

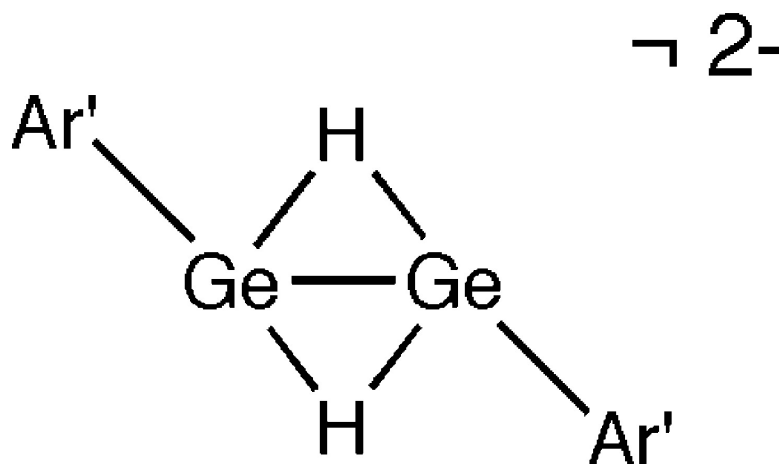
Communication

**Reduction of Digermenes with Alkali Metals: Salts of Formula  $M\{\text{Ge}(\text{H})\text{Ar}'\}$  ( $M = \text{Li}, \text{Na}, \text{or K}, \text{Ar}' = \text{Terphenyl}$ ) with Three Different Structures**

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## Reduction of Digermenes with Alkali Metals: Salts of Formula $M_2\{[Ge(H)Ar']_2\}$ ( $M = Li, Na, \text{ or } K, Ar' = \text{Terphenyl}\}$ with Three Different Structures

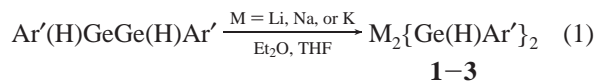
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The synthesis of the stable heavier group 14 element alkyne analogues  $ArMMAr$  ( $M = Ge, Sn \text{ or } Pb; Ar = \text{terphenyl}$ ), by reduction of the halides  $ArMX$  with alkali metals, has shown that their singly and doubly reduced congeners  $[ArMMAr]^-$  and  $[ArMMAr]^{2-}$  are also readily obtained.<sup>1,2</sup> In fact, unless care is exercised in the reaction stoichiometry and conditions, the anionic species are crystallized in preference to the neutral compounds.<sup>2</sup> This is the major reason the ionic species were discovered first.<sup>3</sup> In contrast, less is known about the structures of the reduction products of the corresponding alkene analogues  $R_2MMR_2$  ( $R = \text{alkyl or aryl}; M = Si-Pb$ ). Electrochemical studies on some disilenes showed that they underwent irreversible oxidation and reduction.<sup>4</sup> The reduction of 1,2-dihalo-1,1,2,2-tetraorganodisilanes gave radicals of formula  $[R_2SiSiR_2]^-$ .<sup>5</sup> Similarly, the monomers  $:MR_2$  could be reduced to  $[:MR_2]^-$  ( $M = Ge \text{ or } Sn; R = CH(SiMe_3)_2$ ).<sup>6</sup> Other reductions led to rearrangement and/or disproportionation reactions. Thus, the reduction of  $c\text{-(}SnAr_2)_3$  ( $Ar = C_6H_3\text{-}2,6\text{-Et}_2$ ) gave  $Sn_5Ar_6$  or  $Sn_7Ar_8$ .<sup>7</sup> Reduction of  $R_2MMR_2$  ( $M = Si \text{ or } Ge; R = C_6H_2\text{-}2,4,6\text{-Pr}^i_3$ ) with Li led to  $M-C$  bond cleavage and rearrangement to give cyclic or acyclic products rather than simple  $[R_2MMR_2]^{1-/2-}$  ions.<sup>8</sup> Nonetheless, stable singly or doubly reduced species from the direct reduction of  $R_2MMR_2$  heavier group-14 dimetallenes have not been isolated. We now report the characterization of three alkali metal salts of doubly reduced digermenes and show that the reactions proceed without bond cleavage. The structures obtained are determined by the alkali metal reducing agent.

The compounds  $[Li(THF)_3(OEt_2)][LiAr'(H)GeGe(H)Ar']$  (**1**),  $Na_2\{Ar'(H)GeGe(H)Ar'\}$  (**2**), and  $K_2\{Ar'(H)GeGe(H)Ar'\}$  (**3**) were synthesized as red crystals by treatment of  $Ar'(H)GeGe(H)Ar'$  ( $Ar' = C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-Pr}^i_3)_2$ )<sup>9</sup> with Li powder or with Na or K sand in PhMe (eq 1).

