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Formation of Dimeric σ-Bonded Argentacarboranes Containing Two Types of Closed and Open Ag–H–B Bridge Bonds and Molecular Structure of $[9,9'\text{-}\{Ag(SbPh_3)_2\}_2\text{-}4,9,4',9'\text{-}(\mu\text{-}H)_4\text{-}7,8,7',8'\text{-}\textit{nido}\text{-}(C_2B_9H_{10})_2]$[1]

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Our recent research efforts toward the synthesis of σ-bonded heterodicarboranes of heavier main group elements, initially prompted by the paucity of recent work on the σ-coordination dicarborane chemistry[2-4] and the recent demonstration of the use of $[10\text{-}\textit{endo}\text{-}(AuPPh_3)\text{-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_9Me_2]^-$ anion[3] as a carborane cage transfer reagent,[2,5] led to the observation of σ-bonded group 14 heterodicarboranes $[10\text{-}MPh_3\text{-}10\text{-}\mu\text{-}H\text{-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_{10}]^-$ (M = Ge(IV), Sn(IV)).[6] In an attempt to expand the class of σ-bonded metallacaboranes, a new type of dimeric σ-bonded dicarborane complex of Ag(I) ion has been synthesized. Reported herein is a brief account of the synthesis and characterization of dimeric argentacarboranes $[9,9'\text{-}\{Ag(EPh_3)_2\}_2\text{-}4,9,4',9'\text{-}(\mu\text{-}H)_4\text{-}7,8,7',8'\text{-}\textit{nido}\text{-}(C_2B_9H_{10})_2]$ (E = As, **1**; Sb, **2**).

A reaction mixture generated by stirring AgBr and a 2-fold amount of EPh_3 (E = As, 0.67 mmol; E = Sb, 1.00 mmol) in 15 mL of CH_2Cl_2 for 1 h was added to a slurry of $Tl_2C_2B_9H_{11}$ in 10 mL of CH_2Cl_2. The overall stoichiometric ratio of 1:2:1 was adopted for the reactants. After 12 h of additional stirring, the mixture was filtered and the concentrated filtrate was treated with *n*-heptane. The off-white crystalline solids were collected and recrystallized from CH_2Cl_2–*n*-heptane, yielding analytically pure[7] products **1** and **2** in yields of 14 and 12%, respectively. Various spectroscopic data[7] for these compounds indicate that they are structurally similar.

The molecular structure of **2**,[8] displayed in Figure 1, reveals that two cationic $Ag(SbPh_3)_2$ fragments are incorporated into two anionic *nido*-$C_2B_9H_{12}$ cage via two types of closed and open Ag–H–B bridge bonds, showing that two enantiomeric $(Ph_3Sb)_2AgC_2B_9H_{12}$ units dimerize about a crystallographic center of symmetry via a pair of rather weak open Ag–H–B bridge bonds stemming from terminal B–H bonds in the lower pentagonal belts of carborane cages. The Ag–H′ distance of 2.57 Å for open bridge bonds in **2** can be compared to other Ag–H values in $[PPh_3AgC_2B_8H_{11}]_2$ (2.19 Å),[9] $AgCB_{11}H_{12}\cdot 2C_6H_6$ (1.97 Å),[10] $[(CB_{11}H_{12})AgIr(PPh_3)_2(CO)Cl]$ (1.90 Å),[11] and $[\textit{closo-exo}\text{-}4,8\text{-}\{(\mu\text{-}H)_2Ag(PPh_3)\}\text{-}3\text{-}(PPh_3)\text{-}3,1,2\text{-}CuC_2B_9H_9]$ (2.28, 2.34 Å).[12] For a given $(Ph_3Sb)_2AgC_2B_9H_{12}$ fragment, the $[Ag(SbPh_3)_2]^+$ unit interacts with an asymmetric boron atom in the open C_2B_3 plane of the *nido*-C_2B_9 cage via a σ-Ag–B9 bond [2.451(6) Å] and a Ag–H9–B9 bridge bond with a Ag–H distance of 2.15(3) Å. The IR spectra for **1** and **2**,[7] measured under reduced pressure to avoid any interference owing to the asymmetrical stretching (2350 cm^{-1}) of CO_2, show weak bands at 2332 and 2322 cm^{-1}, respectively, indicating the presence of Ag–H–B bridge interactions in both compounds.

