tempts to solve the structure of B_6H_{12} have been unsuccessful,[24] the ^{11}B and ^1H spectra of B_6H_{12} are in agreement with the structure previously proposed by Gaines and Schaeffer.[6] The 70.6-MHz ^{11}B spectrum (Figure 6) is clearly resolved into a doublet, triplet, and doublet of intensity 2:2:2. The low-field doublet exhibits secondary coupling which probably arises from bridge proton coupling. The pmr spectrum (Figure 7) exhibits the expected axial and equatorial resonances from the $-BH_2$ groups.

As with B_4H_{10} and B_5H_{11}, the low-field quartet has the smaller coupling constant. Although the bridge resonance is not resolved into two separate resonances as would be expected, its structure indicates that it is not arising from only one type of bridge position.

Chemical shift and coupling constant data for B_6H_{12} are presented in Table IV.

Acknowledgments.—The authors at CSCLA and Indiana University gratefully note the support of the National Science Foundation (Grants GP-17704 and GP-4944, respectively).

[24] W. N. Lipscomb, private communication. B_6H_{12} forms a glass at low temperatures and cannot be shocked into the crystalline state.

CONTRIBUTION NO. 1859 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, INDIANA 47401,
AND THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Monocarbon Carboranes. IV.[1] Polyhedral Arsa- and Stibacarbadodecaborane(11) Derivatives and Related 11-Atom Cage Fragments

BY LEE J. TODD,[2] AARON R. BURKE,[3] ALBERT R. GARBER,
HOWARD T. SILVERSTEIN,[4] AND BRUCE N. STORHOFF

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The syntheses of 1,2-, 1,7-, and 1,12-$B_{10}H_{10}CHAs$ as well as 1,2- and 1,7-$B_{10}H_{10}CHSb$ are discussed. The conversions of the appropriate icosahedral derivative to 7,8- or 7,9-$B_9H_{10}CHAs^-$, 7,9-$B_9H_{10}CHAsCH_3$, or 7,8-$B_9H_{10}CHSb^-$ are described. The synthesis and X-ray diffraction study of $(C_5H_5)Co(1,2\text{-}B_9H_9CHAs)$ confirm the relative position of the carbon and arsenic atoms in the 1,2-arsacarboranes and show the distorted nature of these derivatives. Dipole moment and nmr data are presented which aid in elucidating the role of the group V atom in these molecules.

Results and Discussion

Icosahedral Arsa- and Stibacarboranes.—Initial attempts to insert an arsenic or antimony atom into the carbollide ion using the experimental procedure developed for 1,2-$B_{10}H_{10}CHP$[1a] were unsuccessful. Reaction of arsenic trichloride with $Na_3B_{10}H_{10}CH(THF)_2$ in tetrahydrofuran (THF) at room temperature produced a 25% yield of sublimable 1,2-$B_{10}H_{10}CHAs$ which has an odor reminiscent of the phosphacarboranes.[1b] Although antimony trichloride reacted in a very exothermic manner with the $B_{10}H_{10}CH^{3-}$ ion, no 1,2-$B_{10}H_{10}CHSb$ could be isolated. When antimony triiodide was used as the source of antimony and the reaction was run at ice bath temperature, 1,2-$B_{10}H_{10}CHSb$ was obtained in 41% yield by the reaction

$$Na_3B_{10}H_{10}CH(THF)_2 + SbI_3 \xrightarrow[4°]{THF} 1,2\text{-}B_{10}H_{10}CHSb + 3NaI$$

The composition of these heteroatom carboranes was determined by their elemental analyses (Table I). Further confirmation of these molecular formulas was obtained by mass spectral measurement of the parent ion peaks: calcd for $^{11}B_{10}{}^1H_{11}{}^{12}C^{75}As$, 208.1017; found, 208.1010; calcd for $^{11}B_{10}{}^1H_{11}{}^{12}C^{123}Sb$, 256.0833; found, 256.0837.

