Crystal Structure of $Cp_2Mo_2(\eta^2,\mu\text{-}As_3)(\eta^2,\mu\text{-}AsS)$ (5). The structure of 5 is shown in Figure 5; a crystallographic 2-fold rotational axis passes through As(3) and the midpoint of the Sas–Sas(a) bond. The overall structure is that of a triple-decker sandwich in which the middle deck contains one sulfur and four arsenic atoms; deviations from planarity for these five atoms is less than their esd's. The outer decks are Cp rings that are also coplanar. The middle deck is divided into two units: a $\mu,\eta^2\text{-}As_3$ group and a μ,η^2-AsS group. The As–S distance between these groups is very long (2.961 (2) Å) (Table IX) indicating, at best, a weakly bonded interaction. The As_3 group is allylic with an As–As distance of 2.374 (1) Å, which is intermediate between recognized single- and double-bond ranges,[1] and the As–As–As angle is 107.3 (1)°. The crystallographically imposed symmetry creates disorder in the AsS group such that both atoms are 50/50 As/S composites; these are labeled Sas. Although possibly affected by this disorder, the As–S (Sas–Sas(a)) distance is short (2.237 (3) Å) and indicative of a bond order fractionally greater than 1. The distances of the atoms of these groups to Mo are very similar for the 1,3-atoms of the allylic group (2.539 (1) Å) and the AsS composite atoms (2.558 (1) Å); the distance to the central allylic As atom is considerably longer (2.744 (1) Å).

Recently, this class of triple-decker sandwiches has been the subject of two theoretical studies with particular emphasis on structures containing a group 15 or 16 central ring.[31] In 6, the middle layer is also distorted, but to a lesser degree, and in the all-P analogue to 6, $Cp_2Cr_2P_5$,[27a] the central is undistorted. Treme et al.[31b] have postulated that the central As_5 ring distortion from an ideal D_{5h} configuration is due to a second-order Jahn–Teller distortion. On the basis of their calculations, they predicted that as more electronegative atoms are placed in the ring these atoms would have a tendancy to be more "isolated", with ring–ring bonds lengthening and eventually becoming nonexistant. Compound 5 conforms to these expectations. Conversely, less electronegative elements should favor higher symmetry. The substitution of S for As increases the cluster electron count to 28, making it isoelectronic to $Cp_2Mo_2As_5^-$.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work and the National Science Foundation for assistance in the purchase of the diffractometer.

Supplementary Material Available: Tables of complete crystallographic data, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (12 pages); listings of observed and calculated structure factors (47 pages). Ordering information is given on any current masthead page.

---

(29) $[Cp_3Ni_2]^+$: Werner, H.; Salzer, A. *Synth. Inorg. Met.-Org. Chem.* **1972**, *2*, 239. Salzer, A.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 930. $Cp_2V_2C_6R_6$: Duff, A. W.; Jonas, K.; Goddard, R.; Kraus, H.-J.; Kruger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5479. $Cp_2Co_2C_6R_6$: Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295. $Cp_2Cr_2C_6H_6$: Lamanna, W. M.; Gleason, W. B.; Britton, D. *Organometallics* **1987**, *6*, 1583. Lamanna, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 2096. $Cp_2Ru_2Cp^*$: Kudinov, A. R.; Rybinskaya, M. L.; Struchkov, Yu. T.; Yanovskii, A. I.; Petrovskii, P. V. *J. Organomet. Chem.* **1987**, *336*, 187.

(30) Siebert, W.; Renk, T.; Kingberger, K.; Bochmann, M.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 779. Siebert, W.; Rothermel, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 333. Edwin, J.; Bochmann, M.; Bohm, M. C.; Brennan, D. E.; Geiger, W. E.; Kruger, C.; Pebler, J.; Pritzkow, H.; Siebert, W.; Swiridoff, W.; Wadepohl, H.; Weiss, J.; Zennick, U. *J. Am. Chem. Soc.* **1983**, *105*, 2582. Beer, D. C.; Miller, V. R.; Sneddon, L. G.; Grimes, R. N.; Mathew, M.; Palenic, G. *J. Am. Chem. Soc.* **1973**, *95*, 3046. Grimes, R. N.; Beer, D. C.; Miller, V. R.; Sneddon, L. G.; Weiss, R. *Inorg. Chem.* **1974**, *13*, 1138. Herberich, G. E.; Hessner, B.; Huttner, G.; Zsolnar, L. *J. Am. Chem. Soc.* **1983**, *105*, 5479. Wadepohl, H.; Pritzkow, H.; Siebert, W. *Chem. Ber.* **1985**, *118*, 729. Kuhlman, T.; Pritzkow, H.; Zenneck, U.; Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 965.

(31) (a) Jemmis, E. D.; Reddy, A. C. *Organometallics* **1988**, *7*, 1561. (b) Tremel, W.; Hoffmann, R.; Kertesz, M. *J. Am. Chem. Soc.* **1989**, *111*, 2030.

Contribution from the Department of Chemistry and Molecular Structure Center,
Indiana University, Bloomington, Indiana 47405

Synthesis of Icosahedral Boranes Containing Bismuth

John L. Little, Michael A. Whitesell, John G. Kester, Kirsten Folting, and Lee J. Todd*

Received February 1, 1989

The first bismaboranes, $1,2\text{-}EBiB_{10}H_{10}$ (E = P, As, Sb, Bi), have been prepared and characterized. The compound $1,2\text{-}Bi_2B_{10}H_{10}$ has also been characterized by a single-crystal X-ray structure determination (space group $P\bar{1}$, a = 12.174 (1) Å, b = 14.070 (2) Å, c = 12.135 (1) Å, α = 91.07 (0)°, β = 99.51 (0)°, γ = 106.70 (0)°, Z = 8). Two-dimensional ($^{11}B\text{–}^{11}B$) NMR studies have been used to assign boron nuclei to specific resonances. The anion $B_{11}H_{11}Bi^-$ was prepared from $B_{11}H_{14}^-$, $BiCl_3$, and *n*-butyllithium. While these compounds decompose slowly at room temperature in solution, in the solid state they are surprisingly stable to heat.

