an atmosphere of H_2 did lead to slow, but essentially complete, H/D exchange, and the generation of **4** over a period of approximately 1 week. We found that compound **4** can alternatively be prepared in good yield by the reaction of $[L^2GeCl]$ with $Li[HB\mathit{i}Bu_3]$. This prompted us to explore the preparation of the tin analogue of **4** by a similar reaction involving L^2SnCl. However, this, instead, generated a moderate yield of the yellow-orange hydride bridged tin(II) dimer, $[\{L^2Sn(\mu\text{-}H)\}_2]$ (**5**), which is a valence isomer of the anticipated product. Several terphenyl-substituted tin hydride complexes have been reported, and these normally occur in the solid state as the related hydride-bridged tin(II) species, for example, $[\{Ar'Sn(\mu\text{-}H)\}_2]$.[14]

The solution-state NMR spectroscopic data for **4** are consistent with its proposed formulation, and as such, reveal its amide ligands to be chemically equivalent. So as to examine the possibility of its isomerization to the unsymmetrical isomer, $[L^2GeGe(H)_2L^2]$ (compare with **2**), a variable temperature (−60 to 100 °C) ^1H NMR spectroscopic analysis of the compound was carried out. This did not give any evidence for **4** existing in equilibrium with $[L^2GeGe(H)_2L^2]$ in solution, but it did show that the hydride resonance moves downfield significantly, and reversibly, from δ 8.21 ppm at 20 °C to δ 10.60 ppm at 100 °C (Supporting Information, Figure S1). This is intriguing because the hydride resonances for **2** (δ 6.13 ppm)[8] and the terphenyl substituted analogue of **4**, $[Ar'(H)Ge{=}Ge(H)Ar']$ (δ 5.87 ppm),[5] are at markedly higher field than that for **4**. Furthermore, the compound is thermochromic in solution. That is, at −50 °C it is orange, at 20 °C it is yellow-orange, and at 100 °C it is pale yellow. Consistent with this observation, a variable-temperature UV/Vis spectroscopic analysis of a toluene solution of the compound revealed that an absorption band centered at a λ_{max} of 460 nm (0 °C, assigned as the $n_- \rightarrow n_+$ transition) had almost completely diminished at 100 °C (Figure S2). An isosbestic point was observed in the spectrum at 420 nm, which gives strong evidence that there is an equilibrium between only two species in solution. We contend that this equilibrium is between **4** and the two-coordinate hydrido–germylene, $[{:}Ge(H)(L^2)]$ (**6**). Although a similar equilibrium was suggested for $[Ar'(H)Ge{=}Ge(H)Ar']$,[5] to the best of our knowledge no firm experimental evidence has been forthcoming for the existence of $[{:}Ge(H)(Ar')]$, or any other two-coordinate hydrido germylene.[15] It is possible that **4** is instead in equilibrium with the hydride-bridged isomer, $[\{L^2Ge(\mu\text{-}H)\}_2]$ (compare with **5**), although this is unlikely given that calculations have shown such species to be significantly higher in energy than hydrido–digermenes,[6] of which **4** is an example. Similar to the situation with **4**, we propose that **5** partially dissociates to the hydrido-stannylene, $[{:}Sn(H)(L^2)]$ (**7**), when dissolved in aromatic solvents. This view is supported by its ^1H NMR spectrum ($[D_6]$benzene), which exhibits a hydride resonance at an unprecedentedly low field ($\delta = 19.20$ ppm at 40 °C), as might be expected for a two-coordinate system. Indeed, this resonance is more than 10 ppm downfield from that for $[\{Ar'Sn(\mu\text{-}H)\}_2]$, which is thought to not dissociate in solution.[14b]

Further circumstantial evidence to support the dissociation of **4** and **5** in solution comes from their reactions with 4-dimethylaminopyridine (DMAP). These gave good yields of the pale-yellow monomeric, three-coordinate adducts, $[L^2EH(dmap)]$ (E = Ge **8**, Sn **9**).[16,17] Of course, the possibility that **8** and **9** could be formed from the direct reactions of DMAP with **4** or **5** respectively, cannot be discounted.

