As-B, 1.84 mdyn/Å. There appear to have been no other As-B force constants previously reported with which we can compare our value.

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Registry No. $(CH_3)_3As$, 593-88-4; $(CH_3)_3As\cdot BH_3$, 2079-99-4; $(CH_3)_3As\cdot BD_3$, 52003-40-4; $(CH_3)_3As\cdot{}^{11}BH_3$, 52003-41-5; $(CH_3)_3As\cdot{}^{10}BH_3$, 52003-42-6; $(CH_3)_3As\cdot{}^{11}BD_3$, 52003-43-7; $(CH_3)_3As\cdot{}^{10}BD_3$, 52003-44-8.

Contribution No. 3240 from the Department of Chemistry,
University of California, Los Angeles, California 90024

Synthesis of *nido*- and *closo*-Arsacarboranes

HAMPTON D. SMITH, Jr., and M. FREDERICK HAWTHORNE*

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Reaction of $Tl_2 7,8\text{-}C_2B_9H_{11}$ with $RAsX_2$ ($R = CH_3$, $X = Br$; $R = C_6H_5$, $n\text{-}C_4H_9$, $X = Cl$) in diethyl ether solution produced compounds characterized as $3\text{-}R\text{-}3\text{-}As\text{-}1,2\text{-}C_2B_9H_{11}$. Spectral data indicate closo icosahedral structures for these species. Reaction of $3\text{-}C_6H_5\text{-}3\text{-}As\text{-}1,2\text{-}C_2B_9H_{11}$ with BBr_3 afforded $3\text{-}Br\text{-}3\text{-}As\text{-}1,2\text{-}C_2B_9H_{11}$. Reaction of $(CH_3)_2AsBr$ with $Tl_2C_2B_9H_{11}$ in a 2:1 ratio afforded $[(CH_3)_2As]_2C_2B_9H_{11}$. Spectral and chemical data suggest a nido 12-vertex structure for this species with one $(CH_3)_2As$ group terminally bonded to boron.

Introduction

Base degradation of $1,2\text{-}C_2B_{10}H_{12}$ yields the dodecahydro-7,8-dicarba-*nido*-undecaborate(1−) ion[1] which may be subsequently converted to the undecahydro-7,8-dicarba-*nido*-undecaborate(2−) ion, $7,8\text{-}C_2B_9H_{11}^{2-}$.[2] The structure of $7,8\text{-}C_2B_9H_{11}^{2-}$ is that of a nearly regular icosahedron with one vertex missing.[3] A number of reactions of this dianion with various reagents which result in reconstruction of the closed polyhedron have been established over the past few years.[4] However, no such reactions involving group V reagents have been reported, although Todd and coworkers have formally substituted a group V atom for a carbon atom in carborane, obtaining a heteroborane containing ten boron atoms as well as one carbon atom and one arsenic or phosphorus atom.[5]

Our attempts to prepare group V atom heterocarboranes analogous to the $RAlC_2B_9H_{11}$ and $RBC_2B_9H_{11}$ systems, previously prepared and reported by workers from this laboratory,[6,7] have led to the synthesis of two new types of heteroboranes derived from $7,8\text{-}C_2B_9H_{11}^{2-}$ and organoarsenic halides. We report herein the synthesis and characterization of $RAsC_2B_9H_{11}$ ($R = CH_3$, $n\text{-}C_4H_9$, C_6H_5, and Br) and $[R_2As]_2C_2B_9H_{11}$ ($R = CH_3$) species.

Results and Discussion

Synthesis and Characterization of 3-Substituted 3-Arsa-1,2-dicarba-*closo*-dodecaboranes. The general approach to the preparation of group III derivatives of $7,8\text{-}C_2B_9H_{11}^{2-}$ involves proton abstraction from the $7,8\text{-}C_2B_9H_{12}^-$ ion with sodium hydride in tetrahydrofuran (THF) or benzene followed by the addition of the appropriate group III reagent,[6,7] $RAlX_2$ or RBX_2.

$$7,8\text{-}C_2B_9H_{12}^- + NaH \xrightarrow{THF} Na^+\text{-}7,8\text{-}C_2B_9H_{11}^{2-} + H_2 \quad (1)$$

$$Na^+\text{-}7,8\text{-}C_2B_9H_{11}^{2-} + RAlX_2 \xrightarrow{THF} RAlC_2B_9H_{11} + 2X^- \quad (2)$$

Our first attempts to duplicate this sequence for the preparation of arsacarboranes resulted in the formation of yellow solids which we have thus far been unable to characterize. When proton abstraction from the $7,8\text{-}C_2B_9H_{12}^-$ species was carried out by allowing the trimethylammonium salt of $7,8\text{-}C_2B_9H_{12}^-$ to react with *n*-butyllithium in diethyl ether[8] and the resulting solution treated with dibromomethylarsine, a very low yield of a yellow compound identified by mass spectral analysis as the desired $CH_3AsC_2B_9H_{11}$ species was isolated. The yellow gums, which constituted the major reaction product, appeared to be low molecular weight polymers.

$$[(CH_3)_3NH][7,8\text{-}C_2B_9H_{12}] + 2n\text{-}C_4H_9Li \xrightarrow{(C_2H_5)_2O} Li_2[7,8\text{-}C_2B_9H_{11}] + (CH_3)_3N + 2n\text{-}C_4H_{10} \quad (3)$$

$$Li_2[7,8\text{-}C_2B_9H_{11}] + CH_3AsBr_2 \xrightarrow[0°]{(C_2H_5)_2O} CH_3AsC_2B_9H_{11} + \text{yellow polymer} + 2LiBr \quad (4)$$

When the reactions, represented by eq 3 and 4, were carried out in benzene, hexane, toluene, THF, or glyme solutions, none of the desired product was obtained.

