JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
COMMUNICATION
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A Digermyne with a Ge−Ge Single Bond That Activates Dihydrogen in the Solid State

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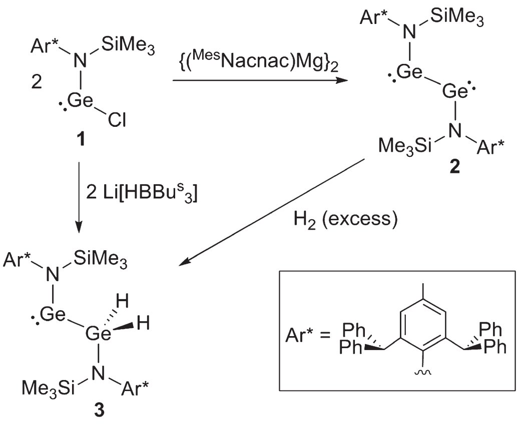
S Supporting Information

ABSTRACT: The reduction of the bulky amido-germanium(II) chloride complex, LGeCl (L = N(SiMe$_3$)(Ar*); Ar* = $C_6H_2Me\{C(H)Ph_2\}_2$-4,2,6), with the magnesium(I) dimer, $[\{(^{Mes}Nacnac)Mg\}_2]$ (^{Mes}Nacnac = $[(MesNCMe)_2CH]^-$; Mes = mesityl), afforded LGeGeL, which represents the first example of a digermyne 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_2 in solution or the solid state, at temperatures as low as −10 °C, to give the mixed valence compound, LGeGe(H)$_2$L.

The past two decades have seen major fundamental advances in the chemistry of low oxidation state p-block compounds.[1] 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°).[2] 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.[3] 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.[2,4] Their resultant high reactivity toward small molecules and unsaturated substrates has led to digermynes being described as main group mimics of transition metal complexes.[1a,d] This reactivity is epitomized by the landmark study of Power et al. who, in 2005, demonstrated for the first time that H_2 can be activated by a main group metal complex, Ar′GeGeAr′ (Ar′ = $C_6H_3(C_6H_3Pr^i_2\text{-}2,6)_2$-2,6), at room temperature and atmospheric pressure.[5] The hydrogenation of Ar′GeGeAr′ yielded mixtures of Ar′(H)GeGe(H)Ar′, Ar′(H)$_2$GeGe(H)$_2$Ar′, and Ar′GeH$_3$, the compositions of which were shown to be dependent upon the reaction stoichiometry.[5] 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_2 at or near ambient temperature.[6]

Although digermynes containing Ge−Ge single bonds are unknown,[7] 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,[8] which would not only provide kinetic protection, but could also circumvent Ge−Ge multiple bonding by offering the possibility of N lone pair → Ge π-interactions in the complex. Here, we report the synthesis, characterization, and bonding analysis of the first amido-substituted digermyne, which possesses a Ge−Ge single bond, and which cleanly activates H_2 in solution or the solid state at atmospheric pressure and temperatures as low as −10 °C.

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



The reduction of the bulky monomeric amido-germanium(II) chloride, LGeCl **1** (L = N(SiMe$_3$)(Ar*); Ar* = $C_6H_2Me\{C(H)Ph_2\}_2$-4,2,6),[9] with half an equivalent of the magnesium(I) dimer, $[\{(^{Mes}Nacnac)Mg\}_2]$ (^{Mes}Nacnac = $[(MesNCMe)_2CH]^-$; Mes = mesityl),[10] 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$_8$, 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: λ_{max} [nm] (ε [L mol^{-1} cm^{-1}]): 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°[2]).

Received: September 30, 2011
Published: October 25, 2011

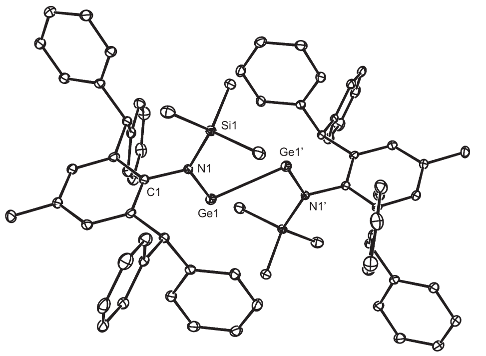


Figure 1. Thermal ellipsoid plot (20% probability surface) of the molecular structure of [LGeGeL] (**2**); hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)−N(1) 1.872(2), Ge(1)−Ge(1)′ 2.7093(7), Si(1)−N(1) 1.762(2), N(1)−C(1) 1.445(3), N(1)−Ge(1)−Ge(1)′ 100.09(6), 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),[4] which is more than 0.4 Å longer than those of other multiply bonded digermynes.[2] It is noteworthy that terphenyl substituted, singly bonded distannynes and diplumbynes related to **2** have been reported.[11] The differences between **2** and other digermynes could result from the fact that its NSiCGe and Ge_2N_2 least-squares planes are essentially coplanar (dihedral angle: 5.2°), thereby potentially allowing N → Ge π-interactions,[12] 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-dicarbenes. There are no significant aryl−Ge contacts (closest: 3.34 Å, cf. 3.03 Å in LGeCl[9]) 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[13] (cf. the Ge−Ge distance in H_3GeGeH_3: 2.403 Å[14]). The LUMO has considerable Ge−Ge π-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[1a]). As expected, several MOs (e.g., HOMO-6) exhibit significant N−Ge π-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 digermyne, 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°).[3b] 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 ΔG = 10.0 kcal/mol higher in energy than **2**.

