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Group 5 Boranes. 4. Icosahedral Stibaboranes and Their Cyclopentadienylcobalt(III) Complexes[1,2]

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Received September 15, 1978

The $B_{10}H_{12}As^-$ ion reacts with triethylamine and $SbCl_3$ in THF to produce 1,2-$B_{10}H_{10}AsSb$. Reacting $B_{10}H_{14}$, $SbCl_3$, triethylamine, and zinc dust in THF produces $B_{10}H_{10}Sb_2$. The $B_{11}H_{11}Sb^-$ ion results when $B_{11}H_{14}^-$ is reacted with $SbCl_3$ and triethylamine in THF. Base degradation of 1,2-$B_{10}H_{10}AsSb$ and 1,2-$B_{10}H_{10}Sb_2$ with piperidine gives anionic 11-particle icosahedral fragments which are too unstable to be purified. Adding freshly cracked cyclopentadiene and anhydrous cobalt chloride to the piperidine solution, however, traps the 11-particle fragments as $C_5H_5Co(7,8\text{-}B_9H_9AsSb)$ or $C_5H_5Co(7,8\text{-}B_9H_9Sb_2)$.

Most of the heavier nonmetals and metalloids have been successfully incorporated into higher boranes. Higher carboranes containing Ga,[4] Tl,[5] Ge,[6-8] Sn,[7] Pb,[7] As,[9] Sb,[9] or Se[17] have been reported, as well as higher boranes containing Ga,[10] Tl,[11] Ge,[12] Sn,[12] As,[13] Se,[14,17] or Te.[14,17]

We now report the preparation and properties of 12-atom heteroboranes containing one or two antimony atoms, their base degradation, and formation of cyclopentadienylcobalt(III) complexes from their 11-particle base degradation products.

Experimental Section

All preparations were carried out in a nitrogen atmosphere. The tetramethylammonium salt of $B_{10}H_{12}As^-$ and $(C_2H_5)_3NHB_{11}H_{14}$ were prepared according to literature methods.[13,15] Anhydrous cobalt chloride was prepared by heating the hexahydrate at 0.1 torr and 100 °C for 2 days. Tetrahydrofuran was distilled from lithium hydroaluminate just prior to use after refluxing overnight. Melting points were taken in sealed, evacuated capillaries and are uncorrected.

Analytical data are reported in Table I. Elemental analyses and osmometric molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY. Infrared spectra (Table II) were obtained on a Perkin-Elmer 621 instrument and are reported as very strong (vs), strong (s), medium (m), or weak (w) intensity. Proton NMR spectra were obtained on a Varian A60A spectrometer, and boron (^{11}B) NMR spectra (Table III) were obtained on a Varian HR-220 spectrometer (externally referenced to $(C_2H_5)_2O\cdot BF_3$). UV–visible spectra were obtained on a Cary 17 instrument.

1,2-$B_{10}H_{10}AsSb$ (I). To a three-necked flask flushed with nitrogen and fitted with a pressure-equalized dropping funnel and a reflux condenser were added 2.0 g of $(CH_3)_4NB_{10}H_{12}As$ and 20 mL of tetrahydrofuran (THF), followed by 2.6 mL of triethylamine. A solution of 2.8 g of $SbCl_3$ in THF was made up in the dropping funnel and added with stirring over 1 h. The solution was then stirred at reflux for 18 h and cooled, and the solvent was removed by rotary evaporation. Extraction with several portions of hot benzene, filtering to remove insoluble solids, and removing the benzene in vacuo gave an off-white solid, which was sublimed at 90 °C and 10^{-1} torr to give 1.08 g of I (46% yield).

1,2-$B_{10}H_{10}Sb_2$ (II). A 500-mL three-necked flask was fitted with a mechanical stirrer, gas inlet, and pressure-equalized dropping funnel. After the system was flushed with nitrogen, 150 mL of dry THF, 4.9 g of $B_{10}H_{14}$, and 5.1 g of zinc dust were added. A solution of 15 g of $SbCl_3$ in 50 mL of THF was prepared in the dropping funnel, and then 22 mL of triethylamine was added by syringe to the flask, which had been cooled in an ice bath. The $SbCl_3$ solution was added over 7 h with stirring while continuing to maintain an ice bath around the flask. After addition was completed, stirring was continued at room temperature for 36 h and then at reflux for 1.5 h. Rotary evaporation gave an oily slurry which was extracted several times with $CHCl_3$, and any insoluble solids were removed by filtration. This solution was allowed to evaporate in a hood, the residues were dissolved in CH_2Cl_2, and the resulting solution was chromatographed on a 2 × 5 *in. silica* gel column with CH_2Cl_2. The eluent was allowed to evaporate in a hood, and the oily solids were collected on a fritted glass funnel to remove the oil. The solids were sublimed at 10^{-4} torr and 130–150 °C to obtain 6.2 g of yellowish solid. This was dissolved in hot benzene (part was insoluble) and the volume of benzene reduced to give 1.58 g of II (11% yield). An analytical sample was obtained by resubliming at 100 °C and recrystallizing from benzene.