During the course of our studies, Spencer, Green, and Stone reported the synthesis of a thallium salt of $7,8\text{-}C_2B_9H_{11}^{2-}$, $Tl_2C_2B_9H_{11}$, which they found to be air and water stable (unlike the alkali metal salts) allowing easy storage and handling.[9] Reaction of $Tl_2C_2B_9H_{11}$ with organodihaloarsines gave the desired 3-alkyl- or 3-aryl-3-arsa-

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(1) R. A. Wiesboeck and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 86, 1642 (1964).

(2) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Amer. Chem. Soc.*, 87, 1818 (1965).

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Table I. Infrared Spectral Data (cm^{-1})[a]

$CH_3AsC_2B_9H_{11}$	3030 m, 2558 vs, 1447 w, 1395 s, 1255 s, 1230 s, 1185 w, 1080 w, 1044 s, 1036 m, 1009 m, 978 s, 939 m, 909 m, 879 s, 855 s, 847 m, sh, 791 s, 775 m, 760 w, 743 w, sh, 730 s, 704 w, 683 w
$CH_3AsC_2B_9H_9(CH_3)_2$	2924 vs, 2564 vs, 1449 s, 1397 m, 1381 s, 1370 s, 1361 m, sh, 1253 w, 1232 s, 1205 w, 1092 w, 1075 m, 1025 s, 996 s, 949 m, 939 m, 909 m, 877 m, 853 s, 803 m, 770 m, 763 s
$C_6H_5AsC_2B_9H_{11}$	3067 m, 2941 vs, 2611 s, 2564 s, 1577 w, 1460 s, 1429 m, 1379 m, 1370 w, sh, 1333 w, 1305 w, 1267 w, sh, 1258 m, 1186 w, 1163 w, 1099 w, 1075 w, 1064 m, 1036 w, 1002 m, 980 m, 971 w, sh, 943 w, 935 w, 917 w, br, 893 w, sh, 889 w, sh, 883 w, 858 w, 849 w, 794 w, 741 s, 709 w, 690 s
n-$C_4H_9AsC_2B_9H_{11}$[b]	3067 m, 2941 s, 2857 s, 2564 s, 1471 s, 1408 m, 1383 m, 1361 w, 1346 w, 1299 w, 1264 s, 1190 m, 1087 m, 1042 m, 1051 m, 980 s, 948 m, 934 w, 913 m, 885 m, 851 s, 794 s, 746 s, 733 s, 699 s
$BrAsC_2B_9H_{11}$	3125 m, 2564 s, 1250 m, 1087 w, 1058 w, 1000 w, 971 m, 939 w, 926 w, 909 w, 889 m, 847 m, 781 m, 727 m, 712 w, 690 w
$[(CH_3)_2As]_2C_2B_9H_{11}$	2857 s, 2500 s, 1449 s, 1399 s, 1370 m, 1250 m, 1176 w, 1087 w, 1020 s, 971 m, 922 s, 909 s, 885 s, 847 s, 823 w, 769 m, 755 m, 722 w
$[(CH_3)_2As]_2C_2B_9H_9(CH_3)_2$[b]	2941 s, 2564 vs, 1453 s, 1418 s, 1389 m, 1372 m, 1282 m, 1266 s, 1250 w, 1205 w, 1093 m, 1064 m, 1026 s, 1010 s, 917 s, 905 s, 881 s, 847 s, 800 m, 769 m, 755 m, 749 m, 738 m, 714 w, 690 w

[a] Spectra recorded as Nujol mulls unless otherwise specified. [b] Liquid smear.