Thermal isomerization of 1,2-$B_{10}H_{10}CHAs$ in a sealed tube at 495° for 22 hr produced 1,7-$B_{10}H_{10}CHAs$ in moderate yield. Elemental analysis (Table I) and

TABLE I
ELEMENTAL ANALYSES FOR ARSA- AND STIBACARBORANE DERIVATIVES

Compound	Analyses
1,2-$B_{10}H_{10}CHAs$	Calcd: C, 5.83; H, 5.38
	Found: C, 5.78; H, 5.18
1,7-$B_{10}H_{10}CHAs$	Calcd: C, 5.83; H, 5.38
	Found: C, 5.82; H, 5.27
$(CH_3)_4N[7,8\text{-}B_9H_{10}CHAs]$	Calcd: C, 22.30; H, 8.56; N, 5.20
	Found: C, 22.09; H, 8.60; N, 4.91
$(CH_3)_4N[7,9\text{-}B_9H_{10}CHAs]$	Calcd: C, 22.30; H, 8.56; N, 5.20
	Found: C, 21.95; H, 8.49; N, 5.33
7,9-$B_9H_{10}CHAsCH_3$	Calcd: C, 11.41; H, 6.70
	Found: C, 11.51; H, 6.66
1,2-$B_{10}H_{10}CHSb$	Calcd: B, 42.73; Sb, 48.10
	Found: B, 42.02; Sb, 48.14
1,7-$B_{10}H_{10}CHSb$	Calcd: C, 4.74; H, 4.38; B, 42.73; Sb, 48.10
	Found: C, 5.18; H, 4.28; B, 42.83; Sb, 47.98
$(CH_3)_4N[7,8\text{-}B_9H_{10}CHSb]$	Calcd: C, 18.95; H, 7.32; N, 4.43
	Found: C, 18.50; H, 7.52; N, 4.13

[1] (a) For the previous paper in this series, see L. J. Todd, J. L. Little' and H. T. Silverstein, *Inorg. Chem.*, **8**, 1698 (1969); (b) for the preliminary communication of this work, see L. J. Todd, A. R. Burke, H. T. Silverstein, J. L. Little, and G. S. Wikholm, *J. Amer. Chem. Soc.*, **91**, 3376 (1969).

[2] Correspondence should be addressed to this author at the Department of Chemistry, Indiana University, Bloomington, Ind. 47401.

[3] National Institutes of Health Fellow, 1967–1969.

[4] National Aeronautics and Space Administration Trainee, 1968–1969.

measurement of the parent ion peak at *m/e* 208.1006 (calcd for $^{11}B_{10}{}^{1}H_{11}{}^{12}C^{75}As$, 208.1017) confirmed the composition of this new isomer. The thermal stability of 1,2-$B_{10}H_{10}CHSb$ is lower than the corresponding phosphorus and arsenic compounds. Isomerization of 1,2-$B_{10}H_{10}CHSb$ at 450° for 13 hr in a sealed tube gave mainly black decomposition products and a 20% yield of nearly pure 1,7-$B_{10}H_{10}CHSb$. Elemental analysis (Table I) and measurement of the parent ion peak at *m/e* 256.0841 (calcd for $^{11}B_{10}{}^{1}H_{11}{}^{12}C^{123}Sb$, 256.0833) determined the molecular formula for this new isomer.

Heating 1,2-$B_{10}H_{10}CHAs$ at 575° for 13 hr in a sealed tube produced a 1:1 mixture of 1,7- and 1,12-$B_{10}H_{10}$-CHAs in moderate yield. The 1,7 isomer was removed from the mixture by selective degradation with piperidine at reflux which converts this isomer to an ionic product (*vide infra*). Mass spectral measurement of the parent ion peak at *m/e* 208.1012 (calcd for $^{11}B_{10}{}^{1}H_{11}$-$^{12}C^{75}As$, 208.1017) confirmed the composition of the 1,12 isomer. The relative gas chromatographic retention times of 1,2-, 1,7-, and 1,12-$B_{10}H_{10}C_2H_2$ and the corresponding phospha- and arsacarboranes are very similar. The retention times increase in the order 1,12, 1,7, and 1,2 isomer, paralleling the increase in polarity of these isomers. Isomerization of 1,2-$B_{10}H_{10}CHSb$ at 500° for 10 hr in a sealed tube gave a very small amount of sublimable product. Gas chromatographic analysis of the product indicated the presence of 1,7-$B_{10}H_{10}CHSb$ and another component with the short retention time expected for 1,12-$B_{10}H_{10}CHSb$. Attempts to increase the amount of 1,12 isomer in the pyrolysate were unsuccessful.

A 1:1 mixture of 1,2-$B_{10}H_{10}C_2H_2$ and 1,2-$B_{10}H_{10}CHP$ was isomerized in a Carius tube at 475° for 4 hr. Gas chromatographic analysis of the products indicated a 91:9 ratio of 1,2- and 1,7-$B_{10}H_{10}C_2H_2$, respectively, and a 5:95 ratio of 1,2- and 1,7-$B_{10}H_{10}CHP$, respectively. It was also determined by the same type of experiment that 1,2-$B_{10}H_{10}CHAs$ isomerized to its 1,7 isomer more easily than 1,2-$B_{10}H_{10}C_2H_2$ does.