Introduction

Boron cage compounds incorporating one or two group 15 elements are known for all the elements of this group with the exception of bismuth.[1-4] Carboranes containing the heavy element lead have been known for several years. While the compound $1,2,3\text{-}SnC_2B_9H_{11}$ could be sublimed at 250 °C under vacuum, the related $1,2,3\text{-}PbC_2B_4H_6$ was found to decompose at room temperature under vacuum.[5,6] Recently reported syntheses of $R_2Bi\text{–}BiR_2$ derivatives indicate that these compounds are thermally unstable as well as air sensitive.[7] The easy thermal decomposition of organolead compounds is well-known.

Despite this unfavorable background information, we have investigated the syntheses of several icosahedral bismaboranes containing one or two bismuth atoms in the cage structure. In this paper, we report the preparation and characterization of these

---

(1) (a) Todd, L. J. In *Metal Interactions in Boron Clusters*; Grimes, R. N., Ed.; Plenum: New York, 1982, pp 145–171. (b) Todd, L. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., et al., Eds.; Pergamon Press: New York, 1982; Vol. I, pp 543–553.

(2) Little, J. L. *Inorg. Chem.* **1979**, *18*, 1598.

(3) Hanusa, T. P.; Roig de Parisi, N.; Kester, J. G.; Arafat, A.; Todd, L. J. *Inorg. Chem.* **1987**, *26*, 4100 and references therein.

(4) Arafat, A.; Baer, J.; Huffman, J. C.; Todd, L. J. *Inorg. Chem.* **1986**, *25*, 3757.

(5) Rudolph, R. W.; Voorhees, R. L.; Cochoy, R. E. *J. Am. Chem. Soc.* **1970**, *92*, 3351.

(6) Wong, K. S.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 2053.

(7) Calderazzo, F.; Poli, R.; Pelizzi, G. *J. Chem. Soc., Dalton Trans.* **1984**, 2365.

(8) Little, J. L.; Pao, S. S.; Sugathan, K. K. *Inorg. Chem.* **1974**, *13*, 1752.

surprisingly heat-stable compounds.

Experimental Section

Physical Measurements. Boron (^{11}B) NMR spectra were obtained at 115.8 MHz with a Nicolet NT-360 spectrometer and were externally referenced to $BF_3 \cdot O(C_2H_5)_2$ (positive values downfield). Two-dimensional NMR (^{11}B–^{11}B) spectra were obtained on the same instrument. Broad-band ^1H decoupling (3 W) was continuously used. A general description for the two-dimensional (^{11}B–^{11}B) NMR technique has been previously reported.[9] Typically, the 2-D t_1, t_2 matrix was collected as 128 × 256 (real plus imaginary) data points. The matrix was zero-filled once in both dimensions after apodization with an exponential function and a sine function. The F_1, F_2 matrix was symmetrized before projecting the contour plot. Proton (^1H) and phosphorus (^{31}P) NMR spectra were obtained at 361.1 and 146.2 MHz, respectively, on the same instrument. The proton NMR spectra were referenced to the proteo solvent impurity, and the ^{31}P NMR were externally referenced to 85% H_3PO_4 (positive values downfield). Infrared spectra were determined by using KBr disks with a Perkin-Elmer 283 spectrometer. Mass spectral data were collected on a Kratos 80 spectrometer. Behavior at high temperatures was observed in sealed, evacuated melting point capillaries. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Materials. All reactions were performed under an atmosphere of prepurified nitrogen. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. Triethylamine was distilled from sodium hydroxide. Phosphorous trichloride was freshly distilled and degassed before use. Decaborane(14) was sublimed at 60 °C and 10^{-2} mmHg. $(CH_3)_4NB_{10}H_{12}P$ was prepared by the literature method.[10] $(CH_3)_3NHB_{11}H_{14}$ was prepared from $NaBH_4$ and $BF_3 \cdot OEt_2$.[11] All other commercially available reagents were used as received.

1,2-$Bi_2B_{10}H_{10}$ (1). To a stirred solution of $B_{10}H_{14}$ (0.61 g) in 30 mL of THF in a 100-mL two-necked flask were added 10 mL of triethylamine and 3.7 g of finely ground $BiCl_3$. After being stirred overnight at room temperature, the solution was filtered and the solids were extracted several times with fresh THF. Combined filtrate and washings were rotary-evaporated onto 5 g of 100–200-mesh silica gel, which was then placed atop a chromatography column made up with 60 g of silica gel slurried in hexane. Elution with toluene gave two bands. Fractions of the second band were combined and rotary-evaporated to a gummy solid, which was extracted several times with small portions of chloroform to remove organic impurities. The extraction residue is pure **1** (0.21 g, 8% yield); the compound was crystallized from acetone/ethylene dichloride. Precise mass (m/e): calcd for $^{11}B_{10}{}^1H_{10}{}^{209}Bi_2$, 538.1321; found, 538.1319. IR (KBr): 2506 (vs), 985 (s), 901 (w), 885 (w), 816 (m), 765 (m), 668 (w) cm^{-1}.

1,2-$PBiB_{10}H_{10}$ (2). When triethylamine (11 mL) was added to a stirred solution of 0.20 g (0.9 mmol) of $(CH_3)_4NB_{10}H_{12}P$ in 25 mL of THF, a precipitate formed. Bismuth trichloride (0.52 g, 16.5 mmol) was added and stirring was continued for 2 h. Refluxing for 1 h darkened the suspension considerably. THF was removed under vacuum and the solid residue extracted several times with hot toluene. The combined toluene extract was stripped onto 230–400-mesh silica gel, which was then placed atop a column made up with 50 g of silica gel slurried in hexane. After removal of a yellow impurity band with hexane, the product was eluted with toluene to give 30 mg of **2** (9.3% yield). Precise mass (m/e): calcd for $^{11}B_{10}{}^1H_{10}{}^{31}P^{209}Bi$, 360.1255; found, 360.1248. ^{31}P NMR (acetone-d_6): δ −51.8 ppm. IR (KBr): 2520 (vs), 1004 (s), 914 (w), 893 (w), 806 (w), 730 (m), 620 (w) cm^{-1}.

