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$[Ph_2Bi-(Ge_9)-BiPh_2]^{2-}$: A Deltahedral Zintl Ion Functionalized by Exo-Bonded Ligands

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The first nine-atom deltahedral Zintl ion of the carbon group, Sn_9^{4-}, was structurally characterized 25 years ago.[1] Since then, the corresponding silicon, germanium, and lead analogues have been also characterized, both in the solid state and in solution (except for silicon).[2,3] These clusters are distorted, monocapped square antiprisms or tricapped trigonal prisms elongated along one or more of the prismatic edges (parallel to the three-fold axis). The bonding in the clusters is achieved by delocalized electrons as in the cagelike boranes. The numbers of electrons needed for bonding follow Wade's rules rather than the octet rule.[4] The clusters are usually made by dissolving a binary compound of the corresponding element and alkali metal in ethylenediamine or liquid ammonia, and a compound containing the cluster is crystallized by addition of cation-sequestering agents such as 2,2,2-crypt(4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo [8.8.8]hexacosane) or crown ethers.[3] Ever since the discovery of these clusters, numerous attempts to use them in various reactions have been made, some successful and some not. Successful has been capping the open-square face of the cluster by transition metals to form *closo*-clusters of $[E_9M(CO)_3]^{4-}$ for E = Sn, Pb and M = Cr, Mo, W.[5] However, the much desired functionalization of the clusters by covalently exo-bonded groups has been elusive until now.[6] The closest to this goal is the recently reported dimerization and polymerization of such Ge_9 clusters to form $[Ge_9-Ge_9]^{6-}$ and $_{1\infty}[-Ge_9-]^{2-}$, respectively, where the clusters are exo-bonded to each other by normal 2-center-2-electron bonds.[7,8] Thus, in a way, this is functionalization of the clusters by each other. This achievement indicated that perhaps other main-group substituents could be exo-bonded in a similar way. We report here the first such species of a nine-atom germanium cluster ligated by two diphenylbismuth groups that are exo-bonded to two opposite germanium vertexes of the open face of the cluster, $[Ph_2Bi-(Ge_9)-BiPh_2]^{2-}$.

The new compound (K-crypt)$_2$[Ge$_9$(BiPh$_2$)$_2$]·en (**1**) was synthesized by reacting ethylenediamine solution of a precursor of nominal composition K_4Ge_9 with $BiPh_3$.[9] The major phase of the precursor was $K_{12}Ge_{17}$, isostructural with $Rb_{12}Si_{17}$,[2d] which contains both Ge_9^{4-} and Ge_4^{4-} clusters. The color of the solution changed quickly from brown-red (for the dissolved precursor) to extremely deep-red upon reacting with $BiPh_3$. The solution was carefully layered with toluene, and in a week bright red crystals of the new compound had grown to sizes suitable for structure determination.[9]

The new compound contains nine-atom germanium clusters with two exo-bonded diphenylbismuth groups (Figure 1).[10] The two Bi−Ge distances, 2.7327(8) and 2.7332(8) Å, are virtually identical, and compare well with other single-bond distances such as those in Bi{μ-Ge(C$_6$F$_5$)$_2$}$_3$Bi and [{(C$_6$F$_5$)$_2$Ge}$_2$Bi−Bi{Ge(C$_6$F$_5$)$_2$}$_2$] with distances in the range of 2.73−2.77 Å, as well as with Pauling's single-bond distance of 2.752 Å.[11,12] The Bi−C distances in $[Ph_2Bi-(Ge_9)-BiPh_2]^{2-}$, 2.257(7)−2.277(8) Å, and the two C−Bi−C angles, 93.6(2) and 93.2(2)°, compare well with those of $BiPh_3$, 2.237−2.273 Å and 92.7−94.7°, respectively.[13] The effect of the inert *s*-pair of electrons at the bismuth makes the Ge−Bi−C angles also very close to orthogonal, 94.7(1)−98.0(1)°.