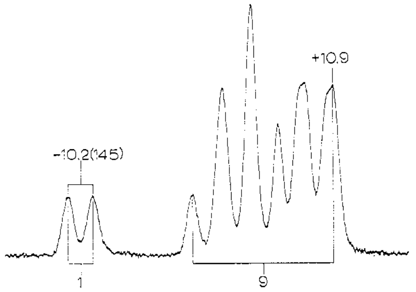

Figure 1.—The 70.6-MHz ^{11}B nmr spectrum of 1,2-$B_{10}H_{10}$-CHAs in acetone solution. Chemical shifts in ppm relative to $BF_3 \cdot (C_2H_5)_2O$ and coupling constants (cps) are indicated.

Boron (^{11}B) and Proton Nmr Data for the Icosahedral Derivatives.—The 70.6-MHz boron spectrum of 1,2-$B_{10}H_{10}CHAs$ (Figure 1) is consistent with a 1:1:2:2:2:2 pattern of doublets expected for this molecule. Two doublets of area 1 are found at lowest field. These signals are due to the two unique boron atoms located on the mirror plane, on the opposite side of the molecule from the heteroatoms. The signals of the two unique boron atoms of all the other 1,2- and 1,7-$B_{10}H_{10}CHE$ (E = P, As, and Sb) derivatives are also found at lowest field. It should be noted that the signal of the analogous boron atoms of 1,2-$B_{10}H_{10}C_2H_2$, B(9,12), was also found at lowest field.[5] The boron nmr spectrum of 1,2-$B_{10}H_{10}CHSb$ (Figure 2) is even easier to separate into a 1:1:2:2:2:2 pattern than that of the arsenic analog.

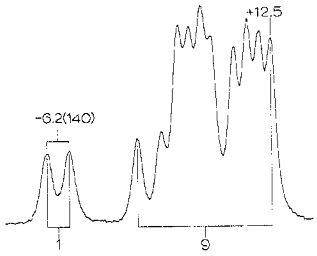

Figure 2.—The 70.6-MHz ^{11}B nmr spectrum of 1,2-$B_{10}H_{10}CHSb$ in acetone solution referenced to $BF_3 \cdot (C_2H_5)_2O$.

In Figure 3 is given the boron nmr spectrum of 1,7-$B_{10}H_{10}CHAs$. The finding that the signals of the unique boron atoms of the arsenic derivative are at lowest field lends support to the earlier suggestion of Beall and Lipscomb[6] that the nmr resonance of B(5,12) of 1,7-$B_{10}H_{10}C_2H_2$ is also at lowest field. The boron nmr spectrum of 1,12-$B_{10}H_{10}CHAs$ at 32 MHz consists of two overlapping doublets of equal area at +6.7 ppm (J = 151 Hz) and +10.4 ppm (J = 168 Hz).

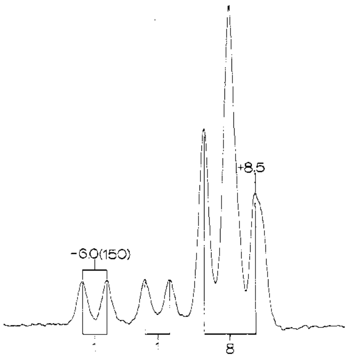

Figure 3.—The 70.6-MHz ^{11}B nmr spectrum of 1,7-$B_{10}H_{10}CHAs$ in acetone solution referenced to $BF_3 \cdot (C_2H_5)_2O$.

The only feature of the 100-MHz proton nmr spectra of the $B_{10}H_{10}CHE$ derivatives which can be easily interpreted is the broad carborane CH signal (see Table II for chemical shift values). This resonance is very solvent dependent as evidenced by the change in the chemical shift values of 1,2-, 1,7-, and 1,12-$B_{10}H_{10}$-C_2H_2 in benzene and chloroform. The chemical shift values in benzene are not concentration dependent. The CH resonance moves to lower field in 1,2-, 1,7-, and 1,12-$B_{10}H_{10}CHE$ isomers, respectively. This suggests

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[5] J. A. Potenza, W. N. Lipscomb, G. D. Vickers, and H. Schroeder, *J. Amer. Chem. Soc.*, **88**, 5340 (1966).