1,2-$AsBiB_{10}H_{10}$ (3). A 100-mL three-necked flask was fitted with a pressure-equalized dropping funnel, a septum, and a gas inlet. The system was evacuated and filled with nitrogen. Decaborane (0.61 g, 5.0 mmol) was added and dissolved in 20 mL of THF and 11 mL of triethylamine added by syringe. Solid $BiCl_3$ (1.8 g, 5.7 mmol) was added and stirring continued for 20 min, yielding a green solution and black precipitate. A solution of 0.42 mL (5 mmol) of $AsCl_3$ in 10 mL of THF was added dropwise over 30 min. Stirring was continued overnight, and then the solution was filtered. The solids were washed several times with 15-mL portions of THF, and the combined washings and filtrate were rotary-evaporated onto 4 g of 230–400-mesh silica gel, which was then placed atop a column made up by slurrying 35 g of silica gel in hexane. Toluene eluted 1,2-$As_2B_{10}H_{10}$, chloroform eluted a mixture of 1,2-$AsBiB_{10}H_{10}$ and 1,2-$Bi_2B_{10}H_{10}$, and acetone eluted 7-$B_{10}H_{12}As^-$. The material eluted with chloroform was fractionally sublimed at 100–105 °C. The first fraction (4 mg) was a mixture, the second fraction (26 mg, 1.3% yield) was pure 1,2-$AsBiB_{10}H_{10}$, and the third fraction (25 mg) was a mixture of 1,2-$AsBiB_{10}H_{10}$ and 1,2-$Bi_2B_{10}H_{10}$, as indicated by ^{11}B NMR spectroscopy. Precise mass (m/e): calcd for $^{11}B_{10}{}^1H_{10}{}^{75}As^{209}Bi$, 404.0733; found, 404.0720. IR (KBr): 2530 (vs), 990 (s), 902 (w), 881 (w), 763 (w), 721 (m), and 332 (w) cm^{-1}.

1,2-$SbBiB_{10}H_{10}$ (4). An apparatus was set up as in the previous experiment and charged with 0.61 g of $B_{10}H_{14}$ (5 mmol), 75 mL of THF, and 11 mL of triethylamine. Solid $BiCl_3$ (1.8 g, 5.7 mmol) was added and stirring was continued for 10 min. The solution turned green, and a black precipitate formed. A slurry of 2.5 g of SbI_3 (5 mmol) in 10 mL of THF was made up in the dropping funnel and added over 30 min. Stirring was continued overnight. The mixture was filtered, and the solids were washed with several small portions of THF. The THF solution was refiltered after several hours to remove solids that had formed. The solution was rotary-evaporated onto 3.5 g of 230–400-mesh silica gel, and the solids were placed atop a column made up with 35 g of silica gel slurried in hexane. Elution with toluene first removed 1,2-$Sb_2B_{10}H_{10}$, then a mixture of 1,2-$Sb_2B_{10}H_{10}$, and 1,2-$SbBiB_{10}H_{10}$, and then 1,2-$Bi_2B_{10}H_{10}$. The second band was rechromatographed, starting with 50% hexane/toluene as eluent, giving 1,2-$Sb_2B_{10}H_{10}$, 1,2-$SbBiB_{10}H_{10}$, and 1,2-$Bi_2B_{10}H_{10}$ as three separate bands. The crude 1,2-$SbBiB_{10}H_{10}$ (57 mg) was crystallized from chloroform to give 20 mg of pure **4** (0.9% yield). Precise mass (m/e): calcd for $^{11}B_{10}{}^1H_{10}{}^{121}Sb^{209}Bi$, 450.0555; found, 450.0558. IR (KBr): 2520 (vs), 992 (s), 909 (w), 887 (w), 827 (m), 772 (m), 724 (m), 675 (w), 310 (w) cm^{-1}.

$(CH_3)_4N[B_{11}H_{11}Bi]$ (5). To a solution of $(CH_3)_3NH[B_{11}H_{14}]$ (0.50 g, 2.6 mmol) in 20 mL of THF was added slowly 4.0 mL of butyllithium solution in hexane (2.5 mmol/mL). After being stirred for 10 min, 1.52 g (4.8 mmol) of $BiCl_3$ was added and the solution rapidly turned black. The solution was stirred for 15 min and refluxed for 4 h. After cooling, 4 mL of water was added and the THF was removed under vacuum. The residues were extracted with water and precipitated with tetramethylammonium chloride solution. The crude precipitate was collected by filtration and crystallized from acetone/water containing a few drops of concentrated HCl added to destroy unreacted starting material. Yield: 0.25 g (25%). Anal. Calcd for $C_4H_{23}NB_{11}Bi$: C, 11.63; H, 5.61; B, 28.78. Found: C, 11.97; H, 5.78; B, 27.28. IR (KBr): 3020 (w), 2500 (vs), 1478 (s), 1018 (m), 945 (m), 733 (w), 712 (w) cm^{-1}.

X-ray Structure Determination for 1,2-$Bi_2B_{10}H_{10}$. Crystals were grown by slow evaporation of an acetone/toluene solution. A small, colorless crystal was selected, mounted on a previously described goniostat,[14] and cooled to −158 °C. A total of 8868 reflections (including standards) were collected, from which a unique set of 5074 unique reflections were obtained. The large linear absorption coefficient (357.18 cm^{-1}) made it imperative to correct the data for absorption. A summary of crystal data and intensity information is given in Table I.