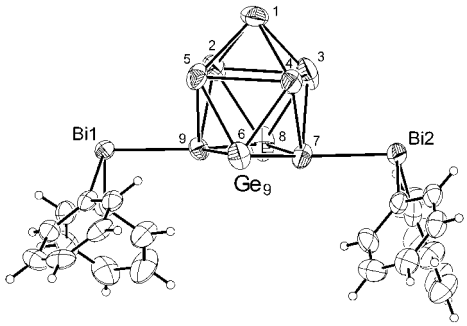

Figure 1. ORTEP drawing of $[Ph_2Bi-(Ge_9)-BiPh_2]^{2-}$ (70% probability thermal ellipsoids). The numbering of the germanium atoms is shown.

The Ge−Ge distances in the cluster follow the general pattern observed for other nine-atom clusters, and are quite similar to those in the various Ge_9 clusters with different charges and connectivity.[2a,3c,14] Thus, they increase in the following order: distances between four-bonded atoms (Ge6, 7, 8, 9), 2.553(1)−2.585(1) Å (Figure 1), distances from four-bonded (Ge1, 6, 7, 8, 9) to five-bonded atoms (Ge2, 3, 4, 5), 2.578(1)−2.653(1) Å, and distances between five-bonded atoms (Ge2, 3, 4, 5), 2.717(1)−2.826(1) Å. The shape of the Ge_9 cluster is reminiscent of both a monocapped square antiprism with distorted open face (rhombic rather than square) and a tricapped trigonal prism with one elongated prismatic edge. The diphenylbismuth ligands are bonded to two opposite vertexes of the distorted open face, specifically the two Ge7 and Ge9 vertexes (Figure 1) along the short diagonal of the rhombus. This diagonal is 2.985(1), while the corresponding long diagonal is 4.169(1) Å. Exactly the same type of distortion is observed in the chains of (−Ge_9−) where the same two vertexes of the open face are exo-bonded to other clusters and the corresponding short and long diagonals of the rhombus are 3.194 and 3.942 Å, respectively.[8] In the dimer of Ge_9-Ge_9, where only one vertex is exo-bonded, the distortion is somewhat less pronounced with distances of 3.433 and 3.848 Å for the two diagonals.[7] Thus, the two exo-bonded vertexes are closer than in typical *nido*-species but are farther than in typical *closo*-species. However, there is clearly no interaction between these two germanium atoms, and therefore, the reason for the distortion should be sought in effects induced by the exo-bonding. The replacement of a lone pair of electrons with a bonding one, the exo-bonds at Ge7 and Ge9, leads naturally to lesser repulsion with the bonds of the cluster, and this translates into larger endo-cluster angles at those atoms. Fenske−Hall (self-consistent field) and extended-Hückel molecular orbital calculations carried out for $[Ph_2Bi-(Ge_9)-BiPh_2]^{2-}$ and the naked

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Ge_9^{4-} cluster with the same shape confirmed the *nido*-character of both,[15] that is, 22 cluster-bonding electrons ($2n + 4$ for $n = 9$), despite the shorter diagonal of the open face. It should be pointed out that although the charge of the former is 2− the bonding within the cluster and its stability have not changed since the number of bonding electrons is the same. What has changed are the two lone pairs of electrons that would have existed at Ge7 and Ge9 had the cluster been naked. They have simply been replaced by bonding pairs of electrons. As it has been discussed elsewhere,[8] the highest occupied orbitals in the naked *nido*-Ge_9^{4-} clusters are exactly the lone pairs of electrons at the atoms of the open face. This is why these particular atoms are most reactive and the first to form exo-bonds.

The diphenylbismuth ligands have their phenyl rings positioned away from the cluster in the solid state (Figure 1) but are very likely fluctional in solution by rotation around the Bi−Ge bond. Crystals of the new compound can be redissolved in ethylenediamine and THF.[16] The solubility of the compound opens venues for further studies of the reactivity of the functionalized clusters toward eventual coordination to transition metals via the lone pairs of the bismuth atoms. Furthermore, similar studies for the phosphorus, arsenic, and antimony analogues are underway, and the initial indications are that they and, likely, the four-substituted species, form as well.[17] These can be very useful ligands in building various transition-metal complexes and extended structures.