[6] H. Beall and W. N. Lipscomb, *Inorg. Chem.*, **6**, 874 (1967).

that the group V atom has a stronger attraction for the available electron density than the carbon atom and that this feature becomes more evident as the heteroatoms are farther apart in the cage.

TABLE II

CHEMICAL SHIFT DATA FOR THE CARBORANE C–H PROTONS OF VARIOUS ICOSAHEDRAL DERIVATIVES

Compound	Solvent	Chemical shift, ppm
1,2-$B_{10}H_{10}C_2H_2$	C_6H_6	7.9 ± 0.1
1,7-$B_{10}H_{10}C_2H_2$	C_6H_6	7.9 ± 0.1
1,12-$B_{10}H_{10}C_2H_2$	C_6H_6	8.0 ± 0.1
1,2-$B_{10}H_{10}C_2H_2$	$CDCl_3$	6.51 ± 0.01
		6.46[a]
1,7-$B_{10}H_{10}C_2H_2$	$CDCl_3$	7.05 ± 0.01
1,12-$B_{10}H_{10}C_2H_2$	$CDCl_3$	7.28 ± 0.01
1,2-$B_{10}H_{10}CHP$	C_6H_6	7.96 ± 0.01
1,7-$B_{10}H_{10}CHP$	C_6H_6	7.56 ± 0.04
1,12-$B_{10}H_{10}CHP$	C_6H_6	7.30
1,2-$B_{10}H_{10}CHAs$	C_6H_6	7.92 ± 0.03
1,7-$B_{10}H_{10}CHAs$	C_6H_6	7.38 ± 0.02
1,12-$B_{10}H_{10}CHAs$	C_6H_6	6.76 ± 0.03
1,2-$B_{10}H_{10}CHSb$	C_6H_6	7.50
1,7-$B_{10}H_{10}CHSb$	C_6H_6	6.88

[a] M. F. Hawthorne, T. D. Andrews, P. M. Garrett, F. P. Olsen, M. Reintjes, F. N. Tebbe, L. F. Warren, P. A. Wegner, and D. C. Young, *Inorg. Syn.*, **10**, 100 (1967).

11-Atom *nido*-Arsa- and -Stibacarboranes.—Reaction of 1,2- or 1,7-$B_{10}H_{10}CHAs$ in piperidine solution at reflux produced 7,8- and 7,9-$B_9H_{10}CHAs^-$, respectively, in good yields.[7] Treatment of 1,2-$B_{10}H_{10}CHSb$ with neat piperidine at reflux produced mainly $B_{10}H_{12}CH^-$ which was identified by comparison of its infrared and ^{11}B nmr spectra with those of an authentic sample.[8] In this case base attack removes the antimony atom from the cage. Reaction of 1,2-$B_{10}H_{10}CHSb$ with piperidine in a 1:4 mole ratio, respectively, in a dilute solution of benzene at reflux produced the 7,8-$B_9H_{10}CHSb^-$ ion in good yield.

Deprotonation of a mixture of 7,8-$B_9H_{10}CHAs^-$ and cyclopentadiene with triethylamine in tetrahydrofuran solution followed by reaction with cobalt(II) chloride gave a low yield of $(C_5H_5)Co(1,2\text{-}B_9H_9CHAs)$. A variety of other arsacarborane complexes of manganese, iron, and cobalt have been prepared.[9] An X-ray diffraction study[10] of this complex has given the structure illustrated in Figure 4. It can be assumed that the carbon and arsenic atoms have not rearranged during the mild reaction required to convert 1,2-$B_{10}H_{10}CHAs$ to the cobalt complex. Thus the structure determination confirms that the carbon and arsenic atoms are nearest neighbors in 1,2-$B_{10}H_{10}CHAs$, 7,8-$B_9H_{10}CHAs^-$, and the cobalt complex.

The 70.6-MHz boron spectrum of Cs[7,8-$B_9H_{10}CHAs$] is given in Figure 5. If the structure of the anion is that of an 11-atom icosahedral fragment, all nine boron atoms would be nonequivalent. Seven of the nine expected boron doublet signals are observed.

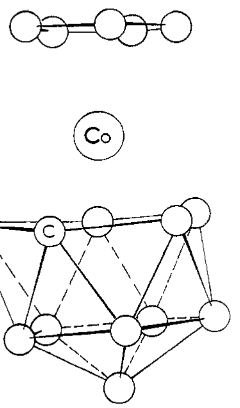

Figure 4.—Schematic drawing of the structure of $(C_5H_5)Co(1,2\text{-}B_9H_9CHAs)$.