The calculated density of 3.64 g/cm³ requires eight molecules of $B_{10}H_{10}Bi_2$ per unit cell, or four molecules in the asymmetric unit. The structure was solved by a combination of direct methods and Fourier techniques. The eight Bi atoms were located from the initial, E map, and the B atoms were located in successive difference maps phased with the already located atoms. The structure was refined by using full-matrix least squares, with isotropic thermal parameters on all Bi and B atoms. The final $R(F)$ was 0.121. All attempts at using anisotropic thermal parameters failed, and it was, of course, not possible to locate any hydrogen atoms. It is possible the difficulties encountered are caused by

---

(9) Veneble, T. L.; Hutton, W. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1984**, *106*, 29.

(10) Little, J. L.; Kester, J. G.; Huffman, J. C.; Todd, L. J. *Inorg. Chem.* **1989**, *28*, 1087.

(11) Dunks, G. B.; Banker, K.; Hedaya, E.; Hefner, C.; Palmer-Ordonez, K.; Remec, P. *Inorg. Chem.* **1981**, *20*, 1692.

(12) (a) Tucker, P. M.; Onak, T.; Leach, J. B. *Inorg. Chem.* **1970**, *9*, 1430. (b) Warren, R.; Paquin, D.; Onak, T.; Dunks, G.; Spielman, J. R. *Inorg. Chem.* **1970**, *9*, 2285. (c) Groszek, E.; Leach, J. B.; Wong, G. T. F.; Ungermann, C.; Onak, T. *Inorg. Chem.* **1971**, *10*, 2770. (d) Siedle, A. R.; Bodner, G. M. *Inorg. Chem.* **1973**, *12*, 2091. (e) Siedle, A. R.; Bodner, G. M.; Garber, A. R.; Beer, D. C.; Todd, L. J. *Inorg. Chem.* **1974**, *13*, 2321. (f) Wikholm, G. S.; Todd, L. J. *J. Organomet. Chem.* **1974**, *71*, 219. (g) Todd, L. J.; Siedle, A. R.; Sato, F.; Garber, A. R.; Scholer, F. R.; Mercer, G. C. *Inorg. Chem.* **1975**, *14*, 1249. (h) Stanko, V. I.; Babushkina, T. A.; Klimova, T. P.; Goltyapin, Y. V.; Klimova, A. I.; Vasilev, A. M.; Alymov, A. M.; Khrapov, V. V. *Zh. Obsch. Khim.* **1976**, *46*, 1071. (i) Babushkina, T. A.; Klimova, T. P.; Anorova, G. A.; Khrapov, V. V.; Stanko, V. I. *Zh. Obsch. Khim.* **1976**, *46*, 1064. (j) Hermanek, S.; Gregor, V.; Stibr, B.; Plesek, J.; Janousek, Z.; Antonovich, V. A. *Collect. Czech. Chem. Commun.* **1976**, *41*, 1492. (k) Todd, L. J.; Siedle, A. R.; Bodner, G. M.; Kahl, S. B.; Hickey, J. P. *J. Magn. Reson.* **1976**, *23*, 301. (l) Hermanek, S.; Plesek, J.; Gregor, V.; Stibr, B. *J. Chem. Soc., Chem. Commun.* **1977**, 561. (m) Little, J. L.; Friesen, G. D.; Todd, L. J. *Inorg. Chem.* **1977**, *16*, 870. (n) Wright, W. F.; Garber, A. R.; Todd, L. J. *J. Magn. Reson.* **1978**, *30*, 595.

(13) Hawthorne, M. F.; Pitochelli, A. R. *J. Am. Chem. Soc.* **1959**, *81*, 5519.

(14) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

Table I. Summary of Crystal Data and Intensity Information for 1,2-$Bi_2B_{10}H_{10}$

empirical formula	$B_{10}H_{10}Bi_2$
color	colorless
cryst dimens	[010], 0.006 cm [0$\bar{1}$0], 0.006 cm [$\bar{1}$02], 0.004 cm [$\bar{1}$0$\bar{2}$], 0.002 cm [100], 0.006 cm [$\bar{1}$10], 0.006 cm
av abs cor	0.109
min tranm; max tranm	0.062; 0.147
space group	$P\bar{1}$
cell dimens (at −158 °C, 44 reflcns)	
a	12.174 (1) Å
b	14.070 (2) Å
c	12.135 (1) Å
α	91.07 (1)°
β	99.51 (1)°
γ	106.70 (1)°
Z (molecules/cell)	8
V	1958.68
d_{calcd}	3.636 g cm^{-3}
wavelength	0.71069 Å
M_r	536.14
linear abs coeff	357.176 cm^{-1}
detector-to-sample dist	22.5 cm
sample-to-source dist	23.5 cm
take-off angle	2.0°
av ω scan width at half-height	0.25°
scan speed	6.0°/min
scan width	1.6° + dispersion
single bkgd time at extremes of scan	8 s
aperture size	3.0 × 4.0 mm
limits of data collcn	
min 2*θ*	6°
max 2*θ*	45°
tot. no. of reflcns collcd	8868
no. of unique intensities	5074
no. with $F > 0.0$	4690
no. with $F > 3.0\sigma(F)$	3491
final results	
$R(F)$	0.121
$R_w(F)$ (*w* based on counting statistics)	0.121
goodness of fit for last cycle	4.587
max Δ/σ for last cycle	0.38

