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Synthesis of Polyhedral Arsaboranes and Their Metal Derivatives

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Methods have been determined to improve the yield of 7-$B_{10}H_{12}As^-$ and 1,2-$B_{10}H_{10}As_2$ to 50% based on $B_{10}H_{14}$. The icosahedral anion $B_{11}H_{11}As^-$ has been obtained in 48% yield from $B_{11}H_{14}^-$. The metalloarsaboranes 3,1,2-(dppe)Ni($As_2B_9H_9$), 3,6,1,2-$[(C_5H_5)Co]_2As_2B_8H_8$, and 1,2-$AsEB_{10}H_{10}^-$ (E = Sn and Pb) have been prepared and characterized.

A few years ago, John Little and co-workers prepared a variety of phosphorus; arsenic- and antimony-containing boranes. From these studies, it appeared that the arsaboranes were the most chemically stable class of compounds of group 15 and offered the most potential for further development.[1-3] The initial report indicated that reaction of $B_{10}H_{14}$ with $AsCl_3$ in diethyl ether with excess sodium hydride or sodium borohydride as base and reducing agent formed 7-$B_{10}H_{12}As^-$ in 34% yield.[1] Unfortunately, this product had to be purified by column chromatography. A second synthetic route seemed to be preferred because the product was obtained in pure form without chromatography, albeit in only 15% yield.[1] This alternate synthesis of 7-$B_{10}H_{12}As^-$ employed THF as solvent, triethylamine as the base, and zinc powder as the reducing agent.

We undertook a detailed study of the synthesis of 7-$B_{10}H_{12}As^-$ and also of 1,2-$B_{10}H_{10}As_2$ with the idea that improved yields of these key arsaboranes would substantially improve our ability to prepare and study a large variety of group 15 heteroatom borane derivatives. In addition, we report here an improved synthesis of $B_{11}H_{11}As^-$, as well as the synthesis and characterization of some new metalloarsaborane compounds.

Experimental Section

Physical Measurements. Boron (^{11}B) NMR spectra were obtained at 70.6 MHz with a Varian HR-220 spectrometer or at 115.85 MHz with a Nicolet NT-360 spectrometer and were externally referenced to $BF_3{\cdot}O(C_2H_5)_2$ (positive values downfield). Proton NMR spectra were recorded on either a Varian HR-220 or a Nicolet NT-360 spectrometer and were referenced to internal Me_4Si. Infrared spectra were determined by using KBr disks with a Perkin-Elmer 283 spectrometer. Low-resolution mass spectral data were collected on a Varian CH-7 spectrometer, and high-resolution data with an AEI-MS-9 spectrometer at The Ohio State University, Columbus, OH. Melting points were obtained in sealed, evacuated capillaries and are uncorrected. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY, or Galbraith Laboratories, Inc., Knoxville, TN.

Materials. All reactions were performed under an atmosphere of prepurified nitrogen. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl; triethylamine and piperidine were distilled from sodium hydroxide. Decaborane(14) was sublimed (60 °C, 10^{-2} mm) prior to use. Arsenic trichloride was distilled under reduced pressure (10^{-2} mm). Arsenic triiodide was prepared from arsenic oxide by following the procedure described in the literature.[4] (1,2-Bis(diphenylphosphino)ethane)nickel(II) chloride was obtained from Strem Chemicals, Inc. Anhydrous cobalt(II) chloride was prepared from the hexahydrate according to the method of King.[5] All other commercially available reagents were used as received.