Table II. 80.5-MHz ^{11}B Nmr Spectra

Compd	Solvent	Chem shift[a] (rel intens)
$CH_3AsC_2B_9H_{11}$	CCl_4	−8.6 (1), −3.2 (2), 0.4 (1), 4.8 (2), 14.5[b] (2), 17.0[b] (1)
$CH_3AsC_2B_9H_9(CH_3)_2$	CCl_4	−4.9 (3), 3.7 (1), 11.9 (5)
$C_6H_5AsC_2B_9H_{11}$	CCl_4	−5.7 (1), −3.7 (2), 0.0 (1), 3.6 (2), 14.1[b] (2), 17.1[b] (1)
n-$C_4H_9AsC_2B_9H_{11}$	CCl_4	−6.6 (1), −2.6 (2), 1.1 (1), 5.6 (2), 16.2 (2), 18.3 (1)
$BrAsC_2B_9H_{11}$	CCl_4	−8.8 (1), −2.1 (2), −1.9 (1), 0.0 (2), 12.4 (2), 14.2 (1)
$[(CH_3)_2As]_2C_2B_9H_{11}$	C_6H_6	3.6 (1), 10.0 (1), 12.0 s (1), 15.4 (1), 16.8 (1), 24.0 (2), 27.9 (1), 35.7 (1)
$[(CH_3)_2As]_2C_2B_9H_9(CH_3)_2$	C_6H_6	5.8 (2), 9.0 br, sh (1), 9.3 s (1), 14.2 (1), 18.1 (1), 24.3 (1), 28.5 (1), 33.7 (1)
$(CH_3)_2AsC_2B_9H_{11}(OC_2H_5)$	$(CH_3)_2CO$-C_2H_5OH	9.0 s (1), 16.0 (1), 20.6 (1), 23.9 (2), 30.0 br (2), 39.0 (1), 44.0 (1)

[a] Ppm from $BF_3 \cdot O(C_2H_5)_2 = 0.0$; doublets showed $J_{B-H} = 130 \pm 40$ Hz. Key: s, singlet; br, broad; sh, shoulder. [b] Overlapping doublets.

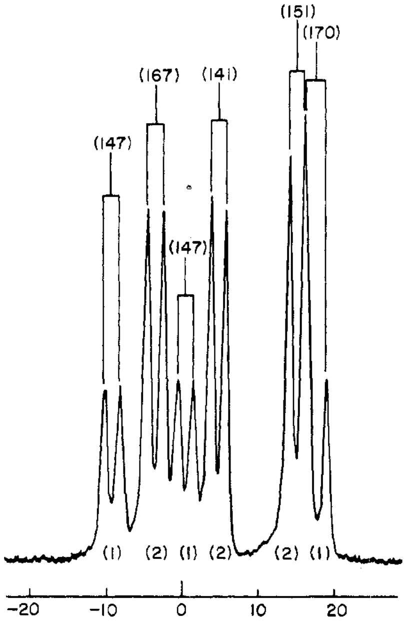

Figure 1. The 80.5-MHz ^{11}B nmr spectrum of $CH_3AsC_2B_9H_{11}$. Scale in ppm relative to $BF_3 \cdot O(C_2H_5)_2 = 0.0$.

1,2-dicarba-*closo*-dodecaborane, $RAsC_2B_9H_{11}$, in up to 30% yield.

Pure 3-CH_3-3-As-1,2-$C_2B_9H_{11}$ was prepared by adding $Tl_2C_2B_9H_{11}$ in small increments to a rapidly stirred solution of CH_3AsBr_2 in diethyl ether at 0°. The product was isolated by removal of the ether solvent by vacuum distillation and subsequent extraction of the residue with hot hexane. The product (mp 77°) crystallized from hexane on cooling.

The mass spectrum consisted of a series of envelopes typical of polyisotopic boranes,[10] with the ion of greatest mass occuring at *m/e* 224, consistent with the $^{75}As^{11}B_9$-$^{12}C_3{}^1H_{14}{}^+$ ion. The 60-MHz ^1H nmr spectrum of CH_3As-$C_2B_9H_{11}$ in carbon tetrachloride solution consisted of a sharp singlet at τ 7.96 (area 3) and a broad singlet at τ 6.39 (area 2). These were assigned respectively to the resonances of the methyl group and the carborane CH protons.

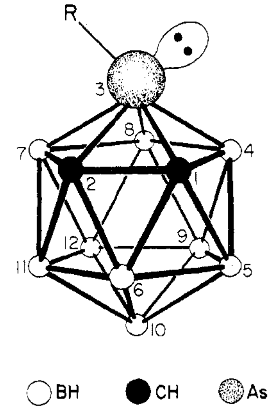

Figure 2. Proposed structure of 3-R-3-As-1,2-$C_2B_9H_{11}$.

The 80.5-MHz ^{11}B nmr spectrum, shown in Figure 1, consisted of three doublets of area 1 and three doublets of area 2. This is consistent with an icosahedral structure in which the arsenic atom occupies position 3, equidistant from and adjacent to the carbon atoms. The accumulated data (Tables I-III) are consistent with our proposed structure, shown in Figure 2. Several other 3-substituted 3-arsa-1,2-carboranes were prepared in a manner similar to that described above for the 3-methyl analog. The relevant data are given in Tables I-III.[11]

When a dilute solution of boron tribromide in carbon tetrachloride was added in small increments to a carbon tetrachloride solution of $C_6H_5AsC_2B_9H_{11}$, the yellow solu-

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(10) R. E. Williams, *Progr. Boron Chem.*, 3, 37 (1970).

(11) Siedle and Todd have recently reported an alternative preparation of $C_6H_5AsC_2B_9H_{11}$ and observed two carborane CH resonances in its ^1H nmr spectrum at −40°: A. R. Siedle and L. J. Todd, *J. Chem. Soc., Chem. Commun.*, 914 (1973). We find that the ^1H nmr spectrum of the methyl analog shows no change to −110° and that the ^{11}B nmr spectra of the methyl and bromo species are unchanged at −40°. Further spectral studies are in progress.