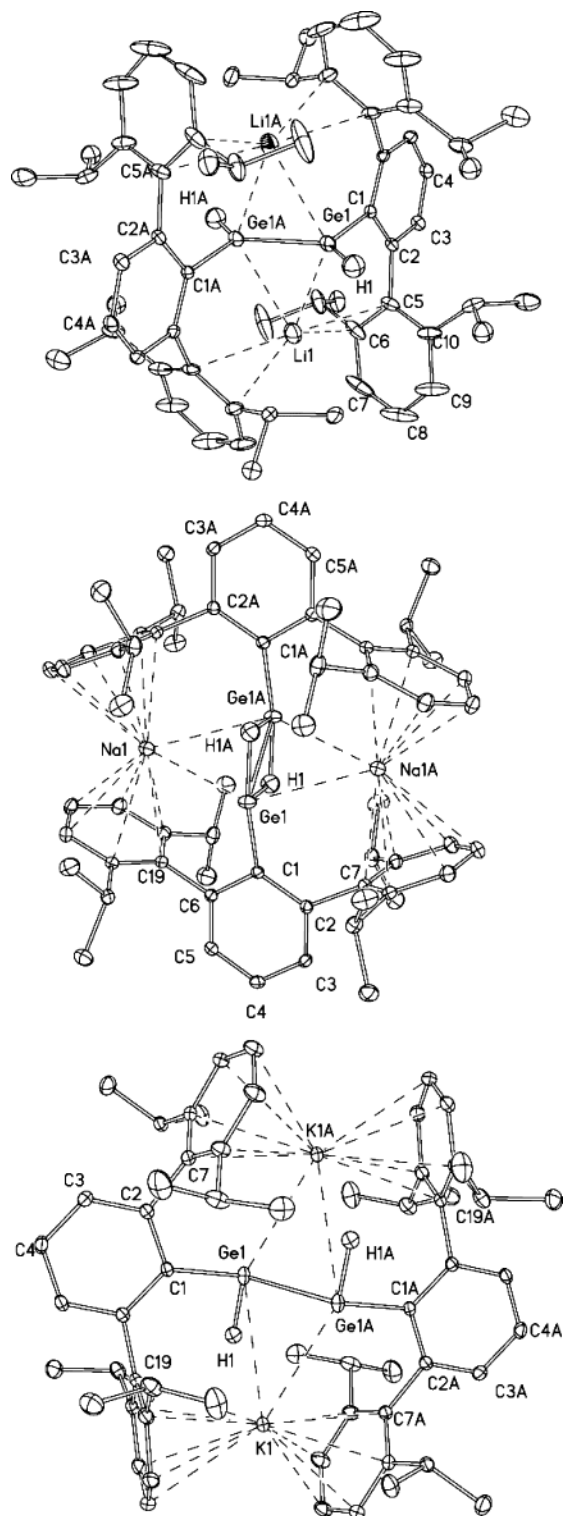


Compounds **1–3** were obtained as deep red or black crystals, which were studied by NMR, IR, and UV-vis spectroscopy and by X-ray crystallography.<sup>10,11</sup> Three distinct structures were observed (Figure 1) that are dependent on the type of alkali metal used. The H atoms bound to Ge were located and allowed to refine freely in **1**, but with fixed parameters in **2** and **3**. In **1**, the anion has a planar  $C(ipso)(H)GeGe(H)C(ipso)$  core. One  $Li^+$  ion is incorporated over two positions (0.5 occupancy) that lie above and below the Ge-Ge bond and bridges it symmetrically ( $Ge-Li = 2.73(3)$  Å). It is further complexed by two flanking  $-C_6H_3\text{-}2,6\text{-Pr}^i_2$  rings of the  $Ar'$  ligands. The other  $Li^+$  ion is solvent separated by complexation to  $Et_2O$  and three THF molecules and is disordered over two positions. The Ge-Ge, Ge-C, and Ge-H distances are

2.395(2), 2.043(6), and 1.58(9) Å, respectively. The structure of the dipotassium salt **3** is related to that of **1**, but the  $[Ar'(H)GeGe(H)Ar']^{2-}$  dianion has a trans-pyramidal rather than a planar structure. Both  $K^+$  ions form a contact ion triple with the dianion in which the  $K^+$  ions are located on either side of the Ge-Ge bond axis almost midway between the germaniums. The Ge-Ge, Ge-C, and Ge-H bond lengths are 2.6468(4), 2.065(2), and 1.52 Å, and the K-Ge distances are 3.5013(7) (K1) and 3.2850(6) (K1A) Å. The angle between the Ge-Ge bond and the (ipso)GeH plane is 67.3°. The structure of **2** differs markedly from those of **1** and **3**. It features a doubly reduced  $[Ar'Ge(\mu-H)_2GeAr']^{2-}$  dianion in which two hydrogens and two  $Na^+$  ions bridge the germaniums. The Ge-Ge separation is 2.5904(5) Å, and the Ge-C and Ge-H distances are 2.047(2) and 1.61 Å. The Na-Ge distances are 3.052(1) and 3.122(1) Å. The <sup>1</sup>H NMR spectra of **1–3** display integrally consistent Ge-H signals at  $\delta$  3.50, 3.91, and 4.34 ppm, respectively. The IR spectra of **1** and **3** as Nujol mulls afford Ge-H absorptions at 1930 and 1940  $cm^{-1}$ , but at 1852  $cm^{-1}$  for **2**.<sup>12</sup>