$N(CH_3)_4[B_{10}H_{12}As]$. To a solution of decaborane(14) (1.0 g, 8.2 mmole) in THF (125 mL) was added triethylamine (4.6 mL, 32.8 mmole) and the solution stirred at room temperature for 1 h. Arsenic triiodide (3.7 g, 8.1 mmol) was loaded into a dropping funnel and THF (50 mL) added. Solid $NaBH_4$ (0.3 g, 8.2 mmol) was added to the stirred solution, and the solution of AsI_3 was added dropwise, over a period of 45 min. The mixture was stirred for 4 h at room temperature, and then the solvent was evaporated under vacuum. The residue was extracted twice with 200-mL portions of 5% NaOH solution, and after filtration to remove the insoluble residue, the filtrate was slightly acidified with 1 N HCl. A saturated solution of Me_4NCl was added to the cooled filtrate (ice–water used) and the solid product filtered and dried under vacuum for several hours. The product ($Me_4NB_{10}H_{12}As$) was pure by ^{11}B NMR[1] and was obtained in 50% yield (1.1 g, 4.1 mmol).

1,2-$B_{10}H_{10}As_2$. To a solution of decarborane(14) (0.57 g, 4.7 mmol) in THF (100 mL) was added excess triethylamine (3.3 mL, 24 mmol) via syringe. The solution was then stirred for 20 min, after which a solution of $AsCl_3$ (0.8 mL, 9.5 mmol) in THF (50 mL) was added dropwise to the stirred solution over a 10-min period. The reaction mixture was heated and maintained at reflux for 15 h. After the mixture was allowed to cool to room temperature, the solvent was removed in vacuo. The resulting orange-brown powder was sublimed at 110 °C, (10^{-2} mm) onto a liquid-nitrogen-cooled probe. Off-white 1,2-$B_{10}H_{10}As_2$ (0.65 g, 51%) was obtained; its ^{11}B NMR spectrum was identical with that previously published.[1]

Preparation of 3,1,2-(dppe)$NiAs_2B_9H_9$. Piperidine (12.5 mL, 0.13 mol) was added via syringe to a sample of 1,2-$B_{10}H_{10}As_2$ (0.62 g, 2.3 mmol), and the resulting mixture was stirred under nitrogen for 6 h. The piperidine was then removed in vacuo, the residue was dissolved in acetone (ca. 25 mL), and any solids were removed by filtration through a medium glass frit. After the acetone was removed in vacuo, dry THF (100 mL) was added to the crude $[C_5H_{12}N]^+[7,8\text{-}B_9H_{10}As_2]^-$ salt. Excess triethylamine (2.8 mL, 20 mmol) was syringed into the stirred reaction mixture, and the stirring continued for 20 min. (1,2-Bis(diphenylphosphino)ethane)nickel(II) chloride, $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]NiCl_2$, (dppe)$NiCl_2$ (1.05 g, 2.0 mmol), dissolved in THF (50 mL) was added dropwise with stirring over a 5-min interval. After being stirred under nitrogen for 9 h, the reaction mixture was opened to air and silica gel (ca. 5 mL dry volume, 60–200 mesh) added. The solvent was removed in vacuo and the solids chromatographed on a short (~13 cm) silica gel column packed with 1:1 (v/v) CH_2Cl_2/hexanes. Elution with the same solvent mixture produced a yellow-green band; removal of the solvent from the eluate yielded 3,1,2-(dppe)$NiAs_2B_9H_9$.

Recrystallization from CH_2Cl_2/pentane produced dark green plates (0.61 g, 37% based on 1,2-$B_{10}H_{10}As_2$), mp 351–352 °C dec. ^1H NMR (361 MHz, $Me_2SO\text{-}d_6$): δ 7.8 (br m, 2), 7.5 br m, 3), 2.94 (d, 1, J = 18.4 Hz). ^{11}B NMR (70.6 MHz, acetone): δ 13.9 (1, J_{BH} = 132 Hz), 7.8(5), −7.4(3). IR: 3045 (w), 2518 (vs, br), 1571 (w), 1481 (m), 1432 (s), 1309 (w), 1262 (w), 1186 (w), 1159 (w), 1098 (s), 998 (s), 876 (w), 809 (w), 740 (s), 689 (s), 672 (m), 647 (w), 520 (s), 482 (m), 429 (w), and 343 (w) cm^{-1}. Anal. Calcd for $C_{26}H_{33}As_2B_9NiP_2$: C, 43.78; H, 4.66. Found: C, 43.86; H, 4.75.