Table III. 60-MHz ^{1}H Nmr Spectra

Compd	Chem shift[a] (rel intens)	Assignment
$CH_3AsC_2B_9H_{11}$	7.96 (3)	CH_3
	6.39 (2)	Carborane CH
$CH_3AsC_2B_9H_9(CH_3)_2$	8.30	Overlapped CH_3's
n-$C_4H_9AsC_2B_9H_{11}$	9.0 (3), 8.3 (4), 7.5 (2)	Butyl group
	6.2 (2)	Carborane CH
$C_6H_5AsC_2B_9H_{11}$	6.3 (2)	Carborane CH
	2.6 (3), 2.3 (2)	Phenyl
$BrAsC_2B_9H_{11}$	6.6	Carborane CH
$[(CH_3)_2As]_2C_2B_9H_{11}$	13.0 (1)[b]	B-H-B Bridge
	9.9 (12)[c]	CH_3's
	8.5 (2)[d]	Carborane CH
$[(CH_3)_2As]_2C_2B_9H_9(CH_3)_2$[b]	12.90 (1)	B-H-B Bridge
	9.19 (3), 9.15 (3), 9.01 (3), 9.00 (3), 8.50 (3), 8.00 (3)	

[a] τ, relative to TMS = 10; deuteriobenzene solvent. [b] 251-MHz data. [c] Resolved into four equal-intensity resonances at 251 MHz. [d] Resolved into two equal-intensity resonances at 251 MHz.

tion gradually became colorless. Subsequent large-scale synthesis, isolation, and mass spectral characterization showed the production of $BrAsC_2B_9H_{11}$.

Prolonged exposure of the pure arsacarboranes to air resulted in extensive decomposition. The 3-bromo-3-arsa-1,2-dicarba-*closo*-dodecaborane species was considerably more stable than the organo-substituted compounds. All of the arsacarboranes reacted rapidly with ethanolic potassium hydroxide quantitatively producing the potassium salt of the 7,8-$C_2B_9H_{12}^-$ ion, which was identified by its characteristic ^{11}B nmr spectrum.[3]

Synthesis and Characterization of Bis(dimethylarsino)-7,8-dicarba-*nido*-undecaborane(13) and Its *C,C'*-Dimethyl Analog. In an attempt to effect the synthesis of $CH_3AsC_2B_9H_{11}$ by a route paralleling the preparation of closo alumina carboranes,[6] bromodimethylarsine was added to a hot benzene solution of the lithio salt of 7,8-$C_2B_9H_{12}^-$. The resulting solution was refluxed for 1 hr and filtered, and the filtrate was evaporated to dryness. In contrast to the aluminum system no methane was evolved when the solid residue was heated *in vacuo* to 100–150°; instead, a white sublimate, identified by its infrared and mass spectra as 7,8-$C_2B_9H_{13}$, was produced. The solid remaining after sublimation exhibited a mass spectral cutoff at m/e 340, corresponding to the $^{75}As_2{}^{11}B_9{}^{12}C_6{}^1H_{23}{}^+$ ion. The overall stoichiometry of the reaction was found to be that shown in eq 5. Identical products were obtained when bromodimethylarsine was treated with $TlC_2B_9H_{12}$ (prepared from $Tl_2C_2B_9H_{11}$ and glacial acetic acid). It was subsequently found that the reaction of $Tl_2C_2B_9H_{11}$ with $(CH_3)_2AsBr$ in a 1:2 ratio afforded $[(CH_3)_2As]_2C_2B_9H_{11}$ as the only major product. This compound, a white waxy solid, mp 128–130°, was obtained in 70% yield.

$$2(CH_3)_2AsBr + 2Li\text{-}7,8\text{-}C_2B_9H_{12} \rightarrow [(CH_3)_2As]_2C_2B_9H_{11} + 7,8\text{-}C_2B_9H_{13} + 2LiBr \quad (5)$$

The 80.5-MHz ^{11}B nmr spectrum of $[(CH_3)_2As]_2C_2B_9H_{11}$, Figure 3, consisted of seven doublets and one singlet and indicated that all of the boron atoms were in unique environments. Substitution of a terminal hydrogen atom by arsenic was suggested by the observation of the singlet, and the breadth of the doublet at *ca.* 28 ppm was indicative of coupling to a bridge hydrogen. The presence of a bridge hydrogen was confirmed by the observation of a broad resonance of relative area 1 at τ 13.0 in the 251-MHz ^{1}H nmr spectrum of $[(CH_3)_2As]_2C_2B_9H_{11}$; two resonances assigned to carborane CH and four methyl resonances were also observed.