Compounds **4**, **5**, and **8** were crystallographically characterized, and the molecular structures of **4** and **8** are shown in Figure 3 (see the Supporting Information for the molecular structure of **5**). Outwardly, the dimeric structure of **4** is similar to that of $[Ar'(H)Ge = Ge(H)Ar']$.[5] However, not only is its Ge–Ge bond (2.4864(4) Å) more than 0.18 Å longer than the double bond in $[Ar'(H)Ge{=}Ge(H)Ar']$ (2.3026(3) Å), but it is longer than many Ge−Ge single bonds (for example, 2.458 Å for cyclo $[(Ph_2Ge)_6]$[18]). Indeed, the only longer Ge=Ge bond (2.5087(7) Å), can be found in the very hindered bromo–digermene, [Bbt(Br)Ge=Ge(Br)Bbt] (Bbt = 2,6-$[C(H)(SiMe_3)]_2$-4-$[C(SiMe_3)_3]C_6H_2$), which exists in equilibrium with the bromo–germylene, $[{:}Ge(Br)(Bbt)]$, in solution (compare with **4**).[19] Another unusual feature of the structure of **4**, is the *trans*-bending angle (54°) the Ge−Ge vector makes with the vector that bisects the N-Ge-H angle. This is markedly more obtuse than the *trans*-bending angle in $[Ar'(H)Ge{=}Ge(H)Ar']$ (45°),[5] and implies that the Ge−Ge bond in **4** has significantly less π character than that in $[Ar'(H)Ge{=}Ge(H)Ar']$. It is possible that, as in **1**, π bonding in **4** is frustrated by a degree of overlap of each of the *p*-orbital lone pairs of its N atoms with the empty *p*-orbital at the adjacent Ge center. The geometry at each Ge center (dihedral angle between H-Ge-N and C-N-Si planes = 7.6°) is certainly amenable to such an overlap. All of these structural features point towards the Ge−Ge interaction in **4** being relatively weak, and are consistent with its proposed dissociation in solution.