Preparation of 3,6,1,2-$[(C_5H_5)Co]_2As_2B_8H_8$. The preparation of 3,1,2-$(C_5H_5)CoAs_2B_9H_9$ was followed as described in the literature (method B),[6] with the use of sublimed 1,2-$B_{10}H_{10}As_2$ (1.00 g, 3.7 mmol) and a reflux time of 20 h. Chromatography of the reaction products with CH_2Cl_2 on a silica gel column generated a yellow band containing 3,1,2-$(C_5H_5)CoAs_2B_9H_9$. An orange band followed more slowly, but moved rapidly off the column upon elution with acetone.

Removal of the solvent from the orange fraction yielded 3,6,1,2-$[(C_5H_5)Co]_2As_2B_8H_8$. Recrystallization from acetone/hexanes produced fire red crystals (5 mg, 0.3%), mp 349–352 °C dec. ^{11}B NMR (70.6 MHz, CD_3CN): δ 28.4 (1, J_{BH} = 132 Hz), 11.2 (2, J_{BH} = 144 Hz), 7.0 (1, J_{BH} = 139 Hz). ^1H NMR (220 MHz, CD_3CN): δ 5.42 (s). IR: 3105 (w), 2502 (vs), 1416 (m, sharp), 1268 (w), 1003 (w), 973 (m), 863 (w), 836 (m), 429 (w), 398 (w), and 356 (w) cm^{-1}.

$(CH_3)_4N[1,2\text{-}B_{10}H_{10}AsPb]$. An excess of *n*-BuLi in hexane (3 mL, 4.44 mmol) was added rapidly to a THF (100 mL) solution of $(CH_3)_3NH[B_{10}H_{12}As]$ (0.282 g, 1.09 mmol) and the mixture stirred at room temperature for 30 min. A solution of lead chloride ($PbCl_2$) (0.452 g, 1.61 mmol) in THF (50 mL) was added dropwise and the mixture refluxed for 5 h. The solvent was removed under vacuum and the residue dried on the vacuum line for several hours. The product was extracted

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into acetonitrile, leaving behind a gray residue upon filtration. The extract solution was evaporated to dryness under vacuum and the crude product washed with several portions of hexane. The lithium salt was dissolved in water, and the product was precipitated by addition of a saturated solution of aqueous tetramethylammonium chloride. The salt was dried under vacuum giving $(CH_3)_4N[B_{10}H_{10}AsPb]$ (0.247 g, 0.52 mmol) in 48% yield. ^1H NMR (361 MHz, Me_2SO-d_6): δ 3.1 (singlet) $[(CH_3)_4N^+]$. ^{11}B NMR (115.85 MHz, Me_2SO-d_6): δ 11.4 (1, J_{BH} = 133 Hz), 7.5 (2, J_{BH} = 127 Hz), 3.6 (2, J_{BH} = 133 Hz), 1.2 (1, J_{BH} = 138 Hz), −5.6 (2, J_{BH} = 119 Hz), −6.7 (2, J_{BH} = 121 Hz). IR: 2490 (s), 1475 (s), 1410 (w), 1260 (w), 1090 (m), 1000 (s), 945 (s), 860 (m), 800 (m), 460 (m) cm^{-1}. Anal. Calcd for $C_4H_{22}NB_{10}AsPb$: As, 15.79. Found: As, 15.58.

$Li[1,2\text{-}B_{10}H_{10}AsSn]$ was made by the same procedure described above. ^{11}B NMR (115.85 MHz, acetone): δ 11.6 (1, J_{BH} = 133), 3.4 (1, J_{BH} = 135 Hz), −0.8 (4, unresolved), −4.9 (2, J_{BH} = 163), −6.8 (2, J_{BH} = 152).