Table II. Interatomic Distances for 1,2-$Bi_2B_{10}H_{10}$

Bi(1)–Bi(2)	2.956 (4)	B(5)–B(6)	1.84 (10)
Bi(1)–B(3)	2.63 (8)	B(5)–B(9)	1.76 (12)
Bi(1)–B(4)	2.39 (8)	B(5)–B(10)	1.74 (14)
Bi(1)–B(5)	2.44 (8)	B(6)–B(10)	1.70 (14)
Bi(1)–B(6)	2.62 (8)	B(6)–B(11)	1.94 (12)
Bi(2)–B(3)	2.51 (8)	B(7)–B(8)	1.72 (13)
Bi(2)–B(6)	2.66 (8)	B(7)–B(11)	1.91 (13)
Bi(2)–B(7)	2.42 (8)	B(7)–B(12)	1.78 (12)
Bi(2)–B(11)	2.41 (9)	B(8)–B(9)	1.76 (14)
B(3)–B(4)	1.81 (11)	B(8)–B(12)	1.76 (14)
B(3)–B(7)	1.75 (11)	B(9)–B(10)	1.71 (15)
B(3)–B(8)	1.69 (13)	B(9)–B(12)	1.84 (12)
B(4)–B(5)	1.89 (11)	B(10)–B(11)	1.80 (15)
B(4)–B(8)	1.71 (13)	B(10)–B(12)	1.90 (15)
B(4)–B(9)	1.82 (12)	B(11)–B(12)	1.86 (12)

the large discrepancy in atomic numbers of the Bi and B atoms, as well as the high ratio of Bi to B, 78% Bi to 20% B (by weight). Attempts were made to establish the presence or absence of disorder by examination of various disorder models. While the results did not indicate the presence of disorder, we cannot rule out this possibility.

Interatomic distances and atomic coordinates and isotropic thermal parameters for one of the independent molecules are shown in Tables II and III, respectively. For the four independent molecules in the asymmetric unit, the average Bi–Bi distance is 2.957 Å, the average Bi–B distance is 2.48 Å, and the average B–B distance is 1.80 Å.

Results and Discussion

Reaction of $BiCl_3$, excess triethylamine, and $B_{10}H_{14}$ at room temperature gave 1,2-$Bi_2B_{10}H_{10}$ (**1**) in 8% yield. These are similar to the conditions used for the preparation of 1,2-$As_2B_{10}H_{10}$,[3,8] except that the solution was not refluxed. If the bismuth reaction was refluxed even for a short time, only approximately 1% yield of **1** was obtained and the major byproduct was $B_{10}H_{10}^{2-}$, with lesser amounts of $B_9H_{14}^-$ and $B_3H_8^-$, as indicated by ^{11}B NMR spectroscopy. It is well-known that $B_{10}H_{14}$ will react directly with excess triethylamine to form $(Et_3NH)_2B_{10}H_{10}$ in high yield.[13]

The structure of **1** was determined by a single-crystal X-ray structure study. An ORTEP drawing for **1** is given in Figure 1. The distorted icosahedral geometry for this molecule is confirmed.

Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10) for 1,2-$Bi_2B_{10}H_{10}$

atom	*x*	*y*	*z*	B_{iso}
Bi(1)	5853 (3)	1719 (2)	9025 (3)	10 (1)
Bi(2)	5886 (3)	3828 (2)	9119 (3)	10 (1)
B(3)	7578 (69)	3252 (58)	9993 (68)	2 (14)
B(4)	7930 (67)	2302 (57)	9222 (66)	0 (13)
B(5)	7202 (66)	2082 (56)	7703 (66)	0 (13)
B(6)	6229 (67)	2862 (57)	7365 (66)	0 (13)
B(7)	7986 (74)	4354 (63)	9315 (73)	7 (15)
B(8)	8778 (94)	3519 (80)	9396 (92)	21 (19)
B(9)	8630 (81)	2883 (69)	8093 (79)	11 (16)
B(10)	7632 (109)	3241 (91)	7167 (106)	31 (23)
B(11)	7201 (82)	4212 (68)	7793 (79)	12 (17)
B(12)	8742 (76)	4217 (64)	8212 (74)	8 (16)

Table IV. ^{11}B NMR Data for Bismaboranes

compd	rel area	δ_B, ppm ($J_{^{11}B-^{1}H}$, Hz)	assgnt	$\omega_{1/2}$, Hz (±2 Hz)
1,2-$Bi_2B_{10}H_{10}$ (**1**)^a	2	14.5 (140)	B(9,12)	80
	2	8.1 (153)	B(3,6)	138
	4	1.4 (142)	B(4,5,7,11)	89
	2	−4.3 (147)	B(8,10)	72
1,2-$PBiB_{10}H_{10}$ (**2**)^a	1	12.6 (∼140)	B(9)	*b*
	1	12.0 (∼140)	B(12)	*b*
	2	6.1 (142)	B(7,11)	81
	2	2.7 (153)	B(3,6)	97^c
	2	−1.2 (146)	B(8,10)	75
	2	−7.1 (148)	B(4,5)	101^c
1,2-$AsBiB_{10}H_{10}$ (**3**)^a	1	15.2 (163)	B(12)	77
	1	13.5 (169)	B(9)	93
	2	6.6 (146)	B(3,6)	90
	2	5.6 (124)	B(7,11)	85
	2	−1.7 (151)	B(8,10)	73
	2	−3.7 (161)	B(4,5)	70
1,2-$SbBiB_{10}H_{10}$ (**4**)^a	1	15.7 (156)	B(12)	78
	1	14.1 (179)	B(9)	109
	2	7.0 (156)	B(3,6)	98
	2	4.1 (142)	B(7,11)	86
	4	−3.6 (146)	B(8,10); B(4,5)	70
$(CH_3)_4NB_{11}H_{11}Bi$ (**5**)^a	1	12.3 (140)	B(12)	88
	5	−5.6 (134)	B(2–6)	91
	5	−6.7 (134)	B(7–11)	67

^{a} Acetone solvent. ^{b} Overlapping peaks. ^{c} Measurement not accurate due to P coupling.