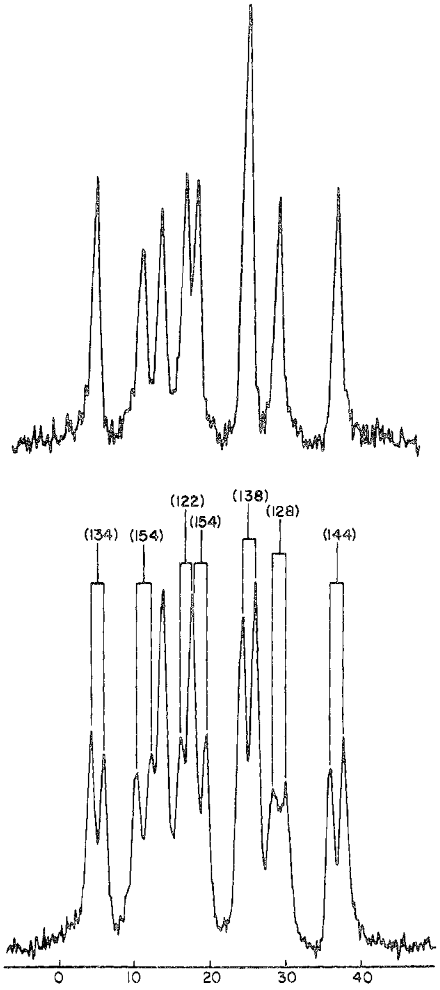

Figure 3. The 80.5-MHz ^{11}B nmr spectrum of $[(CH_3)_2As]_2C_2B_9H_{11}$. The upper spectrum is ^{1}H decoupled. Scale in ppm relative to $BF_3 \cdot O(C_2H_5)_2 = 0.0$.

The *C,C'*-dimethyl analog, $[(CH_3)_2As]_2C_2B_9H_9(CH_3)_2$, was prepared from $Tl_2C_2B_9H_9(CH_3)_2$ and $(CH_3)_2AsBr$ in a similar fashion. The 251-MHz ^{1}H nmr spectrum (Figure 4) showed six equal-area resonances, assigned to six nonequivalent methyl groups, and a bridge hydrogen resonance at τ 12.9. The 80-MHz ^{11}B nmr spectrum was similar to that of the unsubstituted compound. No reaction was observed between $Tl_2C_2B_9H_{11}$ and $(C_6H_5)_2AsCl$; starting materials were recovered after prolonged refluxing in toluene solution.

The unsubstituted and *C,C'*-dimethyl compounds rapidly form boric acid upon exposure to the atmosphere. In the

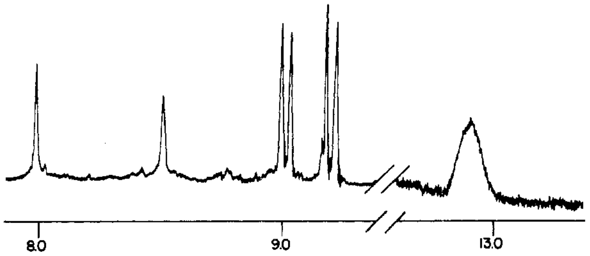

Figure 4. The 251-MHz ^{1}H nmr spectrum of $[(CH_3)_2As]_2C_2B_9H_9(CH_3)_2$ in C_6D_6 solution. Scale in ppm relative to TMS = 10. The bridge hydrogen resonance is not on the same intensity scale of the other resonances.

absence of air an acetone solution of $[(CH_3)_2As]_2C_2B_9H_{11}$ was found to react with ethanolic potassium hydroxide. Removal of solvent, extraction of the solid residue with benzene, and evaporation resulted in a white crystalline solid which exhibited a mass spectral cutoff at *m/e* 284 which corresponds to the $^{75}As^{11}B_9{}^{12}C_6{}^{16}O^1H_{22}{}^+$ ion, in which ethoxide has replaced a $(CH_3)_2As$ group of the starting material. The ^{11}B nmr spectrum of the ethoxy compound showed a gross similarity to that of the starting material, but the singlet resonance was shifted 3 ppm toward lower field. This data are consistent with substitution of a terminally bound $(CH_3)_2As$ group by ethoxide.

Two possible structures consistent with the spectral data are presented in Figure 5. In structure a the cage has been expanded to include the arsenic atom, while structure b has both terminal and bridging dimethylarsino groups. In view of the ready replacement of one but not both of the arsenic functions and of the fact that no $C_2B_9H_{12}{}^-$ was produced by prolonged action of concentrated base, we tend to favor structure a.

Experimental Section

Materials and Apparatus. All operations were conducted under a chemically pure nitrogen atmosphere or in a standard vacuum line. Bromomethylarsines were synthesized using the published procedure.[12] The trimethylammonium salt of $7,8\text{-}C_2B_9H_{12}{}^-$ was prepared as previously described.[1]

All hydrocarbon and ether solvents were purified by distillation from calcium hydride or lithium aluminum hydride. Analytical reagent grade halogenated solvents were used as received unless otherwise specified. Thallium acetate and thallium formate were obtained from Alfa Inorganics. Dichlorophenylarsine, dichloro-*n*-butylarsine, and diiodomethylarsine were obtained from ROC/RIC Chemical Co., Sun Valley, Calif.

Physical Measurements. The 80.5-MHz ^{11}B and 251-MHz ^{1}H nmr spectra were obtained with an instrument designed by Professor F. A. L. Anet of this department. Varian A-60D or T-60 spectrometers were used to record 60-MHz ^{1}H nmr spectra. Infrared spectra were determined using a Perkin-Elmer Model 137 or 257 spectrometer. Mass spectra were obtained with an AEI MS-9 spectrometer. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., or Galbraith Laboratories, Inc., Knoxville, Tenn.