$HNEt_3(B_{11}H_{11}As)$. One-half gram (2.2 mmol) of $HNEt_3[B_{11}H_{14}]$ was dissolved in 20 mL of water containing 1.0 g of KOH. To this solution was added 0.5 g (2.55 mmol) of As_2O_3 in 10 mL of water containing 1.0 g of KOH. The resulting mixture was stirred for 3 days at room temperature, during which time a finely divided, black precipitate was formed. The mixture was filtered and a concentrated solution of NEt_3HCl in water was added to the filtrate to produce a white precipitate. This precipitate was dissolved in CH_2Cl_2, filtered, and reprecipitated with pentane to give 0.31 g (48% yield) of $HNEt_3B_{11}H_{11}As$. ^{11}B NMR spectrum (115.8 MHz, THF): δ 7.7 (1, J_{BH} = 134 Hz), −7.9 (5, J_{BH} = 127 Hz), −9.0 (5, J_{BH} = 138 Hz). The IR spectrum includes absorbances at 3165 (s), 2980 (w), 2525 (vs, br), 1450 (s), 1395 (s), 1355 (w), 1155 (m), 1050 (sh), 1030 (s), 790 (m), 730 (m), 720 (sh), 325 (m), and 315 (w) cm^{-1}.

Results and Discussion

Little has suggested a series of reactions for the insertion of one arsenic atom into the decaborane framework to form $B_{10}H_{12}As^-$.[1] While there is more than one possible multistep pathway by which this chemical transformation could occur, the overall balanced equation is as follows:

$$B_{10}H_{14} + AsI_3 + 2Et_3N + 2e^- \rightarrow Et_3NH[B_{10}H_{12}As] + Et_3NHI + 2I^- \quad (1)$$

One previously reported synthesis of $B_{10}H_{12}As^-$ used zinc dust as the potential reductant.[1] We have found that finely divided, metallic zinc is not effective for this purpose. Some of the decaborane, or a decarborane-derived intermediate, can serve as the reductant. Indeed, we isolated pure $Me_4N[B_{10}H_{12}As]$ in 35% yield with no special reductant added. However, when an equimolar amount of sodium borohydride was added to the reaction, the yield of isolated $B_{10}H_{12}As^-$ was increased to 50%. The reaction takes place at room temperature with no further change upon heating. Excess triethyl-amine beyond that indicated in eq 1 is needed because, with all experimental conditions attempted in this study, some $1,2\text{-}B_{10}H_{10}As_2$ is inadvertently formed (as indicated in eq 2). The choice of arsenic trihalide for this synthesis

$$Et_3NH[B_{10}H_{12}As] + AsI_3 + 2Et_3N \rightarrow 3Et_3NHI + 1,2\text{-}B_{10}H_{10}As_2 \quad (2)$$

was important. The use of $AsCl_3$ or $AsBr_3$ instead of AsI_3 leads to low yields (less than 20%) of $B_{10}H_{12}As^-$ and increased yields of $1,2\text{-}B_{10}H_{10}As_2$.

If the crude product in the $B_{10}H_{12}As^-$ synthesis is extracted with 5% sodium hydroxide solution and then precipitated with Me_4NCl, the resulting precipitate is a mixture of $B_{10}H_{12}As^-$ and $B_{10}H_{11}As^{2-}$. To obtain pure $Me_4N[B_{10}H_{12}As]$, the sodium hydroxide extract is first acidified prior to addition of a saturated solution of Me_4NCl.

If the desired product of the reaction of decaborane-14 and arsenic trihalide is $1,2\text{-}B_{10}H_{10}As_2$, then $AsCl_3$ is the arsenic reagent of choice. With the experimental conditions described in this report for the synthesis of $1,2\text{-}B_{10}H_{10}As_2$, a portion of the decaborane serves as the reductant. With the aid of sodium borohydride as the reductant, we hope to further improve the yield of $1,2\text{-}B_{10}H_{10}As_2$, and such a study is planned.