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Supporting Information Available: An X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Diehl, L.; Khodadadeh, K.; Kummer, D.; Strähle, J. *Chem. Ber.* **1976**, *109*, 3404.

(2) (a) Queneau, V.; Sevov, S. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1754. (b) Queneau, V.; Sevov, S. C. *Inorg. Chem.* **1998**, *37*, 1358. (c) Todorov, E.; Sevov, S. C. *Inorg. Chem.* **1998**, *37*, 3889. (d) Queneau, V.; Todorov, E.; Sevov, S. C. *J. Am. Chem. Soc.* **1998**, *120*, 3263. (e) von Schnering, H. G.; Baitinger, M.; Bolle, U.; Carrilo-Cabrera, W.; Curda, J.; Grin, Y.; Heinemann, F.; Llanos, J.; Peters, K.; Schmeding, A.; Somer, M. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1037. (f) von Schnering, H. G.; Somer, M.; Kaupp, M.; Carrillo-Cabrera, W.; Baitinger, M.; Schmeding, A.; Grin, Y. *Angew. Chem., Int. Ed.* **1998**, *37*, 2359.

(3) Reviews: (a) Corbett, J. D. *Chem. Rev.* **1985**, *85*, 383. (b) Corbett, J. D. *Struct. Bonding* **1997**, *87*, 157. (c) Fässler, T. F. *Coord. Chem. Rev.* **2001**, *215*, 377.

(4) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

(5) (a) Eichhorn, B. W.; Haushalter, R. C.; Pennington, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 8704. (b) Eichhorn, B. W.; Haushalter *J. Chem. Soc., Chem. Commun.* **1990**, 937. (c) Kesanli, B.; Fettinger, J.; Eichhorn, B. W. *Chem. Eur. J.* **2001**, *7*, 5277.

(6) Clusters such as $[E_6\{M(CO)_5\}_6]^{2-}$ for E = Ge, Sn and M = Cr, Mo, W (Renner, G.; Kircher, P.; Huttner, G.; Rutsch, P.; Heinze, K. *Eur. J. Inorg. Chem.* **2001**, 973), $Ga_9(CMe_3)_9$ (Uhl, W.; Cuypers, L.; Harms, K.; Kaim, W.; Wanner, M.; Winter, R.; Koch, R.; Saak, W. *Angew. Chem., Int. Ed.* **2001**, *40*, 566), $[Al_{12}iBu_{12}]^{2-}$ (Hiller, W.; Klinkhammer, K. W.; Uhl, W.; Wagner, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 179), and others of this type are not considered here since they do not exist without the ligands, i.e., as Zintl ions. In all these cases the cluster forms due to the steric protection and stabilization by the ligands.

(7) Xu, L.; Sevov, S. C. *J. Am. Chem. Soc.* **1999**, *121*, 9245.

(8) Downie, C.; Tang, Z.; Guloy, A. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 337.

(9) All operations were carried out in inert atmosphere or under vacuum. The precursor K_4Ge_9 was made from a stoichiometric mixture of the elements (Alfa-Aesar) heated at 900 °C for 2 days in sealed (by arc-welding) niobium containers that were jacketed in evacuated fused-silica ampules. The major phase of the product was $K_{12}Ge_{17}$, isostructural with $Rb_{12}Si_{17}$,[2d] which is known to contain both nine- and four-atom clusters, Ge_9^{4-} and E_4^{4-}. Inside a drybox, approximately 0.0272 mmol of K_4Ge_9 were dissolved in 1 mL of ethylenediamine (redistilled and packaged under nitrogen, 99.5+%, Aldrich) and 0.127 mmol of Kryptofix 222 (98%, Acros) in a test tube (brown-red solution). $BiPh_3$ (Aldrich), 0.068 mmol, was then added, and the resulting bright-red solution was layered with 3 mL of toluene (dried and kept over sodium, 99.5%, Fisher). Bright-red plates formed on the walls and the bottom of the test tube. The mother liquor was decanted after a week, and the crystals were dried (ca. 8 mg product, about 22% yield based on the amount of dissolved precursor). IR (in KBr): 694, 720, and 730 cm^{-1} (out of plane C−H bending); 990, 1010, and 1052 cm^{-1} (in plane C−H bending); 1466 and 1560 cm^{-1} (C−C stretching); 3020 and 3051 cm^{-1} (CH stretching).