$Tl_2C_2B_9H_{11}$. The trimethylammonium salt of $7,8\text{-}C_2B_9H_{12}{}^-$ (19.5 g, 0.1 mol) was dissolved in a solution of 11.2 g of potassium hydroxide (0.2 mol) in 200 ml of water. An aqueous solution of thallous acetate (52.7 g, 0.2 mol, in 100–150 ml of water) was added dropwise under a nitrogen atmosphere. A yellow precipitate formed immediately. The solid was isolated by filtration, washed successively with water, ethanol, and hexane and dried under vacuum. The product melted with decomposition above 300° (yield 54.0 g; approximately 100%).

$Tl_2C_2B_9H_9(CH_3)_2$. This compound was prepared as described above for $Tl_2C_2B_9H_{11}$, from thallium acetate and $[(CH_3)_3NH]C_2B_9H_9(CH_3)_2$. The product precipitated as a yellow crystalline solid. The yield was quantitative. $Tl_2C_2B_9H_9(CH_3)_2$ melted with decomposition above 200°.

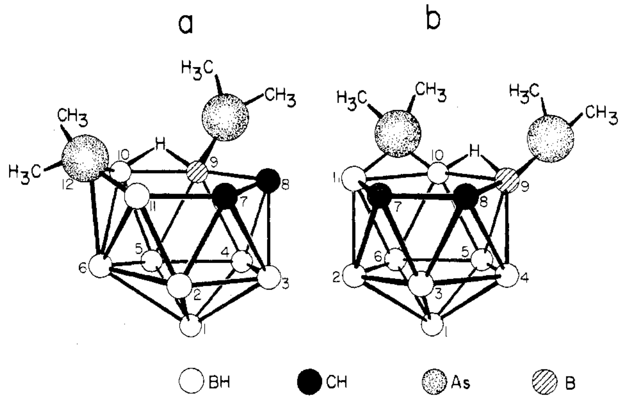

Figure 5. Possible structures of $[(CH_3)_2As)]_2C_2B_9H_{11}$.

$TlC_2B_9H_{12}$. $Tl_2C_2B_9H_{11}$ (5.4 g, 0.01 mol) was dissolved in 100 ml of glacial acetic acid. Benzene (100–150 ml) was added at once. After a few seconds a white crystalline precipitate formed. The crystals were collected by filtration, washed with benzene and hexane, and dried under vacuum at 50°. The product, recrystallized from hot benzene, melted with decomposition at 260°. The yield was quantitative. *Anal.* Calcd for $TlC_2B_9H_{12}$: Tl, 60.51; C, 7.13; H, 3.56; B, 28.75. Found: Tl, 60.44; C, 7.34; H, 3.63, B, 29.23.

3-Arsa-3-methyl-1,2-dicarba-*closo*-dodecaborane(12). Method I. A 1.95-g (0.01-mol) sample of $[(CH_3)_3NH]\text{-}7,8\text{-}C_2B_9H_{12}$ was dissolved in 100 ml of diethyl ether under nitrogen and cooled to 0°. A solution of *n*-butyllithium (1.2 g, 0.022 mol) in hexane (100 ml) was added dropwise with efficient stirring. Evolution of trimethylamine began immediately. The reaction mixture was allowed to stir for 24 hr during which time the ether solvent was removed by evaporation. The resulting white paste was redissolved in dry diethyl ether and cooled to 0°. A solution containing 2.5 g (0.01 mol) of CH_3AsBr_2 in 100 ml of diethyl ether was added to the cold solution resulting in the formation of a yellow solution. Evaporation of the solvent under vacuum yielded a yellow gum. This was extracted several times with hot hexane. On evaporation of the hexane, a yellow crystalline solid was obtained. The product was sublimed at 50° (0.2 mm) followed by recrystallization from hexane. Yellow crystals were obtained (yield 0.2 g, 10%); mp 76–77°. *Anal.* Calcd for $CH_3AsC_2B_9H_{11}$: C, 16.20; H, 6.30; B, 43.80; As, 33.70. Found: C, 16.06; H, 6.43; B, 43.61; As, 33.87.

Method II. A 2.5-g (0.01-mol) sample of CH_3AsBr_2 was dissolved in 100 ml of dry diethyl ether and cooled to 0° under a nitrogen atmosphere. Solid $Tl_2C_2B_9H_{11}$ (5.4 g, 0.01 mol) was added to the cooled, stirred solution from a side arm. The mixture was maintained at 0° for approximately 30 min. At this time, the ether solution was a bright yellow. The mixture was filtered under nitrogen and the filtrate taken to dryness, affording a yellow crystalline product. The product was recrystallized from hexane and dried under vacuum at room temperature; yield 0.7 g, 30%.