A sectional view of **2** given in Figure 2 clearly reveals the *endo* nature of the 12th H atom in a B–H–B bridge as well as a rather unusual steric role for the $[Ag(SbPh_3)_2]$ moiety. Taken alone, the $[7,8\text{-}C_2B_9H_{12}]^-$ anionic fragment in **2** adopts an asymmetric

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(1) Dedicated to Professor M. Frederick Hawthorne on the occasion of his 65th birthday.

(2) Howard, J. A. K.; Jeffery, J. C.; Jelliss, P. A.; Sommerfeld, T.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1664.

(3) Hamilton, E. J. M.; Welch, A. J. *Polyhedron* **1990**, *9*, 2407.

(4) (a) Schubert, D. M.; Bandman, M. C.; Rees, W. S., Jr.; Knobler, C. B.; Lu, P.; Nam, W.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2046. (b) Schubert, D. M.; Rees, W. S., Jr.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2938.

(5) (a) Jeffery, J. C.; Jelliss, P. A.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1993**, 1073. (b) Jeffery, J. C.; Jelliss, P. A.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1993**, 1083.

(6) Kim, J.; Kim, S.; Do, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 938.

(7) Satisfactory elemental analyses were obtained for both compounds. Data for **1**: IR (KBr, 0.20 Torr, cm^{-1}), ν_{BH} 2590, 2545, 2528, and 2478 and ν_{BHAg} 2332; ^1H NMR (CD_2Cl_2, 203 K, ppm), 1.85 (s, carboranyl CH) and –3.19 (s, bridging BH); $^{11}B\{^1H\}$ NMR (CH_2Cl_2–10% CD_3CN, referenced to external $BF_3\cdot OEt_2$, ppm), –15.0, –15.8, –17.0, –18.2, –32.8, and –37.0. Data for **2**: IR (KBr, 0.25 Torr, cm^{-1}), ν_{BH} 2590, 2546, 2526, and 2477 and ν_{BHAg} 2322; ^1H NMR (CD_2Cl_2, 203 K), 2.08 (s, carboranyl CH) and –3.06 (s, bridging BH); $^{11}B\{^1H\}$ NMR (CH_2Cl_2–10% CD_3CN), –15.0, –16.1, –17.9, –32.6, and –36.8.

(8) Crystallographic data for **2**: $C_{76}H_{84}Ag_2B_{18}Sb_4$, $M = 1894.8$, triclinic, space group $P\bar{1}$, $a = 12.399(1)$, $b = 13.406(2)$, $c = 14.204(2)$ Å, $\alpha = 93.80(1)$, $\beta = 110.46(1)$, $\gamma = 111.04(1)°$, $V = 2014.4$, $Z = 2$, $D_c = 1.562$ g cm^{-3}, R (R_w) = 0.0299 (0.0373) for 5136 observed data [$F > 6\sigma(F)$]. The diffraction data of a colorless parallelepiped crystal obtained from a CH_2Cl_2–*n*-pentane solution were collected at 295 K in the $\omega/2\theta$ scan mode on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation to a maximum 2θ value of 50°. The structure was solved with use of the heavy-atom method (SHELXS 86) and blocked-matrix least-squares procedures (SHELX 76) on the CRAY-2S/4-128 supercomputer.

(9) Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1980**, 192.

(10) Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 5955.

(11) Liston, D. J.; Reed, C. A.; Eigenbrot, C. W.; Scheidt, W. R. *Inorg. Chem.* **1987**, *26*, 2739.

(12) Park, Y.-W.; Do, Y.; Knobler, C. B.; Hawthorne, M. F. Manuscript in preparation.