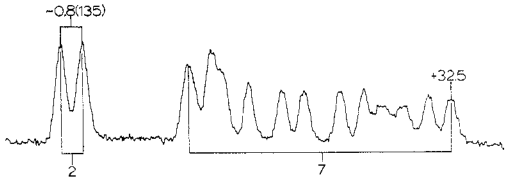

Figure 5.—The 70.6-MHz ^{11}B nmr spectrum of Cs[7,8-$B_9H_{10}CHAs$] in acetone solution referenced to $BF_3\cdot(C_2H_5)_2O$.

Treatment of 7,9-$B_9H_{10}CHAs^-$ with iodomethane produced a good yield of 7,9-$B_9H_{10}CHAsCH_3$. The methyl group is probably attached to the arsenic atom as has been demonstrated for the phosphorus analog.[1a] Methylation of 7,8-$B_9H_{10}CHAs^-$ gave a mixture of volatile products which were difficult to separate. Attempted methylation of 7,8-$B_9H_{10}CHSb^-$ under the conditions used with the phosphorus[1a] and arsenic derivatives gave no observable reaction.

Dipole Moment Measurements.—The dipole moments of several of the icosahedral derivatives measured in benzene solution are given in Table III. It was observed that a methylene chloride solution of 1,2-$B_{10}H_{10}CHSb$ turned yellow upon addition of N,N-dimethylaniline. Although the adduct could not be isolated, an acid–base charge-transfer interaction most likely occurred with the stibacarborane. To a lesser extent, this type of interaction probably also occurs in benzene causing the dipole moments to be unusually large. The dipole moment of $(1,2\text{-}B_9H_9C_2H_2)_2Ni$ was also reported to be larger in benzene than in cyclohexane for the same reason.[11]

TABLE III

DIPOLE MOMENT VALUES OF SOME ICOSAHEDRAL DERIVATIVES MEASURED IN BENZENE SOLUTION

Compound	Dipole moment, D
1,2-$B_{10}H_{10}C_2H_2$	4.25
	4.53
1,2-$B_{10}H_{10}CHP$	8.25
1,7-$B_{10}H_{10}CHP$	3.76
1,2-$B_{10}H_{10}CHAs$	9.53
1,2-$B_{10}H_{10}CHSb$	13.41

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[7] The numbering system employed for these *nido*-carboranes follows the new nomenclature rules which recently appeared: *Inorg. Chem.*, **7**, 1945 (1968).

[8] D. E. Hyatt, F. R. Scholer, L. J. Todd, and J. L. Warner, *ibid.*, **6**, 2229 (1967).

[9] L. J. Todd and A. R. Burke, to be submitted for publication.

[10] The authors wish to thank Professor William E. Streib and Mr. Charles Boss for these structural results received prior to publication.

[11] L F. Warren, Jr., and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **92**, 1157 (1970).

Previous work has shown that the positive end of the cage dipole is located at the carbon atoms in 1,2-$B_{10}H_{10}C_2H_2$.[12] It is likely that the carborane derivatives containing group V elements have similar dipole directions. The observation that 1,2-$B_{10}H_{10}CHE$ (E = P, As, or Sb) is attacked by nucleophilic reagents either at the group V atom or at one of the boron atoms adjacent to both heteroatoms supports this view. In fact the boron atom removal reaction is more facile with the 1,2-$B_{10}H_{10}CHE$ derivatives than it is with 1,2-$B_{10}H_{10}C_2H_2$. The increase in the dipole moment of the $B_{10}H_{10}CHE$ derivatives relative to the corresponding $B_{10}H_{10}C_2H_2$ isomer can be partly explained by the increased distortion of the icosahedral framework caused by the large group V atom. In addition the 1,2 isomers have the atoms with the larger nuclear charges concentrated on one side of the cage. Probably the available bonding electrons are not able to compensate for the positive nuclear charge imbalance in the cage structure.

Experimental Section

Apparatus and Materials.—The infrared spectra for which a solvent is not indicated have been recorded as KBr disks. All infrared spectra were measured on a Perkin-Elmer 521 or 621 instrument. Intensities of absorptions are reported as strong (s), medium (m), or weak (w). Mass spectra were obtained with an AEI MS-9 instrument. Boron (^{11}B) nmr spectra at 70.6 MHz were obtained with a Varian HR-220 spectrometer equipped with an experimental probe built by Mr. A. O. Clouse of the department. The spectra were obtained by a digitized linear sweep of the main radiofrequency carrier developed by a Hewlett-Packard 5100 B frequency synthesizer. The receiver local oscillator was replaced with a coherent phase locked difference frequency which was always precisely 5 MHz removed from the detection frequency. This gives a capability of greater than 20-kHz linear receiver gain. Spectral integrals were measured with a planimeter. Boron chemical shift data were measured relative to external $BF_3 \cdot (C_2H_5)_2O$. Proton nmr spectra were obtained with a Varian HA-100 spectrometer.

