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Effects of the alkali metal counter ions on the germanium–germanium double bond length in a heavier group 14 element ethenide salt

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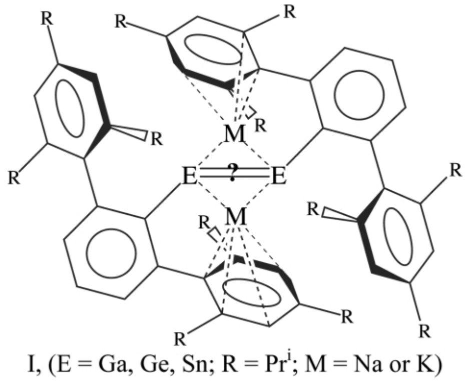
The first, well-characterized 1,2-dilithium salt of a group 14 element ethenide species, [{(dioxane)$_{0.5}$(Et$_2$O)LiGeC$_6$H$_3$-2,6-Mes$_2$}$_2$]$_\infty$, shows that the positions of the cations have a large effect on the length of the Ge–Ge double bond.

Sterically encumbered terphenyls have proven successful ligands for the stabilization of a variety of compounds with unusual coordination or bonding.[1] Prominent among these are the doubly reduced salts, **I**, in which two alkali metals (M) bridge the E–E multiple bond in an [ArEEAr]$^{2-}$ (Ar = terphenyl) dianion.[2,3] In these complexes the flanking aryl groups also coordinate the M$^+$ cations which may affect the stability of the complex as well as the E=E bond length. Calculations by Cotton, Cowley and Feng[4] for the gallium species Na$_2$ArGaGaAr,[2] using C$_6$H$_3$-2,6-Ph$_2$, as a model terphenyl ligand[4] suggested that complexation by the flanking aryl exerted a significant shortening effect on the Ga–Ga distance. This result was supported by detailed calculations by Schaefer, Nagase and their coworkers.[5,6] The corresponding M$^+$ salts of Ge and Sn, M$_2$[ArEEAr], (Ar = Ar′ = C$_6$H$_3$-2,6(C$_6$H$_3$-2,6-Pr$^i_2$)$_2$ or Ar* = C$_6$H$_3$-2,6(C$_6$H$_2$-2,4,6-Pr$^i_3$)$_2$) have similar structures, in which Na$^+$ or K$^+$ ions complexed by flanking aryls, bridge the Ge or Sn centers.[3] There are no theoretical data available for models of these reduced group 14 species. Furthermore, there are no experimental data on either the group 13 or 14 compounds that examine the rôle played by the location of the M$^+$ ions. In other words, the experimental effects of moving the M$^+$ ion to terminal positions, or their removal to give solvent separated ion pairs, are unknown. We now describe the synthesis, structural characterization and calculations on the *trans*-1,2-dilithio-1,2-diaryl species [{(dioxane)$_{0.5}$(Et$_2$O)LiGeC$_6$H$_3$-2,6-Mes$_2$}$_2$]$_\infty$, **1**, in which, for the first time, the alkali metal is terminally bound to the germaniums and show that the displacement of the alkali metals from the bridging positions exert a large shortening effect on the Ge–Ge bond length.



I, (E = Ga, Ge, Sn; R = Pr^i; M = Na or K)

Compound **1** was synthesized† by the reduction of Ge(Cl)C$_6$H$_3$-2,6-Mes$_2$, generated *in situ* from GeCl$_2$·dioxane and Ge(C$_6$H$_3$-2,6-Mes$_2$)$_2$.[7] It was obtained in moderate (47%) yield as orange crystals which were characterized by ^{1}H, ^{13}C NMR and IR spectroscopy and by X-ray crystallography. The solution NMR spectra afforded absorptions due to the terphenyl ligand and coordinating ethers. X-ray crystallography‡ yielded the structure shown in Fig. 1. The asymmetric unit consists of half the dimeric molecule {(dioxane)$_{0.5}$(Et$_2$O)LiGeC$_6$H$_3$-2,6-Mes$_2$}$_2$. Each half molecule is related to its partner by an inversion center such that the core consists of a planar Li$_2$Ge$_2${C(*ipso*)}$_2$ array. The lithiums are solvated by oxygens from ether (O(1)) and a dioxane (O(2)). The other O of the dioxane is coordinated to Li from a neighboring molecule. In this way the structure is propagated along the *b* axis as a one-dimensional polymer. The central aryl ring is perpendicular to the coordination plane at Ge. The Li coordination is trigonal planar and is coplanar with the molecular core. The Ge=Ge, Ge–C and Ge–Li distances are 2.3278(7), 2.011(3) and 2.554(6) Å. The Ge–Ge–C and Ge–Ge–Li angles differ sharply having the values 100.24(9) and 134.04(13)°.