New Synthesis of the $B_{11}H_{11}As^-$ Ion. Previously, the $B_{11}H_{11}As^-$ ion had been prepared by pyrolysis of $CsB_{10}H_{12}As$ at 350–370 °C (12.7% yield) or by treatment of $N(CH_3)_4(B_{10}H_{12}As)$ with $Et_3N{:}BH_3$ in refluxing diglyme (52% yield).[1] We had reported some time ago that certain element oxides can be used to insert Se, Te, or As into boron anion or carborane anion structures.[7] Thus, $B_{11}H_{14}^-$ reacted with $NaHSeO_3$ or TeO_2 in heptane/water to form $B_{11}H_{11}Se$ or $B_{11}H_{11}Te$ in moderate yield. In addition, it was found that $Na(B_{10}H_{12}CH)$ reacted with As_2O_3 in 0.03M aqueous KOH/heptane to form $1,2\text{-}B_{10}H_{10}CHAs$ in low yield.

The $B_{11}H_{14}^-$ ion is readily available in good yield by the reaction of $NaBH_4$ with $BF_3{\cdot}O(C_2H_5)_2$ in diglyme at 105 °C.[8] Treatment of $HNEt_3(B_{11}H_{14})$ with As_2O_3 in aqueous KOH formed $B_{11}H_{11}As^-$ in 48% isolated yield.

Metal Arsaborane Derivatives. Having developed reasonable yield syntheses for the key arsaborane compounds $N(CH_3)_4[7\text{-}B_{10}H_{12}As]$ and $1,2\text{-}As_2B_{10}H_{10}$, we have started to explore the chemical capabilities of these materials and report here our initial studies involving some metal-containing derivatives.

$3,1,2\text{-}(dppe)NiAs_2B_9H_9$. Treatment of $1,2\text{-}B_{10}H_{10}As_2$ with excess piperidine removed a boron atom adjacent to both arsenic atoms in the cage to form the piperidinium salt of $7,8\text{-}B_9H_{10}As_2$. The salt was reacted with $(dppe)Ni^{II}Cl_2$ [dppe = 1,2-bis(diphenylphosphino)ethane] in the presence of excess triethylamine at room temperature to give green $3,1,2\text{-}(dppe)NiAs_2B_9H_9$ in 37% yield. The air-stable molecule represents the first known nickel complex of the $7,8\text{-}B_9H_9As_2^{2-}$ ion and has been satisfactorily characterized by elemental analysis, IR data, and its low-resolution mass spectrum, which contains the parent peak at *m/e* 714, corresponding to the $^{12}C_{26}{}^{1}H_{33}{}^{75}As_2{}^{11}B_9{}^{58}Ni^+$ ion.

Its ^{11}B NMR spectrum deserves some comment, as the three resonances (two of them badly overlapped) with a roughly 1:5:3 area are considerably broader and less well resolved than is usually the case for spectra obtained at 70–80 MHz of other closo complexes of the $B_9H_9As_2^-$ or $B_9C_2H_{11}^{2-}$ ions.[6,9] In the present case, the poor resolution probably stems from a peculiarity of the (dppe)Ni moiety itself, which has been associated with ill-defined spectra in other cage complexes as well.[10] The broad spectral lines have been attributed to anisotropic tumbling of the molecules in solution,[11] the consequences of which should then become less marked as the temperature is raised. With *closo*-$(dppe)NiSe_2B_8H_8$, for example, this is in fact the case, and its resonances are nearly completely resolved at 63 °C.[12] Spectra of the disarsaborane complex were negligibly improved up to 74 °C, however, and characterization of the compound has rested on other than NMR data.