Elemental analyses (C, H, N, and Sb) were obtained from the University of Illinois Microanalytical Laboratory. Boron analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

The dielectric constants of dilute benzene solutions of the icosahedral derivatives were determined by use of the capacity bridge method, with a General Electronics 1650A impedance bridge. The cell was a 50-mm air condenser. The indices of refraction were obtained with a Bausch and Lomb Abbé-56 refractometer. The dipole moments were calculated by use of a modification of the Guggenheim method.[12] The equation used to calculate the dipole moments is

$$\mu^2 = 1.47 \times 10^{-1}\left[\frac{1}{d_1(\epsilon_1 + 2)}\right](a_\epsilon - a_n)M_2$$

where a_ϵ and a_n are the slopes of the equations

$$\epsilon_{12} = a_\epsilon(w_2) + \epsilon_1$$

$$n_{12}^2 = a_n(w_2) + n_1^2$$

The various terms in the above equations are defined as follows: ϵ_{12} is the dielectric constant of the solutions, n_{12} is the refractive index of the solutions, w_2 is the weight fraction of solute, and ϵ_1 is the dielectric constant of the solvent obtained by extrapolation of the appropriate equation to $w_2 = 0$. The measurements were conducted in the range of w_2 from 0.0100 to 0.002. All measurements were conducted at 25°. There are possible errors in the dipole moment values of up to 10% inherent in the method of calculation. As a check of the procedure, the dipole moment of 1,2-$B_{10}H_{10}C_2H_2$ was redetermined and found in close agreement with the literature value[13] (see Table III).

1,2-$B_{10}H_{10}$CHAs.—A sample of the $B_{10}H_{10}CH^{3-}$ ion was prepared *in situ* from 55 g (0.288 mol) of $B_{10}H_{12}CN(CH_3)_3$ by the previously described procedure. A solution of 25 ml (0.3 mol) of freshly distilled arsenic trichloride in 200 ml of tetrahydrofuran was slowly added to the stirred reaction mixture at room temperature. Stirring was continued for 4 hr after addition of the arsenic compound. The solvent was removed by rotary evaporation at reduced pressure and the brown residue was extracted overnight in a Soxhlet apparatus with high-boiling petroleum ether. Evaporation of the petroleum ether extract and sublimation of the residues at 130° (0.01 mm) gave 15 g (25% yield) of white 1,2-$B_{10}H_{10}$CHAs, mp 399–399.5°. The infrared spectrum (in CS_2 solution) contained absorptions at λ_{max} 3046 (w), 2580 (s), 1116 (w), 1048 (m), 993 (m), 933 (w), 735 (m), and 661 cm^{-1} (w).

1,7-$B_{10}H_{10}$CHAs.—A 1.08-g sample of 1,2-$B_{10}H_{10}$CHAs was sealed in an evacuated Carius tube and maintained at 495° for 22 hr. The pyrolysate was sublimed at 60° (0.01 mm) to give a 65% yield by weight of sublimate, mp 351–352°. Gas chromatographic analysis indicated the product was a 99:1 mixture of 1,7- and 1,2-$B_{10}H_{10}$CHAs, respectively. The infrared spectrum (CS_2 solution) showed absorptions at λ_{max} 3047 (w), 2580 (s), 1134 (w), 1059 (w), 993 (m), and 735 cm^{-1} (m).

1,12-$B_{10}H_{10}$CHAs.—A 2-g sample of 1,2-$B_{10}H_{10}$CHAs was sealed in an evacuated Carius tube and maintained at 575° for 13 hr. The pyrolysate was sublimed at 60° (0.01 mm) to give 1 g of sublimate. Gas chromatographic analysis indicated the product was a 56:44 mixture of 1,7- and 1,12-$B_{10}H_{10}$CHAs. The sublimate was refluxed in 10 ml of piperidine for 24 hr. The piperidine was removed under vacuum and the residues were treated with methanol until gas evolution ceased. The mixture was treated with dilute aqueous HCl until acidic and the solution was extracted with pentane. The pentane layer was evaporated under vacuum and the solid residue sublimed at 40° (0.01 mm) to give 0.3 g of 1,12-$B_{10}H_{10}$CHAs, mp 335–337°. The infrared spectrum (CS_2 solution) contained absorptions at λ_{max} 3055 (w), 2590 (s), 1142 (m), 1070 (m), 1042 (m), 985 (m), 915 (w), 880 (w), and 735 cm^{-1} (m).