3-Arsa-1,2,3-trimethyl-1,2-dicarba-*closo*-dodecaborane(12). $Tl_2C_2B_9H_9(CH_3)_2$ was prepared by treating $[(CH_3)_3NH]C_2B_9H_{10}(CH_3)_2$ in KOH solution with thallium acetate in water. The product was isolated and handled in a manner similar to that described above for $Tl_2C_2B_9H_{11}$. A 2.9-g (5-mmol) sample of $Tl_2C_2B_9H_9(CH_3)_2$ was added to a solution of 1.3 g (5.2 mmol) of CH_3AsBr_2 in 100 ml of diethyl ether at 0°. The work-up of the reaction was identical with that described above for $CH_3AsC_2B_9H_{11}$. The product was obtained as yellow crystals (mp 110°) from hexane solution; yield 0.05 g, 3.5%.

3-Arsa-3-phenyl-1,2-dicarba-*closo*-dodecaborane(12). The addition of 7.5 g (13.2 mmol) of $Tl_2C_2B_9H_{11}$ to a solution of $C_6H_5AsCl_2$ (3.0 g, 13.5 mmol, in 100 ml of diethyl ether), resulted in the formation of a yellow solution and an off-white solid. Filtration followed by evaporation of the filtrate yielded yellow crystals of the desired product, $C_6H_5AsC_2B_9H_{11}$; yield 0.2 g, 5.2%; mp 127–128°. *Anal.* Calcd for $C_8H_{16}B_9As$: C, 33.80; H, 5.63; B, 34.20; As, 26.38. Found: C, 33.55; H, 5.71; B, 34.61; As, 26.18.

3-Arsa-3-bromo-1,2-dicarba-*closo*-dodecaborane(12). A 0.2-g (0.72-mmol) sample of $C_6H_5AsC_2B_9H_{11}$ was dissolved in 10 ml of carbon tetrachloride under a nitrogen blanket and a solution of 0.2 g (0.8 mmol) of BBr_3 in 10 ml of carbon tetrachloride was added dropwise. The resulting solution was allowed to stir for 20 min and the solvent was removed under vacuum. The $C_6H_5BBr_2$ was distilled out of the reaction flask at 50° (1 mm). The residue was extracted

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[12] L. Maier, *Inorg. Syn.*, 7, 82 (1963).

with hot hexane and the extract concentrated until crystals formed; yield 95%; mp 129–130°. The product was identified by mass, ^{11}B nmr, and infrared spectra (Tables I–III).

3-Arsa-3-*n*-butyl-1,2-dicarba-*closo*-dodecaborane(12). The addition of a solution of 2.0 g (10 mmol) of n-$C_4H_9AsCl_2$ in diethyl ether to a suspension of 5.4 g (9 mmol) of $Tl_2C_2B_9H_{11}$ in diethyl ether resulted in the formation of TlCl and a clear, light yellow solution. The solution was concentrated under vacuum and the residue distilled. The major fraction distilled at 120° (0.4 mm) as a heavy clear liquid. The ^1H nmr spectrum (Table III) identified the product as n-$C_4H_9AsC_2B_9H_{11}$. The mass, ^{11}B nmr, and infrared spectra (Tables I–III) confirmed its identity; yield ~1.0 g (38%).

Bis(dimethylarsino)-7,8-dicarba-*nido*-undecaborane(13). Method I. A 1.0-g (3-mmol) sample of $TlC_2B_9H_{12}$ was suspended in 100 ml of benzene under a nitrogen blanket at 0° and a solution of 0.54 g (2.9 mmol) of $(CH_3)_2AsBr$ in 20 ml of benzene was added at a moderate rate. The reaction mixture was allowed to warm to room temperature over a 12-hr period. The mixture was filtered and the filtrate was concentrated, yielding a yellow oil. The oily product was next heated to 70° under vacuum in a sublimator; a white solid sublimed out of the reaction flask and was identified by its mass, ^{11}B nmr, and infrared spectra as 7,8-$C_2B_9H_{13}$. The residue was identified by its mass spectrum as $[(CH_3)_2As]_2C_2B_9H_{11}$.

Method II. A 5.0-g (0.01-mol) sample of $Tl_2C_2B_9H_{11}$ was weighed into a 250-ml boiling flask and 100 ml of dry benzene was added. The system was purged with nitrogen and a solution of $(CH_3)_2AsBr$ (3.4 g, 0.02 mol) in 50 ml of benzene was added dropwise over a 10-min period. The mixture was allowed to stir for 1 hr after which it was filtered to remove the TlBr, and the filtrate was concentrated to approximately 50 ml. Dry hexane was added slowly to the hot concentrate until cloudiness appeared. On cooling to room temperature a yellow semisolid formed. The mixture was filtered and the semisolid residue was washed with hexane and dried at 50° under vacuum. The resulting off-white waxy solid was sublimed at 150° (0.1 mm) to a −80° cold finger. The product was obtained as a white sublimate, mp 128–130°; yield 2.3 g, 70%. *Anal.* Calcd for $[(CH_3)_2As]_2C_2B_9H_{11}$: C, 21.05; H, 6.77; B, 28.42; As, 43.76. Found: C, 21.23; H, 7.04; B, 28.01; As, 44.11.