$3,6,1,2\text{-}[(C_5H_5)Co]_2As_2B_8H_8$. By prolonging the reaction time during the synthesis of $3,1,2\text{-}(C_5H_5)CoAs_2B_9H_9$ from the mixture of $1,2\text{-}B_{10}H_{10}As_2$, piperidine, $CoCl_2$, and C_5H_6,[6] we obtained a previously unreported side product in low yield, which crystallized as bright red, air-stable plates. Its ^{11}B NMR spectrum consisted of three doublets in a 1:2:1 intensity ratio, and its ^1H NMR spectrum contained only a single peak at δ 5.42, assignable to η^5-C_5H_5 protons. Its low-resolution mass spectrum cut-off at *m/e* 494 corresponded to the $^{12}C_{10}{}^{1}H_{18}{}^{75}As_2{}^{11}B_8{}^{59}Co_2^+$ ion; the high-resolution, mass determination of the ion (*m/e* 493.9262; calcd 493.9249) confirmed the assigned composition. Thus, the compound appears to be an isomer of the previously unknown bimetallodiarsaborane, *closo*-$[(C_5H_5)Co]_2As_2B_8H_8$.

The NMR data alone do not uniquely define the particular isomer under consideration; barring accidental degeneracies, however, the observation of only 3 ^{11}B NMR resonances suggests the presence of a high degree of symmetry in the polyhedral framework, and the singlet in the proton NMR spectrum indicates

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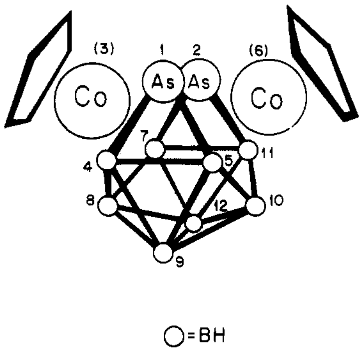

Figure 1. Proposed structure of 3,6,1,2-$[(C_5H_5)Co]_2As_2B_8H_8$.

that the $(C_5H_5)Co$ units lie either on, or on opposite sides of, a mirror plane. Taken together, the spectra eliminate all except six of the 37 possible isomers. If we further assume that no migration of the arsenic atoms has occurred, i.e., that they are still adjacent as in the starting 1,2-$B_{10}H_{10}As_2$, three more configurations can be discarded. Finally, Hawthorne has described an empirical correlation between the structure and electronic spectra of $[(C_5H_5)Co]_2C_2B_nH_{n+2}$ (n = 6–8) complexes, which proposes that those species which do not have absorptions at wavelengths longer than 540 nm (i.e., those visibly red or orange) are not expected to contain a cobalt–cobalt bond; those which do absorb at low frequencies and are visibly green probably contain such a bond.[13] If the relationship holds as well for metallodiarsaboranes, the red color of $[(C_5H_5)Co]_2As_2B_8H_{10}$ suggests that the cobalt atoms in the complex are not, in fact, adjacent; hence, one more isomer can be eliminated. Of the two remaining possibilities (8,10,1,2 and 3,6,1,2; see Figure 1 for the numbering scheme), we prefer the latter, since the ^{11}B NMR resonances are deshielded appropriately (12.7 ppm (average)) from those of the previously assigned metallocarbaborane analogue 3,6,1,2-$[(C_5H_5)Co]_2C_2B_8H_{10}$.[14]

The metalloarsaborane is probably formed analogously to the isoelectronic carbaborane complex, which itself was originally isolated as a low yield (2%) byproduct from the synthesis of 3,1,2-$(C_5H_5)CoC_2B_9H_{11}$.[14] Apparently, a formal BH^{2+} unit is extracted by the excess base from the initially formed $(C_5H_5)CoAs_2B_9H_9$, generating a transient "$(C_5H_5)CoAs_2B_8H_8^{2-}$" species that then incorporates the additional cobalt and cyclopentadienide ion present in the reaction mixture.