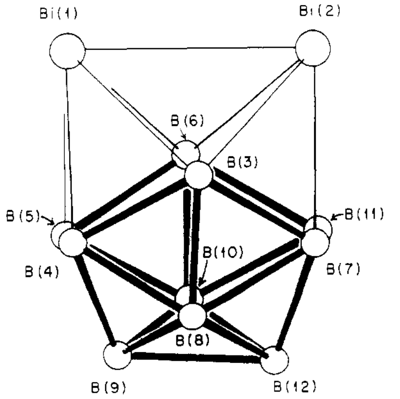

Figure 1. ORTEP drawing of 1,2-$Bi_2B_{10}H_{10}$.

Table V. Bi-Bi Bond Distances of Recently Reported Compounds

compd	Bi-Bi dist, Å	ref
$Ph_2Bi-BiPh_2$	2.990 (2)	7
$Mo_2(CO)_4(\eta-C_5H_4Me)_2(\mu-\eta^2-Bi_2)$	2.838 (1)	15
$Os_4(CO)_{12}(\mu_4-Bi)_2$	3.017 (2)	16
$Bi_2Fe_2Co(CO)_{10}$	3.092 (2)	17

There are four molecules in the asymmetric unit. The average Bi-Bi distance is 2.957 Å. Recently, there has been considerable interest in molecules containing Bi-Bi bonds. The Bi-Bi bond distances for some of these molecules are collected in Table V. This is by no means an exhaustive list of all known compounds containing a Bi-Bi structural unit. However, the data of Table V clearly show that the Bi-Bi bond distance of **1** is similar to an element-element single bond and is not too unlike the Bi-Bi units found in tetrahedral and octahedral transition-metal clusters.

Reaction of piperidine with 1,2-$As_2B_{10}H_{10}$ or 1,2-$Sb_2B_{10}H_{10}$ removes a boron atom to form the $B_9H_{10}E_2^-$ (E = As, Sb) anions.[2,8] However, when neat piperidine was reacted with **1** at room temperature for several hours, the major product was $B_{10}H_{10}^{2-}$. No NMR evidence was found for the presence of either $B_{10}H_{12}Bi^-$ or $B_9H_{10}Bi_2^-$ in the reaction mixture. Compound **1** was treated with triethylamine in acetone/DMF at 60 °C for 1 h, and **1** was recovered unchanged. Thus, the tertiary amine does not degrade **1** once it is formed during the synthesis; however, a secondary amine easily leads to bismuth removal from compound **1**.

The only icosahedron containing two different group-15 atoms that has been reported to date is 1,2-$AsSbB_{10}H_{10}$.[2] We have been able to synthesize all the mixed derivatives 1,2-$EBiB_{10}H_{10}$ (where E = P, As, or Sb).

The phosphorus-containing molecule 1,2-$PBiB_{10}H_{10}$ (**2**) was made in moderate yield by reaction of $B_{10}H_{12}P^-$,[10] triethylamine, and $BiCl_3$ in THF. Attempts to synthesize **2** by reaction of $B_{10}H_{14}$, triethylamine, PCl_3, and $BiCl_3$ gave 1,2-$P_2B_{10}H_{10}$ and 1,2-$Bi_2B_{10}H_{10}$ in low yield, but no **2** was found.

The mixed compounds 1,2-$B_{10}H_{10}AsBi$ (**3**) and 1,2-$B_{10}H_{10}SbBi$ (**4**) were synthesized in low yield by reaction of $B_{10}H_{14}$, triethylamine, $AsCl_3$ or SbI_3, and $BiCl_3$. The desired products **3** and **4** were separated from the mixture of hetero boranes by column chromatography. The precise mass detemination of the parent ion peaks in the high-resolution mass spectra verified the molecular formulas of **1**-**4**.

Since $B_{11}H_{11}Sb^-$ is readily formed from $B_{11}H_{14}^-$, a base, and $SbCl_3$,[2] we tried the synthesis of the bismuth-containing icosahedral anion under similar conditions. Thus, treating $B_{11}H_{14}^-$ with butyllithium and adding solid $BiCl_3$ gave a black solution from which $(CH_3)_4N[B_{11}H_{11}Bi]$ (**5**) was isolated in 25% yield.

^{11}B NMR Studies. Compound **1** exhibited a ^{11}B NMR spectrum containing four doublets in a 2:2:4:2 ratio, which is consistent with the C_{2v} symmetry of an icosahedral molecule with two equivalent heteroatoms. The ^{11}B NMR data for all the bismaboranes are given in Table IV. Two-dimensional (^{11}B-^{11}B) NMR was used to assign boron nuclei to specific resonances. Only the resonances at 1.4 and -4.3 ppm show cross peaks in the 2-D contour plot with all other resonances. This suggests that the resonance at -4.3 ppm is due to B(8,10) and, by its intensity, the resonance at 1.4 ppm is due to B(4,5,7,11). (See Figure 2 for the numbering of 1,2-$Bi_2B_{10}H_{10}$ and related molecules. Note that this figure is rotated relative to Figure 1 and this icosahedral structure does not show the actual distortion caused by the heteroatoms in the cage.) There is no possibility of using 2-D NMR spectroscopy to determine the assignments of the resonances at 14.5 and 8.1 ppm, since both signals show cross peaks in the 2-D contour plot with B(8,10) and B(4,5,7,11). Since bismuth-209 is 100% spin active ($I = {}^9/_2$), there should be a broadening of the line widths of the resonances of boron atoms adjacent to the bismuth atoms in the cage. The line widths at half the peak height ($\omega_{1/2}$) (see Table IV) are slightly larger for the resonance assigned to B(4,5,7,11) at 1.4 ppm and significantly larger for the resonance at 8.1 ppm, which can therefore be assigned to B(3,6). This, then, assigns the resonance at 14.5 ppm to B(9,12), which is consistent with the antipodal effect observed in closo hetero boranes.[12]

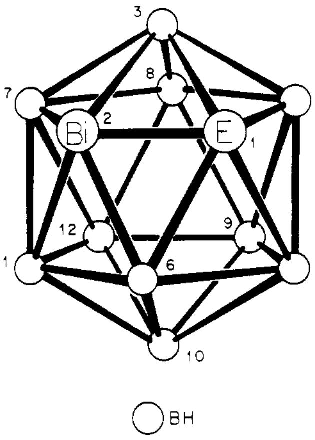

Figure 2. Structure and numbering of the bismaboranes of the general formula 1,2-$EBiB_{10}H_{10}$ (E = P, As, Sb, Bi).