The synthesis of **1** stemmed from several experiments to synthesize dianionic species in which the Li$^+$ ions are not in the bridging positions as they are in Li$_2$Ar′GeGeAr′ (Ar′ = C$_6$H$_3$-2,6-(C$_6$H$_3$-2,6-Pr$^i_2$)$_2$), **2**, which has a bridged structure like **I** with Ge–Ge, Ge–C and Ge–Li distances of 2.455(9), 2.060(3) and 2.88(1) Å and a Ge–Ge–C angle of 102.97(9)°.[3] It was found that the use of 1,4-dioxane in the solvent mixture as well as C$_6$H$_3$-2,6-Mes$_2$ as the Ge substituent enabled such a species to be isolated and purified. Possibly, the tendency of dioxane to form infinite chain structures (due to its 1,4-oxygen donor configuration) favored the formation of crystalline species involving only terminally bound Li$^+$ ions. Moving the Li$^+$ ions to the 1,2 bonding configuration seen in **1** results in major shortening of the Ge–Ge bond by 0.13 Å in comparison to that in **2**. The Li–Ge bond is also shortened by *ca.* 0.33 Å and it has a similar length to the 2.518(7) Å in LiGe(SiMeBu$^t_2$)$_3$[8] which has quasi one coordination at Li. Some of the Ge–Ge and Li–Ge bond shortening in **1** could be due to steric effects because of the smaller size of –C$_6$H$_3$-2,6-Mes$_2$. However, **1** also includes Et$_2$O and dioxane donors which increase crowding at Li. The Ge–Ge bond length in **1** (2.3278(7) Å) is in the middle of the currently known range for digermenes[9] and is similar to the 2.3173(5) Å in Ar′(Me)GeGe(Me)Ar′ suggesting that steric effects in the two compounds are similar.[10] The planar core in **1** indicates a Ge–Ge double bond, whereas the Ge–Ge bond length in the bridged species **2** at 2.455(9) Å is more typical of a single bond.

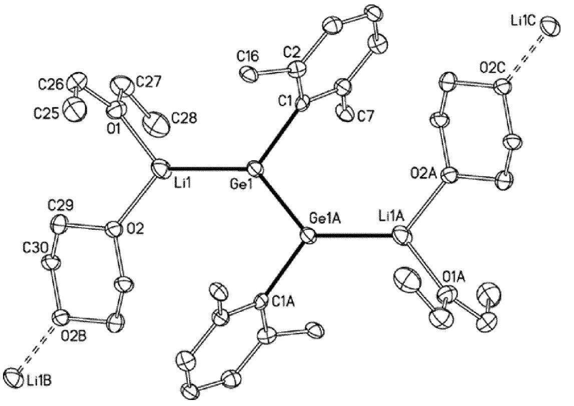


Fig. 1 Thermal ellipsoid (30%) plot of **1**. H atoms are not shown. Bond distances (Å) and angles (°): Ge(1)–Ge(1A) = 2.3278(7), Ge(1)–C(1) = 2.011(3), Ge(1)–Li = 2.554(6), Li–O(1) = 1.931(6), Li–O(2) = 1.945(6), Ge(1A)–Ge(1)–C(1) = 100.24(9), Ge(1A)–Ge(1)–Li(1) = 134.04(13), Li(1)–Ge(1)–C(1) = 125.63(16), Ge(1)–Li–O(1) = 131.2(3), Ge(1)–Li–O(2) = 130.3(3), O(1)–Li(1)–O(2) = 98.4(3).