0020-1669/94/1333-0001$04.50/0

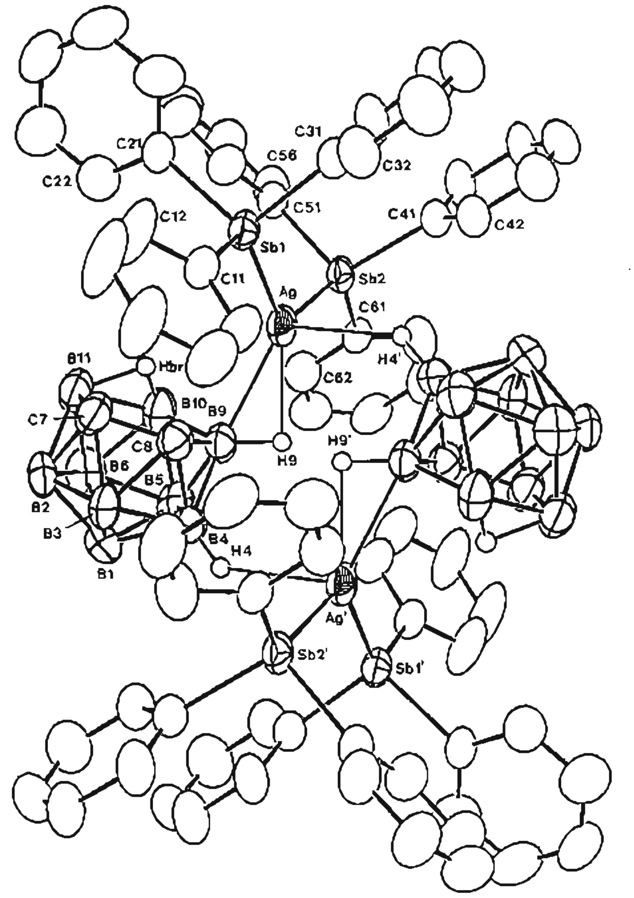

Figure 1. Molecular structure of [9,9'-{Ag(SbPh$_3$)$_2$}$_2$-4,9,4',9'-(μ-H)$_4$-7,8,7',8'-*nido*-(C$_2$B$_9$H$_{10}$)$_2$] (**2**) and the atom-numbering scheme. All hydrogen atoms except the bridging hydrides have been omitted for clarity. Dimensions: Ag–Sb1 = 2.711(1) Å, Ag–Sb2 = 2.679(1) Å, Ag–B9 = 2.451(6) Å, Ag–H9 = 2.152(33) Å, Ag–H4' = 2.558 Å, C7–C8 = 1.538(7) Å, B10–Hbr = 1.127(50) Å, B11–Hbr = 1.389(65) Å, ⟨B–B$_{\text{facial}}$⟩ = 1.827 Å, ⟨B–C$_{\text{facial}}$⟩ = 1.617 Å; Sb1–Ag–Sb2 = 118.5(<1)°, Sb1–Ag–B9 = 112.4(2)°, Sb2–Ag –B9 = 126.4(2).

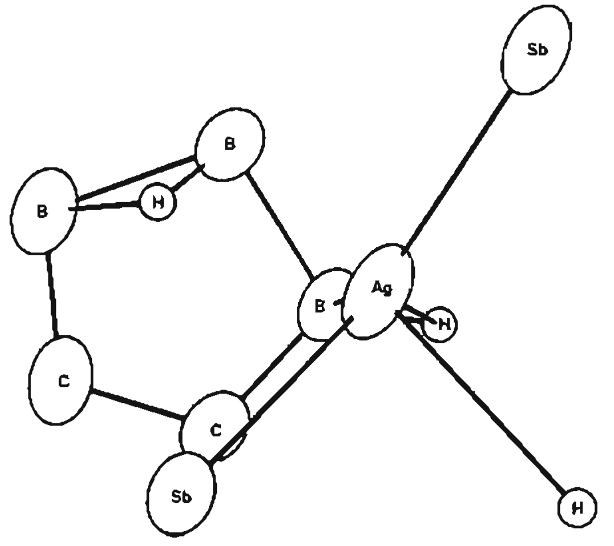

Figure 2. Projection of the AgSb$_2$ fragment of **2** onto the open C$_2$B$_3$ pentagonal plane.

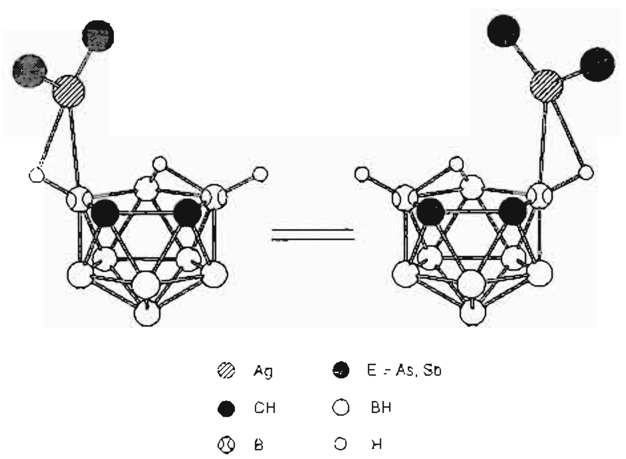

Figure 3. Wigwag fluxional process of the monomeric (Ph$_3$E)$_2$AgC$_2$B$_9$H$_{12}$ (E = As, Sb) units in solution.