$(CH_3)_4$N[7,8-B_9H_{10}CHAs].—A mixture of 2 g (0.009 mol) of 1,2-$B_{10}H_{10}$CHAs in 20 ml of piperidine was stirred at reflux for 4 hr. The piperidine was removed under vacuum and the residue was treated with methanol until gas evolution ceased. The solution was filtered and then treated with saturated aqueous tetramethylammonium chloride until precipitation was complete. The precipitate was crystallized from acetone–methanol to give 1.83 g (70% yield) of $(CH_3)_4$N[7,8-B_9H_{10}CHAs]. The infrared spectrum showed absorptions at λ_{max} 3013 (w), 2510 (s), 1477 (s), 1066 (w), 1032 (m), 1010 (m), 984 (w), 948 (m), 829 (w), and 629 cm^{-1} (w). The proton nmr spectrum (acetone-d_6) showed a sharp singlet at τ 6.6 (12 H) and a broad singlet at τ 8.7 (1 H).

$(CH_3)_4$N[7,9-B_9H_{10}CHAs].—This compound was prepared in 80% yield by the same procedure used for $(CH_3)_4$N[7,8-B_9H_{10}CHAs). The infrared spectrum of $(CH_3)_4$N[7,9-B_9H_{10}CHAs] contained absorptions at λ_{max} 3013 (w), 2525 (s), 1480 (s), 1086 (w), 1066 (m), 1025 (w), 988 (m), 951 (s), 866 (w), and 745 cm^{-1} (w). The proton nmr spectrum (acetone-d_6) showed a sharp singlet at τ 6.6 (12 H) and a broad singlet at τ 8.2 (1 H).

7,9-B_9H_{10}CHAsCH_3.—A mixture of 0.92 g (0.0034 mol) of $(CH_3)_4$N[7,9-B_9H_{10}CHAs] and iodomethane, 4.83 g (0.034 mol), in 50 ml of tetrahydrofuran was refluxed for 24 hr. The precipitated $(CH_3)_4$NI was removed by filtration and the filtrate was evaporated to dryness under vacuum. The residues were

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[12] R. Maruca, H. Schroeder, and A. W. Laubengayer, *Inorg. Chem.*, **6**, 572 (1967).

[13] A. W. Laubengayer and W. R. Rysz, *ibid.*, **4**, 1513 (1965).

sublimed at 40° (0.01 mm) to give 0.69 g (96% yield) of colorless crystalline 7,9-$B_9H_{10}CHAsCH_3$, mp 134–134.5°. The infrared spectrum contained absorptions at λ_{max} 3028 (w), 2930 (w), 2580 (s), 1835 (w), 1402 (w), 1252 (w), 1161 (w), 1061 (m), 969 (m), and 739 cm^{-1} (m). The proton nmr spectrum (acetone-d_6) showed a broad singlet at τ 7.5 (1 H) and a sharp singlet at τ 7.8 (3 H).

$(C_5H_5)Co(7,8\text{-}B_9H_9CHAs)$.—A mixture of 2.0 g (0.007 mol) of $C_5H_{10}NH_2(7,8\text{-}B_9H_{10}CHAs)$, 3 ml (0.036 mol) of freshly cracked C_5H_6, 10 ml (0.1 mol) of triethylamine, and 2.7 g (0.02 mol) of anhydrous cobalt(II) chloride in tetrahydrofuran solution was refluxed overnight. The solvent was removed *in vacuo* and the solids were chromatographed on a silica gel column with benzene as eluent. Recrystallization from benzene–heptane gave 0.11 g of yellow crystalline $(C_5H_5)Co(7,8\text{-}B_9H_9CHAs)$, mp 250–251°. The mass spectrum of this compound contained a parent ion peak at *m/e* 320.0559 (calcd for ${}^{11}B_9{}^{1}H_{15}{}^{12}C_6{}^{75}As{}^{59}Co$, 320.0559).