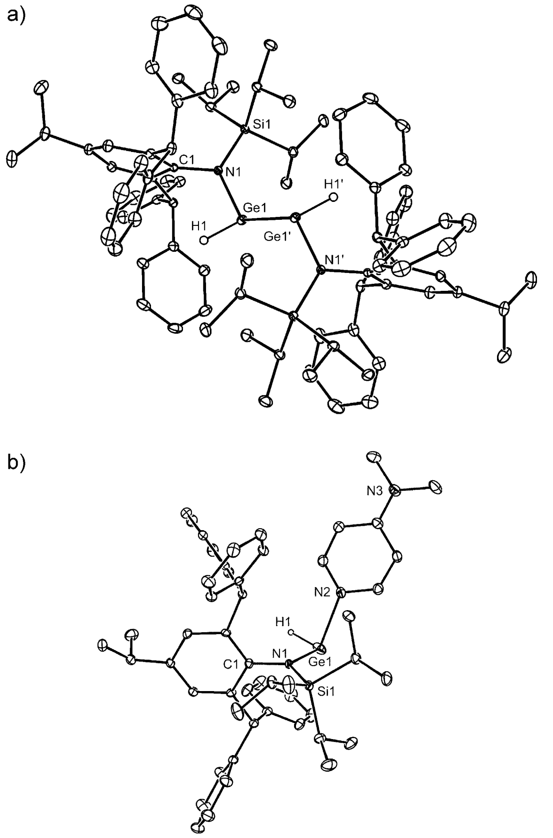


Figure 3. Molecular structures of a) **4** and b) **8** (ellipsoids set at 25% probability, non-hydride hydrogen atoms omitted). Relevant bond lengths (Å) and angles (°) for **4** (Calculated values at BP86 + D3/def2-TZVPP in square brackets): Ge1–N1 1.8564(13) [2.510], Ge1–Ge1′ 2.4864(4) [2.510], Ge1–H1 1.470(8) [1.572], N1-Ge1-Ge1′ 117.85(4) [116.18], N1-Ge1-H1 98.2(9) [97.22], C1-N1-Si1 116.58(10) [119.19]. Symmetry operation: $'-x+1, -y+2, -z+1$. Relevant bond lengths (Å) and angles (°) for **8** (Calculated values at BP86 + D3/def2-TZVPP in square brackets): Ge1–N1 1.933(3) [1.983], Ge1–N2 2.204(4) [2.241], Ge1–H1 1.494(8) [1.607], N1-Ge1-N2 107.98(13) [104.33], N1-Ge1-H1 99.9(14) [102.73], N2-Ge1-H1 89.5(13) [91.96], C1-N1-Si1 120.8(3) [116.48].

The molecular structure of **5** shows it to be an unsymmetrically hydride-bridged dimer that is closely related to several previously reported terphenyl-substituted systems, for example, $[\{Ar'Sn(\mu\text{-}H)\}_2]$.[14] However, the Sn⋯Sn separation in **5** (3.35 Å) is considerably greater than in all of the terphenyl tin(II) hydrides, for example, 3.13 Å for $[\{Ar'Sn(\mu\text{-}H)\}_2]$.[14] Similar to **4**, this difference probably results from some overlap of the p-orbital lone pairs of the N atoms of **5** with the empty *p*-orbitals of the Sn centers (dihedral angle between H-Sn-N and C-N-Si planes = 20.9°). This, in turn, could lead to a weakening of the hydride bridges in **5**, and its proposed equilibrium with $[:Sn(H)(L^2)]$ (**7**) in solution. The structure of **8** reveals it to be the first example of a monomeric, three-coordinate, acyclic germanium(II) hydride complex, although it is related to two cyclic systems in which the Ge center is *N,N′*-chelated by a delocalized β-diketiminate ligand, for example, $[(^{Mes}Nacnac)GeH]$.[20]

DFT calculations were carried out on **4** and **8**, and their geometries optimized to be in good agreement with those in the solid state (Figure 3). An analysis of the frontier orbitals of **4** revealed them to be similar to those described for other digermenes (Figure S8). The geometry of the mixed-valence isomeric form of **4**, $[L^2GeGe(H)_2L^2]$, was also optimized and found to be slightly higher in energy ($\Delta H = 2.59$ kcal mol^{-1}, $\Delta G = 1.92$ kcal mol^{-1}) than **4**. This is the reverse of the situation for **2** and $[L^1(H)GeGe(H)L^1]$, the former of which is energetically favored ($\Delta H = 3.08$ kcal mol^{-1}, $\Delta G = 0.08$ kcal mol^{-1}), thereby providing an explanation for the isomeric differences between **2** and **4**. Moreover, a comparison of the energies of **3** and **4** shows the hydrogenation of the former to be exergonic by $\Delta G = -6.65$ kcal mol^{-1} (vs. $\Delta G = -9.35$ kcal mol^{-1} for the hydrogenation of **1**). Finally, the gas-phase structures of the germylene, $[:Ge(H)(L^2)]$ (**6**), and stannylene, $[:Sn(H)(L^2)]$ (**7**), were optimized, which allowed the calculation of the dissociation energies for **4** and **5**. Both are only mildly endergonic processes at 298 K ($\Delta G = 19.4$ kcal mol^{-1} for **4**, 15.4 kcal mol^{-1} for **5**; vs. 14.2 kcal mol^{-1} for [Bbt(Br)Ge=Ge(Br)Bbt]), which indicates that they may well dissociate to some degree in solution, especially at elevated temperatures, as the experimental evidence suggests.