bridge position of the B10–B11 connectivity as a site for the 12th H atom whereas the non-ligating parent anion in [H(dmso)$_2$]-[7,8-C$_2$B$_9$H$_{12}$][13] contains the 12th H atom predominantly bound terminally to B(10). The Ag(SbPh$_3$)$_2$ group is bound to the carborane cage in an intermediate fashion between *endo* and *exo*, suggesting that the silver ion interacts with the cage agostically to form a closed Ag–H–B bridge. Among the geometric parameters for Ag(SbPh$_3$)$_2$, the Ag–Sb bond distance of 2.678(1) and 2.711(1) Å are compatible with other observed distances between coinage metals and group 15 elements.[14,15] The Sb–Ag–Sb angle of 118.5(1)° is quite acute compared to values for As–Ag–As and P–Ag–P.[14]

Upon dissolution, the dimeric argentacarboranes **1** and **2** dissociate into monomeric (Ph$_3$E)$_2$AgC$_2$B$_9$H$_{12}$ (**3**, E = As, Sb) units which then display fluxionality. The molecular structure of **2** in Figure 1 suggests the presence of nine, in principle, distinguishable boron atoms and two magnetically inequivalent carboranyl C–H protons in each argentacarborane. The 96.3-MHz ^{11}B{^{1}H} NMR spectra[7] of **1** and **2** consist of six and five distinct resonances with 2:2:1:2:1:1 and 2:3:2:1:1 relative ratios, respectively, going from downfield to upfield, indicating the C_s symmetry nature of the C$_2$B$_9$ cage in solution. The observations of one carboranyl CH proton signal in the low temperature (203 K) ^{1}H NMR spectra[7] are also supportive of the same solution symmetry nature of **1** and **2**. The foregoing solution spectroscopic properties can be ascribed to a kind of wigwag fluxional motion, suggested in Figure 3, of monomeric **3** generated by dissociation of **1** and **2**. A similar wigwag process has been previously observed in [*closo-exo*-4,8-{(μ-H)$_2$Cu(PPh$_3$)}-3-(PPh$_3$)-3,1,2-CuC$_2$B$_9$H$_9$].[16]

The relatively low yield for the formation of **1** and **2** may imply a rather complicated nature of the reaction system AgBr/2EPh$_3$/Tl$_2$C$_2$B$_9$H$_{11}$ (E = As, Sb). With E = P and a 2:1:1 reactant ratio, the formation of a charge-compensated carborane [*nido*-9-PPh$_3$-7,8-C$_2$B$_9$H$_{11}$] has been observed,[17] indicating that the route to **1** and **2** might compete with the formation of EPh$_3$ (E = As, Sb) derivative of the dicarbollide anion. The reaction system of AgBr/EPh$_3$/Tl$_2$C$_2$B$_9$H$_{11}$ (E = As, Sb) with varying relative stoichiometric ratios is under investigation.

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Supplementary Material Available: Tables giving details of the crystallographic data collection, positional and thermal parameters, and bond distances and angles for **2** (7 pages). Ordering information is given on any current masthead page.

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(13) Buchanan, J.; Hamilton, E. J. M.; Reed, D.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1990**, 677.

(14) Baiada, A.; Jardine, F. H.; Willett, R. D. *Inorg. Chem.* **1990**, *29*, 3042.

(15) Rheingold, A. L.; Fountain, M. E. *J. Crystallogr. Spectrosc. Res.* **1984**, *14*, 549.

(16) (a) Do, Y.; Kang, H. C.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1987**, *26*, 2348. (b) Kang, H. C.; Do, Y.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1988**, *27*, 1716.

(17) Kim, K. M.; Do, Y.; Knobler, C. B.; Hawthorne, M. F. *Bull. Korean Chem. Soc.* **1989**, *10*, 321.