The ^{11}B NMR spectrum of **2** contained a 1:1:2:2:2:2 pattern of resonances expected for this icosahedral molecule with two nonequivalent heteroatoms. The 2-D ^{11}B-^{11}B COSY spectrum of **2** showed that the resonance at -1.2 ppm could be assigned to B(8,10), since it exhibited cross peaks with all of the other boron resonances. The area 2 resonance at 2.7 ppm was assigned to B(3,6), since there was no cross peak between it and the two area 1 resonances at 12.6 and 12.0 ppm (assigned to B(9) and B(12)).

An ^{11}B NMR line-narrowing experiment, with proton decoupling, resolved the 2.7 ppm signal into a doublet ($J_{^{11}B-^{31}P}$ = 67 Hz). The resonance at -7.1 ppm was resolved into a doublet as well ($J_{^{11}B-^{31}P}$ = 62 Hz).

The observation of phosphorus coupling to the 2.7 ppm signal is consistent with our assignment of this resonance to B(3,6). The ^{31}P coupling observed at the most upfield resonance at -7.1 ppm assigns this signal to B(4,5). The remaining area 2 resonance at 6.1 ppm is then assigned to B(7,11). Since the resonance of area 1 at 12.0 ppm shows a cross peak with the resonance at 6.1 ppm, this assigns this peak to B(12). The peak at 12.6 ppm is then due to B(9).

Compound **3** exhibits an ^{11}B NMR spectrum containing resonances in a 1:1:2:2:2:2 pattern similar to that seen for **2**. In the 2-D ^{11}B COSY contour plot of **3**, the resonance at -1.7 ppm shows cross peaks with all other resonances and is assigned to B(8,10). The resonance at 6.6 ppm shows no cross peak with the two area 1 resonances (B(9) and B(12)) and is assigned to B(3,6). The resonance at 15.2 ppm shows a cross peak with the resonance at 5.6 ppm, while the resonance at 13.5 ppm shows a cross peak with the resonance at -3.7 ppm. However, since the area 2 resonances and the area 1 resonances are related by symmetry (C_2 axis and a mirror plane), it is not possible, using 2-D NMR, to determine the exact assignments of these four resonances.

However, in **2**, the resonance assigned to B(4,5) occurred at a higher field than that of B(7,11). Thus, we tentatively assign the resonance at -3.7 ppm in the ^{11}B NMR spectrum of **3** to B(4,5) and the resonance at 5.6 ppm to B(7,11). This then leads to the assignment of the area 1 signal at 15.2 ppm to B(12) and the signal at 13.5 ppm to B(9). These assignments are consistent with the general observation that ^{11}B signals of boron atoms adjacent or antipodal to bismuth-209 ($I = {}^9/_2$) are broader ($\omega_{1/2}$) than other ^{11}B signals of these molecules.

The assignments for the ^{11}B NMR spectrum of compound **4** follow from results for the 2-D ^{11}B-^{11}B COSY spectrum similar to that observed for **3**.

The ^{11}B NMR spectrum for compound **5** consists of resonances in a 1:5:5 ratio, which is consistent with an icosahedral cage

---

(15) Clegg, W.; Compton, N. A.; Errington, R. J.; Norman, N. C. *Polyhedron* **1988**, *7*, 2239.

(16) Ang, H. G.; Hay, C. M.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Whitton, A. J. *J. Organomet. Chem.* **1987**, *330*, C5.

(17) Whitmire, K. H.; Raghuveer, K. S.; Churchill, M. R.; Fettinger, J. C.; See, R. F. *J. Am. Chem. Soc.* **1986**, *108*, 2778.

containing one heteroatom. The 2-D ^{11}B COSY spectrum shows a cross peak between the resonance at 12.3 ppm (area 1, B(12)) and the resonance at −6.7 ppm (thus assigned to B(7−11)).

The antipodal effect for nido and closo boron cage compounds has been well documented.[12] In general, it is observed, for a given periodic table group (e.g., P, As, Sb, Bi) of hetero boranes, that the more electronegative the heteroatom, the more shielded is the antipodal boron atom of the icosahedral structure. The ^{11}B chemical shift values for the antipodal boron atoms of the $AsB_{11}H_{11}^-$, $SbB_{11}H_{11}^-$, and $BiB_{11}H_{11}^-$ ions are +7.9, +9.4, and +12.3 ppm, respectively, in accord with this generality. For heteroboranes from different periodic groups, the shielding of the antipodal atom (with the limited data available) appears to decrease in the order group 13 > group 14 > group 15 > group 16. A more detailed discussion on the chemical shift trends of group 14−16 icosahedral heteroatom boranes will be published in the near future.

Thermal Properties. In the solid state, none of the compounds melts up to 500 °C. **2** starts darkening above 250 °C, while **1** and **3**−**5** darken above 350 °C. Thus, these compounds are much more stable thermally than known lead-containing carboranes[5,6] but not as thermally stable as group-15 boranes containing one or two group-15 atoms other than bismuth in the cage. With the exception of **2**, however, they are surprisingly heat stable.

Acknowledgment. This work was supported by the Army Research Office.