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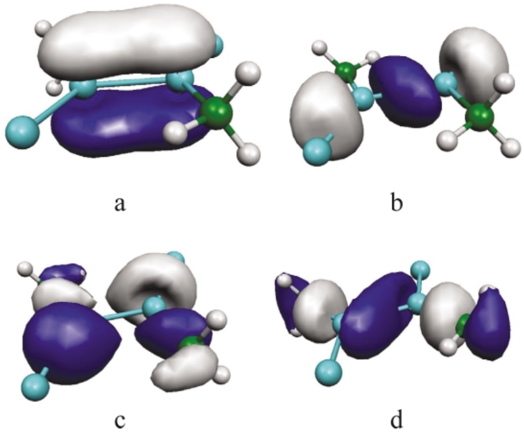

Fig. 2 Electron density surfaces of the Kohn–Sham orbitals of (a) HOMO (π-bond),(b) HOMO-1 (n_+ lone pair + Ge–Ge σ), (c) HOMO-2 (n_- lone pair + Ge–C σ), and (d) HOMO-3 (Ge–Ge σ + Ge–C σ) levels in the model species *trans*-Li(Me)GeGe(Me)Li.

DFT calculations§ on the model species $Li_2Ge_2R_2$ (R = H or Me) show that *trans*-1,2-Li(R)GeGe(R)Li structure analogous to **1** is the global minimum. The Ge–Ge and Ge–Li distances were calculated to be 2.276 (H) or 2.277 Å (Me) and 2.415 (H) or 2.432 Å (Me). These are shorter than those experimentally observed which can be explained on the basis of the much larger size of the Ge substituent and the coordination of Li by ether donors in **1**. The HOMO, HOMO-1, HOMO-2 and HOMO-3 orbitals correspond to π, lone pair (Li), lone pair (Li) and σ bonding consistent with the presence of a conventional Ge–Ge σ and π double bond (Fig. 2). Interestingly, the symmetric bridged configuration analogous to **I** is not a minimum on the potential surface and its observation in the structure of **2** may be due to the stabilizing effect of Li coordination by the aryl rings of the terphenyl group.

The structure of **1** shows that the Ge–Ge bond is shortened considerably in comparison to that in **2** and this finding is in agreement with the DFT calculations. It seems likely that Ge=Ge bonds in **2** are longer than those in **1** due to weakening of the Ge–Ge π bond by bonding to the bridging Li^+ ions. Ge–Ge lone pair–lone pair repulsions present in **2** are also diminished in **1** due to their direct coordination to the Li^+ ions. The experimental and theoretical findings for the Ge system are opposite to those calculated for the Ga species $Na_2ArGaGaAr$ where the bridging alkali metals shorten the Ga–Ga bond.[4] The different effects of the bridging alkali metal ions on the Ga–Ga and Ge–Ge bond lengths in $M_2ArEEAr$ species underline the inherent weakness of the Ga–Ga bonding. Thus the interaction of the putative Ga–Ga multiple bond with the bridging M^+ ions causes no lengthening. Instead, the Ga–Ga distance is shortened by M^+-aryl interactions. This finding is in agreement with the conclusions of Nagase *et al.*, *i.e.* that the core in $Na_2Ar^*GaGaAr^*$ is best viewed as a Na_2Ga_2 cluster with a weak Ga–Ga bond.[6]

Finally it is notable that the structure of **1** is of further interest because structures of 1,2-dilithio salts of an ethenide-like species have been hitherto unknown for derivatives of the heavier group 14 elements as well as carbon.