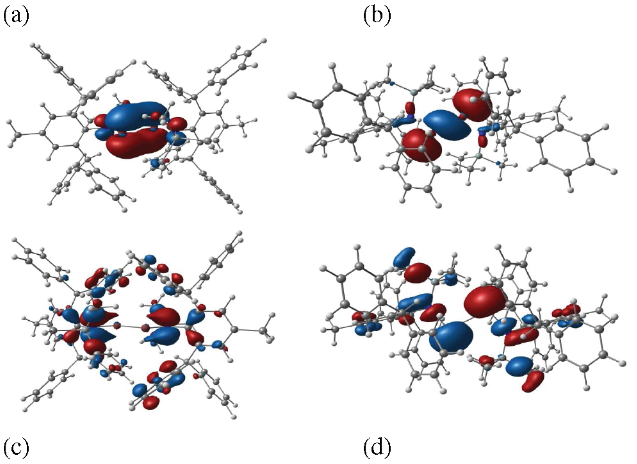


Figure 2. (a) LUMO (−2.934 eV), (b) HOMO (−3.557 eV), (c) HOMO-6 (−5.844 eV), and (d) HOMO-23 (−6.623 eV) of **2**.

Given the emerging "transition metal-like" reactivity of multiply bonded digermynes,[1a,d] reactions of **2** with dihydrogen were examined. When toluene or d_6-benzene solutions of the compound were exposed to an excess of H_2 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_2 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_2 up to 100 °C.[15] It is of note, however, that mixtures of the formal double hydrogenation product, $L(H)_2GeGe(H)_2L$ **4**, and **3** were obtained from the reactions of LGeCl with either $Li[HBBu^s_3]$ or $K[HBEt_3]$.[16] 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, $LGe^{II}H$, in these reactions. The other product, **3**, can easily be envisaged as ultimately resulting from the dimerization of $LGe^{II}H$ (vide infra).

Both compounds **3** and **4** display two Ge−H stretching bands in their infrared spectra (**3**: ν 1990, 2031 cm^{-1}; **4**: ν 2030, 2076 cm^{-1}), which lie in the expected region for terminal tetravalent germanium hydrides.[17] In their ^1H NMR spectra, hydride resonances appear at δ 6.13 ppm (**3**) and δ 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_8-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 $Ar'(H)_2Ge$ GeAr′,[1a] evidence for which comes from the addition of PMe_3 to a solution of Ar′(H)GeGe(H)Ar′, which leads to the base stabilized mixed valence compound, $Ar'(H)_2GeGeAr' \cdot PMe_3$.[18]

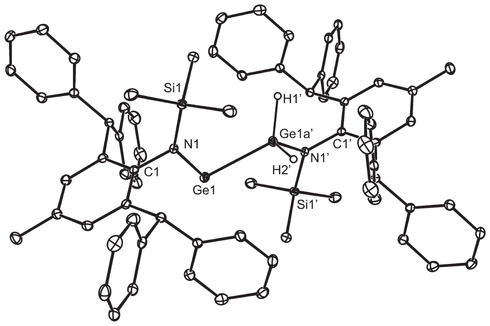


Figure 3. Thermal ellipsoid plot (20% probability surface) of the molecular structure of [LGeGe(H)$_2$L] (**3**); hydrogen atoms (except hydrides) are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)−Ge(1A)′ 2.5507(8), Ge(1)−N(1) 1.8802(16), Ge(1A)′−N(1)′ 1.8748(16), Ge(1A)′−H(1)′ 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)$_2$GeGeAr′·PMe$_3$ (2.5304(7) Å),[18] yet significantly longer than the double bond in Ar′(H)GeGe(H)Ar′ (2.3026(3) Å).[5] 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′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[5]). 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′GeGeAr′, which involves interaction of its frontier π-bonding HOMO and nonbonding LUMO (n+ combination) with the H_2 σ*- and σ-orbitals, respectively.[1d] Instead, it could be similar to the mechanism proposed for the hydrogenation of the germylene, Ar$^{\#}_2$Ge: (Ar$^{\#}$ = $C_6H_3(C_6H_2Me_3\text{-}2,4,6)_2\text{-}2,6$), which proceeds only at 65 °C to give Ar$^{\#}_2$GeH$_2$. This mechanism is thought to entail an initial interaction of the H_2 σ-orbital with the empty 4p orbital at Ge, with concomitant back-donation from the Ge lone pair into the H_2 σ*-orbital.[19] 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

Ⓢ 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)$_2$GeGe(H)(OH)L] and [L(H)$_2$GeGe(H){K(OEt$_2$)$_2$}L]. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

C.J. thanks the Australian Research Council (DP0665057) and the US Air Force Asian Office of Aerospace Research and Development for financial support. G.F. acknowledges the Deutsche Forschungsgemeinschaft (grant FR641/25-1). C.S. thanks the Alexander von Humboldt Foundation for a Feodor-Lynen Fellowship. The EPSRC Mass Spectrometry Service at Swansea University is also thanked. Part of this research was undertaken on the MX1 beamline at the Australian Synchrotron, Victoria, Australia. Dr. Andreas Stasch is acknowledged for the refinement of the X-ray crystal structure of compound **2**. This paper is dedicated to Professor Matthias Driess on the occasion of his 50th birthday.

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