(10) X-ray diffraction data were collected from a red, platelike crystal of **1** (0.35 mm × 0.28 mm × 0.06 mm) with graphite-monochromated Mo Kα radiation on a Bruker APEX diffractometer with a CCD area detector at −100 °C. The structure was solved by direct methods in *P*-1 and refined on F^2 (full matrix, absorption corrections with SADABS) using the SHELXTL V5.1 package. Crystal data: triclinic, *P*-1, $a = 13.5216(9)$ Å, $b = 13.6028(9)$ Å, and $c = 24.498(1)$ Å, $\alpha = 79.700(1)°$, $\beta = 77.003(1)°$, and $\gamma = 65.881(1)°$, $V = 3988.1(5)$ Å^3, $Z = 2$, $\mu = 78.94$ cm^{-1}, $d_{calc} = 1.891$ g/cm^3, R1/wR2 = 4.57/11.33% for 11680 unique observed reflections ($I \geq 2\sigma I$) and 826 variables (R1/wR2 = 5.64/11.75% for all data).

(11) (a) Bochkarev, M. N.; Razuvaev, G. A.; Zakharov, L. N.; Struchkov, Y. T. *J. Organomet. Chem.* **1980**, *199*, 205. (b) Pankratov, L. V.; Zakharov, L. N.; Bochkova, R. I.; Fukin, G. K.; Struchkov, Y. T. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1994**, 921.

(12) Pauling, L. In *Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 403.

(13) Jones, P. G.; Blaschette, A.; Henschel, D.; Weitze, A. *Z. Kristallogr.* **1995**, *210*, 377.

(14) (a) Belin, C. H. E.; Corbett, J. D.; Cisar, A. *J. Am. Chem. Soc.* **1977**, *99*, 7163. (b) Somer, M.; Carillo-Cabrera, W.; Peters, E. M.; Peters, K.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1915. (c) Fässler, T. F.; Schütz, U. *Inorg. Chem.* **1999**, *38*, 1866. (d) Fässler, T. F.; Hunziker, M. *Inorg. Chem.* **1994**, *33*, 5380. (e) Belin, C.; Mercier, H.; Angilella, V. *New J. Chem.* **1991**, *15*, 931.

(15) (a) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768. (b) Hoffmann, R. J. *J. Chem. Phys.* **1963**, *39*, 1397.

(16) ^{1}H NMR (300 MHz, 297 K, ethylenediamine and THF-d_8) δ 7.07−7.17 (m, 12H) and 7.17−7.24 (m, 8H). ^{13}C NMR δ 126.14 (p-C_6H_5), 129.03 (m-C_6H_5), 129.74 (o-C_6H_5), C-1 was not found, most likely because of broadening due to the quadrupole effect of the bismuth.

(17) While the manuscript was reviewed, we isolated and structurally characterized the antimony analogue, (K-crypt)[Ph_2Sb−(Ge_9)−$SbPh_2$]•en. The compound is isostructural with **1** ($a = 13.5062(9)$ Å, $b = 13.5444(9)$ Å, and $c = 24.485(1)$ Å, $\alpha = 79.440(1)°$, $\beta = 77.228(1)°$, and $\gamma = 65.753(1)°$, $V = 3961.3(5)$ Å^3; R1/wR2 = 3.99/9.03 and 5.67/9.75% for the observed and all data, respectively). The distances within the Ge_9-cluster are virtually the same as in **1** but the Sb−Ge distances are quite shorter, 2.6483(5) and 2.6505(5) Å.

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