Bis(dimethylarsino)-7,8-dimethyl-7,8-dicarba-*nido*-undecaborane(13). A 3.0-g (5.3-mmol) sample of $Tl_2C_2B_9H_9(CH_3)_2$ prepared from thallium acetate and $[(CH_3)_3NH]C_2B_9H_{10}(CH_3)_2$ was placed in a 250-ml boiling flask under a dry nitrogen atmosphere. Benzene (100 ml) was added and the mixture was stirred while a solution of 1.9 g (10.2 mmol) of $(CH_3)_2AsBr$ in 20 ml of benzene was added dropwise over a 10-min period. The reaction was instantaneous as evidenced by the change in color of the solid phase from yellow to white. The mixture was filtered under nitrogen and the filtrate was concentrated to 75 ml. Dry hexane was added until cloudiness occurred. The mixture was then cooled to 0° and a yellow solid precipitated. The mixture was filtered and the filter cake was washed with hexane and dried under vacuum. The product was identified as $[(CH_3)_2As]_2C_2B_9H_9(CH_3)_2$ by its mass, nmr, and infrared spectra (Tables I–III). Attempts to obtain an analytically pure sample *via* sublimation or recrystallization from benzene–hexane were unsuccessful. The melting range was 60–90°. The yield of crude product was quantitative.

Reaction of $[(CH_3)_2As]_2C_2B_9H_{11}$ with Ethanolic Potassium Hydroxide. A 0.5-g sample of $[(CH_3)_2As]_2C_2B_9H_{11}$ was dissolved in approximately 15 ml of an ethanol solution containing 20 g of potassium hydroxide /300 ml of ethanol. The solution was refluxed for 30–60 min. After cooling of the mixture to room temperature the solvent was removed under vacuum and the solid residue was extracted with benzene. Evaporation of the benzene yielded approximately 0.3 g (72%) of a white crystalline solid. This product has not been completely characterized. However, mass spectral and ^{11}B nmr data are consistent with the proposed substitution of a terminally bound $(CH_3)_2As$ group by ethoxide.

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Registry No. $[(CH_3)_3NH]$-7,8-$C_2B_9H_{12}$, 12305-36-1; CH_3AsBr_2, 676-70-0; $CH_3AsC_2B_9H_{11}$, 52175-48-1; $Tl_2C_2B_9H_{11}$, 41721-58-8; $Tl_2C_2B_9H_9(CH_3)_2$, 41721-60-2; $CH_3AsC_2B_9H_9(CH_3)_2$, 52175-47-0; $C_6H_5AsCl_2$, 696-28-6; $C_6H_5AsC_2B_9H_{11}$, 52175-49-2; BBr_3, 10294-33-4; $BrAsC_2B_9H_{11}$, 52175-50-5; n-$C_4H_9AsCl_2$, 692-23-9; n-$C_4H_9AsC_2B_9H_{11}$, 52175-51-6; $TlC_2B_9H_{12}$, 52216-81-6; $(CH_3)_2AsBr$, 676-71-1; ^{11}B, 14798-13-1.

Contribution from the Department of Chemistry,
Tufts University, Medford, Massachusetts 02155

Nitrile Addition to Polyhedral Boranes in the Presence of Iron(III) Chloride

ANDREA H. NORMAN[1] and A. KACZMARCZYK*

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The reactions of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ with $FeCl_3$ in the presence of nitriles were investigated. In addition to $B_{20}H_{18}^{2-}$, $B_{24}H_{23}^{3-}$, $B_{12}H_{11}Cl^{2-}$, $B_{24}H_{22}Cl^{3-}$, and $B_{12}H_{11}NH_3^-$, nitrile adducts were produced in reactions with acetonitrile, ethyl cyanoacetate, malononitrile, and cyanomethyl benzenesulfonate. The adducts were recovered in the partially hydrolyzed form $B_nH_{n-a}(NH_2COR)_a^{a-2}$, where $a = 1$ or 2, and R = CH_3, $CH_2COOC_2H_5$, CH_2CONH_2, or $CH_2OSO_2C_6H_5$.

Introduction

Acetonitrile has been used as a solvent in numerous reactions of polyhedral boranes, but at elevated temperatures and under strongly acidic conditions it can also act as a reactant by displacing hydrogen from the boron cage. Monosubstituted derivatives of $B_{10}H_{10}^{2-}$ have been obtained from acid-catalyzed reactions with acetonitrile and benzonitrile.[2] The acetonitrile derivative of $B_{12}H_{12}^{2-}$ has been prepared in a similar fashion.[3] Whether a second nitrile can be attached to the cage under such conditions has not been reported. A disubstituted derivative, $B_{10}H_8(NCCH_3)_2$, has been made by heating 1,10-$B_{10}H_8(N_2)_2$ in the presence of CH_3CN at 150°.[4]

Since a number of polyhedral boranes having functional groups separated from the cage by several bonds exhibit biological activity,[5] we decided to look for reactions leading to more such compounds. The large number of commercially available substituted nitriles suggested that nitrile addition might lead to such products in a one-step reaction if the other functional group can be protected from loss, decomposition, or direct attachment to the cage. At elevated temperatures and in the presence of protonic acids most functional groups of biological interest, particularly those

[1] National Defense Education Act Fellow, 1969–1972.

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