1,2-$B_{10}H_{10}CHSb$.—Six grams (0.031 mol) of $B_{10}H_{12}CN(CH_3)_3$ was converted to $Na_3B_{10}H_{10}CH(THF)_2$ by the procedure previously described. The reaction flask was cooled in an ice bath and 17.9 g (0.035 mol) of antimony triiodide, stirred in 200 ml of tetrahydrofuran, was added to the reaction mixture over a 5-hr period. The dark brown solution was allowed to stir at room temperature for an additional 2 hr. The mixture was filtered under nitrogen and the filtrate was evaporated under vacuum. The resulting residues were sublimed at 120–150° at 10^{-2} mm to give a red-yellow sublimate. The crude product was crystallized three times from benzene to give 3.4 g (41% yield) of white crystalline 1,2-$B_{10}H_{10}CHSb$. The compound decomposed above 240° without melting. The infrared spectrum contained absorptions at λ_{max} 3020 (m), 2530 (s), 1095 (w), 1010 (m), 960 (m), 895 (m), 750 (w), 720 (m), 660 (w), 630 (w), and 240 cm^{-1} (w). The molecular weight was determined osmometrically in benzene: calcd, 253; found, 252.

1,7-$B_{10}H_{10}CHSb$.—1,2-$B_{10}H_{10}CHSb$ (0.20 g) was sealed into an evacuated thick-wall glass tube and maintained at 450° for 13 hr. The pyrolysate was sublimed at 60° at 10^{-2} mm pressure to give 0.04 g (20% yield) of colorless 1,7-$B_{10}H_{10}CHSb$, mp 403.5–404.5°. Gas chromatographic analysis indicated the product was 99.9% the 1,7 isomer. The infrared spectrum contained absorptions at λ_{max} 3038 (m), 2550 (s), 1100 (m), 1025 (m), 960 (m), 890 (m), 870 (w), 700 (m), 640 (w), 620 (w), and 235 cm^{-1} (m).

$(CH_3)_4N[7,8\text{-}B_9H_{10}CHSb]$.—A solution of 0.211 g (0.0008 mol) of 1,2-$B_{10}H_{10}CHSb$ in 50 ml of benzene was brought to reflux, and 0.28 g (0.0033 mol) of piperidine in 50 ml of benzene was added dropwise over 2 hr. The solvent was removed under vacuum and methanol was slowly added to the residue until gas evolution ceased. A saturated solution of tetramethylammonium chloride was added until precipitation was complete. The solids were crystallized from acetone–methanol to give 0.209 g (74% yield) of colorless crystalline $(CH_3)_4N[7,8\text{-}B_9H_{10}CHSb]$. The infrared spectrum contained absorptions at λ_{max} 3001 (m), 2960 (m), 2510 (s), 1485 (s), 1475 (m), 1450 (m), 1434 (m), 1413 (w), 1392 (m), 1290 (w), 1190 (w), 1171 (s), 1055 (m), 997 (s), 900 (w), 873 (w), 858 (w), 784 (s), 755 (w), 734 (w), 685 (w), and 488 cm^{-1}.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTHEASTERN UNIVERSITY, BOSTON, MASSACHUSETTS 02115

The Reaction of Bis(fluoroxy)difluoromethane with Cesium Trifluoromethoxide[1]

BY DARRYL D. DESMARTEAU

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The reaction of bis(fluoroxy)difluoromethane, $CF_2(OF)_2$, with cesium trifluoromethoxide, $CsOCF_3$, in the presence of cesium fluoride forms CF_3OF, CF_3OOOCF_3, and the new compound $CF_3OOOCF_2OOCF_3$. When excess carbonyl fluoride is added, CF_3OF and $CF_3OOC(O)F$ are the products. The characterization of $CF_3OOOCF_2OOCF_3$ is discussed along with a possible mechanism for the reaction.

Introduction

The reaction of carbonyl fluoride with strong oxidizing agents in the presence of metal fluorides forms a variety of interesting compounds in high yields. For example the following reactions are known[2-7]

$$COF_2 + F_2 \xrightarrow{CsF} CF_3OF$$

$$COF_2 + OF_2 \xrightarrow{CsF} CF_3OOOCF_3$$

$$COF_2 + ClF \xrightarrow{CsF} CF_3OCl$$

$$COF_2 + S_2O_6F_2 \xrightarrow{KF} CF_3OOSO_2F$$

The reactive species in these reactions appears to be trifluoromethoxide salt which can be preformed from metal fluoride and carbonyl fluoride or formed *in situ* in the presence of the oxidizing agent. While CF_3OF does not react with $CsOCF_3$ at 22° to form the peroxide, CF_3OOCF_3,[7-9] the reaction of OF_2 suggests that other

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