In summary, an extremely bulky amide ligand has been used to stabilize the first multiply bonded amido–digermyne, $[L^2GeGeL^2]$, thereby demonstrating steric control over Ge–Ge bond orders. The digermyne activates H_2 below 0 °C, quantitatively yielding a hydrido–digermene with a very long Ge–Ge double bond, $[L^2(H)Ge{=}Ge(H)L^2]$. Spectroscopic and theoretical evidence indicate that this exists in equilibrium with the hydrido–germylene, $[:Ge(H)(L^2)]$, in solution. We are currently examining the use of the hydrido–germylene as a powerful, ambiphilic hydrogermylating agent towards unsaturated substrates, and will report on this, and a comparison of the mechanisms of hydrogenation for both $[L^1GeGeL^1]$ and $[L^2GeGeL^2]$, in due course.

Received: July 2, 2013

Keywords: DFT calculations · digermene · digermyne · hydride ligands · hydrogen activation

---

[1] For selected reviews on ditetrelyne chemistry, see: a) C. A. Caputo, P. P. Power, *Organometallics* **2013**, *32*, 2278 – 2286; b) A. Sekiguchi, *Pure Appl. Chem.* **2008**, *80*, 447 – 457; c) P. P. Power, *Organometallics* **2007**, *26*, 4362 – 4372; d) E. Rivard, P. P. Power, *Inorg. Chem.* **2007**, *46*, 10047 – 10064.

[2] M. Lein, A. Krapp, G. Frenking, *J. Am. Chem. Soc.* **2005**, *127*, 6290 – 6299.

[3] a) Y. Peng, R. C. Fischer, W. A. Merrill, J. Fischer, L. Pu, B. D. Ellis, J. C. Fettinger, R. H. Herber, P. P. Power, *Chem. Sci.* **2010**, *1*, 461 – 468; b) Y. Sugiyama, T. Sasamori, Y. Hosoi, Y. Furukawa, N. Takagi, S. Nagase, N. Tokitoh, *J. Am. Chem. Soc.* **2006**, *128*, 1023 – 1031; c) M. Stender, A. D. Phillips, R. J. Wright, P. P. Power, *Angew. Chem.* **2002**, *114*, 1863 – 1865; *Angew. Chem. Int. Ed.* **2002**, *41*, 1785 – 1787.

[4] For selected recent reviews, see: a) S. S. Sen, S. Khan, P. P. Samuel, H. W. Roesky, *Chem. Sci.* **2012**, *3*, 659 – 682; b) P. P. Power, *Acc. Chem. Res.* **2011**, *44*, 627 – 637; c) M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111*, 354 – 396; d) P. P. Power, *Nature* **2010**, *463*, 171 – 177.

[5] G. H. Spikes, J. C. Fettinger, P. P. Power, *J. Am. Chem. Soc.* **2005**, *127*, 12232 – 12233.

[6] L. L. Zhao, F. Huang, G. Lu, Z.-X. Wang, P. v. R. Schleyer, *J. Am. Chem. Soc.* **2012**, *134*, 8856 – 8868.

[7] J. Li, A. Stasch, C. Schenk, C. Jones, *Dalton Trans.* **2011**, *40*, 10448 – 10456.

[8] J. Li, C. Schenk, C. Goedecke, G. Frenking, C. Jones, *J. Am. Chem. Soc.* **2011**, *133*, 18622 – 18625.

[9] a) J. Hicks, T. J. Hadlington, C. Schenk, J. Li, C. Jones, *Organometallics* **2013**, *32*, 323 – 329; b) J. Hicks, C. Jones, *Inorg. Chem.* **2013**, *52*, 3900 – 3907; c) J. Li, C. Schenk, F. Winter, H. Scherer, N. Trapp, A. Higelin, S. Keller, R. Pöttgen, I. Krossing, C. Jones, *Angew. Chem.* **2012**, *124*, 9695 – 9699; *Angew. Chem. Int. Ed.* **2012**, *51*, 9557 – 9561; d) A. V. Protchenko, K. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2012**, *134*, 6500 – 6503; e) D. Dange, J. Li, C. Schenk, H. Schnöckel, C. Jones, *Inorg. Chem.* **2012**, *51*, 13050 – 13059.

[10] W. D. Woodul, E. Carter, R. Müller, A. F. Richards, A. Stasch, M. Kaupp, D. M. Murphy, M. Driess, C. Jones, *J. Am. Chem. Soc.* **2011**, *133*, 10074 – 10077.