Supplementary Material Available: Tables of fractional coordinates, isotropic thermal parameters, bond distances, and intramolecular angles (25 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2,
and Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Phosphoranimine Phosphines and Arsines as Heterodifunctional Coordinating Ligands. Synthesis and Characterization of New Palladium(II) Metallacycles $\overline{\mathrm{RN{=}PPh_2(CH_2)_nEPh_2Pd}}\mathrm{Cl_2}$ (R = $SiMe_3$, $GeMe_3$, H; n = 1, 2; E = P, As) and the Crystal and Molecular Structure of $\overline{\mathrm{HN{=}PPh_2CH_2PPh_2Pd}}\mathrm{Cl_2}$, the First Structural Example of a Phosphoranimine Phosphine Complex

K. V. Katti,[†] R. J. Batchelor,[‡] F. W. B. Einstein,[‡] and R. G. Cavell*[,†]

Received May 31, 1989

Reaction of the *N*-(trimethylsilyl)- or *N*-(trimethylgermyl)phosphoranimine phosphines $Me_3ENPPh_2CH_2PPh_2$ (E = Si, Ge) or the *N*-(trimethylsilyl)phosphoranimine arsine $Me_3SiNPPh_2CH_2CH_2AsPh_2$ with $PdCl_2(PhCN)_2$ gave metallacyclic Pd^{II} derivatives $\mathrm{Me_3E}\overline{\mathrm{NPPh_2(CH_2)_nQPh_2Pd}}\mathrm{Cl_2}$ (Q = P, n = 1, E = Si or Ge; Q = As, n = 2, E = Si). Water reacts with $\mathrm{Me_3Si}\overline{\mathrm{NPPh_2CH_2PPh_2Pd}}\mathrm{Cl_2}$ to form the parent imine complex $\overline{\mathrm{HNPPh_2CH_2PPh_2Pd}}\mathrm{Cl_2}$ (**12**), the structure of which has been determined. (Crystal data for **12** (as a 1:1 adduct with CH_2Cl_2): monoclinic $P2_1/n$ (No. 14), a = 8.953 (3) Å, b = 21.151 (4) Å, c = 14.773 (2) Å, β = 93.98 (2)°, Z = 4, final $R(F)$ = 0.034, $R_w(F)$ = 0.037.) The imine ligand adopts an "envelope" five-membered chelate ring configuration bonded at N and P. The Pd—N (2.021 (6) Å) and N=P (1.599 (6) Å) bond lengths are in accord with expectations for Pd—N single and P=N double bonds. The nitrogen atom is pyramidal. **12** is also formed by reaction of $Me_3SiNPPh_2CH_2PPh_2$ with K_2PdCl_4 in the presence of water. Activated fluoroaromatics (e.g. pentafluorobenzonitrile) replace Me_3Si or Me_3Ge groups on the ligand framework by elimination of Me_3SiF and attachment of the fluoroaromatic exclusively at the para position. Full spectral characterization of all complexes is given. The Me_3Ge phosphoranimine phosphine shows conformational behavior similar to that of the Me_3Si analogue reported earlier. All conformers in the mixture however give a metal complex with only one conformation. We also describe a more efficient synthesis of Me_3GeN_3, which was developed in the course of the study.

Introduction

Synthesis of appropriate heterodifunctional ligands for development of homogeneous catalyst applications[1] is often the major barrier to progress; frequently the synthesis of ligands with chemically diverse donating (or bonding) atoms requires multistep manipulations with concomitantly poor yields or difficult separations. An example is the partial oxidation of dppm to the catalytically useful ligand $Ph_2PCH_2P(O)Ph_2$, which involves a multistep sequence of reactions employing organolithium or Grignard reagents.[2] Additional advantages would be provided by the possibility of easily making modifications to the reactivity of the ligand by systematic alteration of its substituents, a flexibility that could strongly influence the design of catalytic complexes with appropriate chemical selectivity and stereoselectivity.

We recently reported a new approach to the preparation of heterodifunctional ligands based on the partial oxidation of diphosphines such as dppm (**1**) by means of a Staudinger reaction with Me_3SiN_3 (eq 1).[3a] This reaction represents the first example

---

* To whom correspondence should be addressed.
[†] University of Alberta.
[‡] Simon Fraser University.

(1) For leading references illustrating the catalytic potential of different types of heteroatomic chelated transition-metal compounds, see: (a) Kraft, M. E.; Wilson, L. J.; Onan, K. D. *Organometallics* **1988**, *7*, 2528. (b) Anderson, M. P.; Casalnuovo, A. L.; Johnson, B. J.; Mattson, B. M.; Mueting, A. M.; Pignolet, L. H. *Inorg. Chem.* **1988**, *27*, 1649. (c) Wang, H. H.; Casalnuovo, A. L.; Johnson, B. J.; Mueting, A. M.; Pignolet, L. H. *Inorg. Chem.* **1988**, *27*, 325. (d) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167. (e) Wegman, R. W.; Abatjoglou, A. G.; Harrison, A. M. *J. Chem. Soc., Chem. Commun.* **1987**, 1891. (f) Bonnet, M. C.; Stitou, B.; Tkatchenko, I. *J. Organomet. Chem.* **1985**, *279*, C1. (g) Brunner, H.; Rahman, A. F. M. M. *Chem. Ber.* **1984**, *117*, 710. (h) Organ, G. J.; Cooper, M. K.; Henrick, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1984**, 2377. (i) Breque, A.; Santini, C. C.; Mathey, F.; Fischer, J.; Mitschler, A. *Inorg. Chem.* **1984**, *23*, 3463. (j) Roundhill, D. M.; Bechtold, R. A.; Roundhill, S. G. N. *Inorg. Chem.* **1980**, *19*, 284.

(2) (a) Grim, S. O.; Satek, L. C.; Tolman, C. A.; Jesson, J. P. *Inorg. Chem.* **1975**, *14*, 656. (b) Carr, S. W.; Colton, R. *Aust. J. Chem.* **1981**, *34*, 35. (c) Grim, S. O.; Walton, E. D. *Inorg. Chem.* **1980**, *19*, 1982.

0020-1669/90/1329-0808$02.50/0