The lengthening of the Ge-Ge distances that occurs on reduction of **1–3** is noteworthy. Calculations for the model digermene precursor  $Me(H)GeGe(H)Me$  show that it has a trans-bent  $C_{2h}$  geometry with pyramidally coordinated germaniums and  $Ge-Ge = 2.187$  Å. This is shorter than the 2.372(1) Å observed in the neutral precursor  $Ar'(H)GeGe(H)Ar'$ <sup>9</sup> probably for steric reasons. DFT calculations on the model anion of **1**,  $[LiMe(H)GeGe(H)Me]^-$ , confirm the planar structure, but a Ge-Ge distance, 2.449 Å, is over 0.26 Å longer than that in  $Me(H)GeGe(H)Me$ . The lengthening is due to the addition of a pair of electrons to the  $\pi^*$ -LUMO in  $Me(H)GeGe(H)Me$ . Surprisingly, the experimental Ge-Ge distance (2.395(1) Å) in **1** is ca. 0.05 Å shorter than that calculated for  $[LiMe(H)GeGe(H)Me]^-$ . This is contrary to what is expected on steric grounds, but the calculations do not take into account the complexation of the  $Li^+$  ion by the aryl rings which can shorten the Ge-Ge distance through strong interactions with the aryl rings.<sup>13,14</sup> The calculated Ge-Ge bond length (2.561 Å) in the  $K_2\text{-}Me(H)GeGe(H)Me$  model for the potassium salt **3** is also shorter than the experimentally observed 2.6468(4) Å for the same reason, i.e. because the  $K^+$ -aryl contacts are not considered in the calculation. The other pyramidal Ge coordination is reproduced fairly accurately by the calculations, which is consistent with the much longer (by ca. 0.25 Å) Ge-Ge distance observed.

The H-bridging character of **2** is unique for a stable Ge-Ge-bonded species. The X-ray data for **2** do not afford exact structural parameters for the bridging hydrides and cannot confirm that they are symmetrically bound. However, computations by Trinquier on the model species  $HGe(\mu-H)_2GeH$  have shown that it is a minimum on the potential surface just 9 kcal  $mol^{-1}$  above the lowest-energy trans-pyramidal form  $H_2GeGeH_2$ .<sup>15</sup> It is thus probable that the doubly reduced  $[HGe(\mu-H)_2GeH]^{2-}$  is close in energy to its  $[H_2GeGeH_2]^{2-}$  isomer. As a result, it is possible that the size of



**Figure 1.** Thermal ellipsoid drawings of **1** (anion, top 50% Li occupancy), **2** (middle), **3** (bottom). Selected bond lengths (Å) and angles (deg): **1**, Ge–Ge = 2.395(2), Ge–C = 2.043(6), Ge–H = 1.58(9), Ge–Ge–C = 100.7(2), Ge–Ge–H = 133(3); **2**, Ge–Ge = 2.590(5), Ge–C = 2.047(2), Ge–H = 1.61, Ge–Ge–C = 108.09(6), C–Ge–H = 71.2; **3**, Ge–Ge = 2.6468(3), Ge–C = 2.065(2), Ge–H = 1.52, Ge–Ge–C = 111.10(5), Ge–Ge–H = 97.3(8), C–Ge–H = 97.7(8).

$\text{Na}^+$ , and its complexation by the aryl rings of the terphenyl ligand, could stabilize a H-bridged structure in **2**. Calculations on the simple

model species  $\text{Na}_2\text{Ge}_2\text{H}_2\text{Me}_2$  indicate that the bridged structure is not a minimum on the potential surface. Seemingly, the stability **2** is due to complexation of the  $\text{Na}^+$  ions by the aryl rings. A detailed explanation of the factors that govern the stability of **2** await higher-level calculations on more sophisticated model species incorporating the terphenyl ligands used experimentally.<sup>14</sup> The bonding between the two  $[\text{Ge}(\text{H})\text{Ar}]^-$  units comprising the dianion  $[\text{Ar}'\text{Ge}(\mu\text{-H})_2\text{GeAr}]^{2-}$  involves coupling of the unpaired electrons from the putative  $[\text{Ge}(\text{H})\text{Ar}]^-$  radical anion. It remains to be seen if this is a genuine Ge–Ge bond or an instance of singlet biradical character as recently observed in several main-group species.<sup>16</sup> The lower Ge–H infrared frequencies observed for **2** are also consistent with the bridged configuration in the X-ray crystal structure. The synthesis of **1–3** underlines the ability of terphenyl ligands to complex cations to the centers of anionic charge and provide the stabilization necessary to isolate these unstable dianionic species.

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**Supporting Information Available:** X-ray crystallographic data in CIF format. Synthetic data for **1–3** and details of DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>

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