Although 3,6,1,2-$[(C_5H_5)Co]_2As_2B_8H_8$ is an icosahedral species, it is the first example of a diarsaborane complex containing less than nine boron atoms; in the context of the metal–ligand analogy, it could be considered a derivative of the *arachno*-$B_8H_8As_2^{4-}$ ion, although the uncomplexed anion is unknown. Its synthesis suggests that lower arsaboranes or their complexes might be accessible under the proper conditions.

1,2-$B_{10}H_{10}AsSn^-$ and 1,2-$B_{10}H_{10}AsPb^-$ Ions. Rudolph and co-workers initially reported the syntheses of 1,2,3-$C_2EB_9H_{11}$ (E = Ge, Sn or Pb) in which the E atoms were believed to be in the +2 oxidation state.[15] Several other similar tin- and lead-containing carborane and metallocarborane compounds have been reported more recently.[16] Such derivatives have served in certain cases as intermediates used to form other desired products. Thus, reaction of 7,9-$B_9C_2H_{11}^{2-}$ and stannous chloride gave a thermally unstable product, which decomposed to form tin, metal, and *closo*-$B_9C_2H_{11}$ in good yield.[17] More recently, it has been found that one of these Sn(II) reagents can be used as a carborane-transfer reagent, which is illustrated in the following equation:[18]

$$Sn(Me_3Si)_2C_2B_4H_4 + {}^1/_3Os_3(CO)_{12} \xrightarrow{150\ ^\circ C} CO + Sn + Os(CO)_3(Me_3Si)_2C_2B_4H_4$$

The $B_{10}H_{12}As^-$ ion was deprotonated with excess n-BuLi and then treated with $SnCl_2$ or $PbCl_2$ to form 1,2-$B_{10}H_{10}AsSn^-$ and 1,2-$B_{10}H_{10}AsPb^-$, respectively. The ^{11}B NMR spectrum of $N(CH_3)_4[1,2\text{-}B_{10}H_{10}AsPb]$ has a 1:2:2:1:2:2 pattern of doublets consistent with the C_s symmetry of this icosahedral anion. The two doublets of area one can be assigned to the two unique boron atoms antipodal to the arsenic and lead atoms in the cage. A similar ^{11}B NMR spectral pattern is found for 1,2-$B_{10}H_{10}AsSn^-$. Two-dimensional ^{11}B–^{11}B NMR experiments will allow specific structural assignments for all the signals in these two ^{11}B NMR spectra. Interesting ortho and antipodal shielding correlations should result, and such a study is planned. Thermal decomposition of solid $N(CH_3)_4[1,2\text{-}B_{10}H_{10}AsPb]$ in an evacuated Pyrex glass tube occurs at 300 °C, giving a very dark residue. This may lead to the formation of *closo*-$B_{10}H_{10}As^-$ and studies of this product are in progress.

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Registry No. $N(CH_3)_4[B_{10}H_{12}As]$, 52668-45-8; AsI_3, 7784-45-4; 1,2-$B_{10}H_{10}As_2$, 51292-90-1; $AsCl_3$, 7784-34-1; 3,1,2-(dppe)$NiAs_2B_9H_9$, 110934-54-8; $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]NiCl_2$, 14647-23-5; 3,6,1,2-$[(C_5H_5)Co]_2As_2B_8H_8$, 110904-90-0; $(CH_3)_4N[1,2\text{-}B_{10}H_{10}AsPb]$, 110934-56-0; $(CH_3)_3NH[B_{10}H_{12}As]$, 110904-92-2; $Li[1,2\text{-}B_{10}H_{10}AsSn]$, 110934-57-1; $HNEt_3(B_{11}H_{11}As)$, 110904-94-4; $HNEt_3[B_{11}H_{14}]$, 12106-44-4; $[C_5H_{12}N]^+[7,8\text{-}B_9H_{10}As_2]^-$, 110904-96-6; As_2O_3, 1327-53-3; decaborane(14), 17702-41-9.

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