[11] E. W. Y. Wong, D. Dange, L. Fohlmeister, T. J. Hadlington, C. Jones, *Aust. J. Chem.*, DOI: 10.1071/CH13175.

[12] a) A. Stasch, C. Jones, *Dalton Trans.* **2011**, *40*, 5659 – 5672; b) S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, *Chem. Eur. J.* **2010**, *16*, 938 – 955.

[13] The nature of Si–Si bonding in tetra(amido)disilenes has been shown to be similarly dependent on the bulk of the ligands involved; see: M. Takahashi, S. Tsutsui, K. Sakamoto, M. Kira, T. Müller, Y. Apeloig, *J. Am. Chem. Soc.* **2001**, *123*, 347 – 348.

[14] a) Y. Peng, B. D. Ellis, X. Wang, P. P. Power, *J. Am. Chem. Soc.* **2008**, *130*, 12268 – 12269; b) E. Rivard, R. C. Fischer, R. Wolf, Y. Peng, W. A. Merrill, N. D. Schley, Z. Zhu, L. Pu, J. C. Fettinger, S. J. Teat, I. Nowik, R. H. Herber, N. Takagi, S. Nagase, P. P. Power, *J. Am. Chem. Soc.* **2007**, *129*, 16197 – 16208; c) B. E. Eichler, P. P. Power, *J. Am. Chem. Soc.* **2000**, *122*, 8785 – 8786.

[15] It has been proposed that $[\mathrm{Ar'GeH_3}]$ formed in the reaction of $[\mathrm{Ar'GeGeAr'}]$ with $\mathrm{H_2}$, may arise from the hydrogenation of a germylene intermediate, $[\mathrm{:Ge(H)(Ar')}]$ (Ref. [5]). However, the results of a recent theoretical study (Ref. [6]) indicate that the hydrogenation of another intermediate, $[\mathrm{Ar'GeGe(H)_2Ar'}]$, may instead give $[\mathrm{Ar'GeH_3}]$.

[16] The reaction of $[\mathrm{Ar'(H)Ge{=}Ge(H)Ar'}]$ with $\mathrm{PMe_3}$ does not lead to Ge–Ge bond cleavage, but instead to the mixed valence adduct, $[\mathrm{Ar'(Me_3P)GeGe(H_2)Ar}]$; see: A. F. Richards, A. D. Phillips, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 3204 – 3205.

[17] In an attempt to access a two-coordinate hydrido–germylene in the solid state, an amide of unprecedented steric bulk was developed and used to prepare the precursor complex, $[\mathrm{L^3GeCl}]$ ($\mathrm{L^3 = N(Ar^3)(Si}i\mathrm{Pr_3)}$, $\mathrm{Ar^3 = 2{,}6\text{-}[C(H)(4\text{-}}t\mathrm{BuC_6H_4)_2]_2\text{-}4\text{-}}i\mathrm{PrC_6H_2}$). However, treatment of this with $\mathrm{K[HB(}s\mathrm{ec\text{-}Bu)_3]}$ gave a complex product mixture, from which only a few crystals of the germanium(III) hydride, $[\mathrm{L^3(H)_2GeGe(H)_2L^3}]$ were isolated (see the Supporting Information for details).

[18] M. Drager, L. Ross, D. Simon, *Z. Anorg. Allg. Chem.* **1980**, *466*, 145 – 156.

[19] T. Sasamori, Y. Sugiyama, N. Takeda, N. Tokitoh, *Organometallics* **2005**, *24*, 3309 – 3314.

[20] a) S. L. Choong, W. D. Woodul, C. Schenk, A. Stasch, A. F. Richards, C. Jones, *Organometallics* **2011**, *30*, 5543 – 5550; b) L. W. Pineda, V. Jancik, K. Starke, R. B. Oswald, H. W. Roesky, *Angew. Chem.* **2006**, *118*, 2664 – 2667; *Angew. Chem. Int. Ed.* **2006**, *45*, 2602 – 2605.