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Notes and references

† **1**: All manipulations were carried out under anaerobic and anhydrous conditions. $Ge(C_6H_3\text{-}2,6\text{-}Mes_2)_2$ (0.5 mmol, 0.35 g) and $GeCl_2$(dioxane) (1 mmol 0.232 g) were dissolved in diethyl ether (30 mL) and stirred for 1 h. The solution was added dropwise to a −78 °C ether suspension of Li powder (0.10 g). A rapid color change was observed and the deep red solution was allowed to reach ambient temperature. Stirring was maintained for 16 h, after which time the reaction mixture was allowed to settle. The red solution was filtered from the excess Li and LiCl. The solution was concentrated to *ca*. 10 mL. Storage at *ca*. 5 °C yielded **1** as orange/red needles in 47% yield. M.p. 148–151 °C, ^1H NMR (C_6D_6, 400 MHz, 25 °C): δ 1.022 (s, 12H, *o*-CH_3), 2.280 (s, 6H, *p*-CH_3), 3.35 (s, CH_2, dioxane), 6.845 (s, 4H, *m*-Mes), 6.878 (d, 2H, *m*-C_6H_3, *J*H–H = 7.2 Hz), 7.425 (t, ^1H, *p*-C_6H_3, ^1JH–H = 7.2 Hz). ^{13}C NMR {^1H} (C_6D_6, 100.59 MHz, 25 °C): δ 21.357, (*p*-CH_3), 21.569 (*o*-CH_3), 67.176 (CH_2, dioxane), 128.745 (*o*-Mes), 129.003 (*m*-Mes), 131.310 (*o*-C_6H_3), 136.243 (*m*-C_6H_3), 136.843 (*p*-C_6H_3), 136.964 (*p*-Mes), 142.634 (*i*-Mes), 149.533 (*i*-C_6H_3), $^7Li\{^1H\}$ 0.413 (NaCl plates, ν cm^{-1}) 1345 (m), 1360 (m), 810 (w), 750 (s), 640 (m), 550 (m).

‡ Diffraction data for **1** at 90 K with Mo–Kα (λ = 0.71073 Å) radiation: a = 22.275(2), b = 11.5462(8), c = 23.434(2) Å, β = 98.272(1)°, monoclinic, space group $C2/c$, Z = 4, $R1$ = 0.049 for 4206 ($I > 2\sigma(I)$) data.

CCDC 230338. See http://www.rsc.org/suppdata/cc/b4/b401507j/ for crystallographic data in .cif or other electronic format.

§ The geometry optimizations were performed using DFT theory with hybrid B3LYP functional. The molecular structures were first pre-optimized with Los Alamos LanL2DZ basis set using an effective core potential (ECP) approximation; a subsequent full optimization of the geometry to the real minima was performed with 6-31g* basis set. All the calculations were performed with Gaussian03 package[(a)] and the representations of the molecular structures and molecular orbitals were generated with the MOLEKEL program[(b)]. (a) Gaussian 98, Revision A.7. Gaussian, Inc., Pittsburgh PA, 1998, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomeli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ciolowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Koramomi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogе, E. S.; Pople, J. A. (b) MOLEKEL 4.3, Flukiger, P.; Luthi, H. P.; Portmann, S.; Weber, J. Swiss Center for Scientific Computing, Manno (Switzerland), 2000–2002.

1 B. Twamley, S. T. Haubrich and P. P. Power, *Adv. Organomet. Chem.*, 1999, **44**, 1; J. A. C. Clyburne and N. McMullen, *Coord. Chem. Rev.*, 2000, **210**, 73.
2 J. Su, X.-W. Li, C. Crittendon and G. H. Robinson, *J. Am. Chem. Soc.*, 1997, **119**, 5471.
3 L. Pu, A. D. Phillips, A. F. Richards, M. Stender, R. S. Simons, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 2003, **125**, 11626.
4 F. A. Cotton, A. H. Cowley and X. Feng, *J. Am. Chem. Soc.*, 1998, **120**, 1795.
5 Y. Xie, H. F. Schaefer and G. H. Robinson, *Chem. Phys. Lett.*, 2000, **317**, 174.
6 N. Takagi, M. W. Schmidt and S. Nagase, *Organometallics*, 2001, **20**, 1646.
7 L. Pu, M. M. Olmstead and P. P. Power, *Organometallics*, 1997, **16**, 1920.
8 M. Nakamoto, T. Fukawa, V. Y. Lee and A. Sekiguchi, *J. Am. Chem. Soc.*, 2002, **124**, 15160.
9 J. Escudie and H. Ranaivonjatovo, *Adv. Organomet. Chem.*, 1999, **44**, 114.
10 M. Stender, L. Pu and P. P. Power, *Organometallics*, 2001, **20**, 1820.