$(CH_3)_4NB_{11}H_{11}Sb$ (III). To 100 mL of THF in a two-necked 250-mL flask under a nitrogen blanket were added 1.0 g of $(C_2H_5)_3NH^+B_{11}H_{14}^-$ and 2.4 mL of triethylamine. Then a solution of $SbCl_3$ (1.21 g) in 25 mL of THF was added from a pressure-equalized dropping funnel over 1 h to the stirred solution in the flask. After the solution had been stirred for 18 h, the THF was removed on a rotary evaporator and the crude solids were extracted several times with small portions of acetone. To the acetone solution was added water and $(CH_3)_4NCl$ solution, and dilution with water was continued until precipitation was complete. The crude solid was isolated by filtration, air-dried, and then dissolved in acetone and stripped onto 10 mL of neutral alumina. Chromatography was carried out on a 2 × 5 in. neutral alumina column with ethyl alcohol (discarded) and 25% acetone–75% ethyl alcohol. The last fractions collected were the purest, so they were recrystallized from acetone/methanol to give 0.18 g (13% yield) of III.

$C_5H_5CoB_9H_9AsSb$ (IV). To a 50-mL two-necked flask fitted with a reflux condenser were added 40 mL of piperidine and 0.574 g of 1,2-$B_{10}H_{10}AsSb$. The solution was stirred at 75 °C for 2 h and cooled in an ice bath. Then, 3.0 mL of freshly cracked C_5H_6 and 2.0 g of $CoCl_2$ were added. After the solution had been stirred at room temperature for 1 h, the temperature was raised to 90–95 °C for 18 h and the solution finally refluxed for 1 h. After oxygen was bubbled through the solution for 1 h, the excess piperdine was removed on a rotary evaporator. The solids were chromatographed on silica gel with methylene chloride. Benzene was added to the eluent and the mixture boiled to decompose an air-sensitive impurity. The benzene solution was stripped onto silica gel and the solids placed atop a 2 × 5 in. silica gel column. Chromatography with benzene gave a yellow-orange band. Rotary evaporation of the benzene solution with recrystallization of the solids from ethylene dichloride–heptane gave 0.193 g of orange plates of IV (25% yield).

The ^1H NMR spectrum consists of a singlet at τ 4.40 assigned to C_5H_5. The UV–visible spectrum (acetonitrile solution) shows the following absorptions [λ_{max}, nm (ϵ)]: 451 (313), 317 (8140), and 252 (10 600).

$C_5H_5CoB_9H_9Sb_2$ (V). To a 50-mL two-necked flask fitted with a nitrogen inlet and a reflux condenser were added 0.70 g of 1,2-$B_{10}H_{10}Sb_2$ and 30 mL of piperidine. The solution was stirred to dissolve the borane, the flask was cooled in an ice bath, and 3.5 mL of freshly cracked C_5H_6 was added by syringe. Then 2.0 g of $CoCl_2$ was added, and the solution was first stirred at 60–65 °C for 10 h, then stirred at room temperature for 12 h, and finally refluxed for 1 h. After O_2 was bubbled through the solution for 1 h, excess piperidine was removed on a rotary evaporator, and the solids were extracted with several portions of methylene chloride. This solution was stripped onto a 2 × 5 in. silica gel column and eluted with benzene to give a yellow-orange band. Rotary evaporation of the solution and recrystallization of the solids from ethylene dichloride–heptane gave 0.202 g of V (22% yield).

The ^1H NMR spectrum contains a singlet at τ 4.40 assigned to the C_5H_5 group. The UV–visible spectrum (acetonitrile solution) shows

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Table I. Analytical Data

			calcd					found				
no.	compd	mp, °C	% C	% H	% M[a]	% Co	mol wt	% C	% H	% M[a]	% Co	mol wt[b]
I	1,2-$B_{10}H_{10}AsSb$	>500		3.20	23.80		315		3.32	23.19		317
II	1,2-$B_{10}H_{10}Sb_2$	>400		2.78	67.32		362		2.91	66.98		357
III	$(CH_3)_4NB_{11}H_{11}Sb$		14.83	7.16				14.60	7.04			
IV	$C_5H_5CoB_9H_9AsSb$	270–272	14.06	3.40		13.80	427	14.08	3.43		13.79	407
V	$C_5H_5CoB_9H_9Sb_2$	296–298	12.67	2.98		12.44	474	12.97	3.05		11.77	468

[a] As or Sb. [b] Osmometric in benzene.

Table II. Infrared Spectra (KBr Pellets) (cm^{-1})

I	2520 vs, 995 s, 908 w, 886 w, 840 w, 767 w, 726 m, 663 w, 598 w
II	2515 vs, 992 s, 909 w, 890 w, 834 w, 775 w, 724 m, 646 w
III	2510 vs, 1477 s, 1013 s, 948 m, 731 m, 717 w
IV	3105 w, 2505 vs, 1416 m, 1060 w, 1000 s, 876 w, 847 s, 756 w, 725 w, 492 w, 403 w
V	3100 w, 2495 vs, 1415 m, 996 s, 980 m, 925 w, 878 w, 847 s, 765 w, 727 w, 566 w, 482 w, 453 w, 433 w, 398 w

Table III. ^{11}B NMR Spectra at 70.6 MHz

no.	rel intens	chem shifts, δ^a (J_{BH}, Hz)
I[b]	1:1:2:2:2:2	14.2 (140), 12.3 (130), 3.0 (160), −0.1 (140), ~−2.0 (~130), −3.5 (130)
II[b]	2:2:4:2	13.9 (140), 3.9 (155), −1.7 (155), ~−4.6 (~150)
III[b]	1:5:5	9.4 (135), −6.9 (110), −9.3 (120)
IV[c]	1:3:2:2:1	~15.8 (~130), 13.7 (150), ~11.2 (~140), ~−5.7 (~130), −7.3 (125)
V[c]	2:3:1:1:2	15.7 (140), 13.8 (130), 9.5 (145), −4.0 (160), −7.5 (145)

[a] Relative to $(C_2H_5)_2O\cdot BF_3 = 0$. [b] Dimethylformamide solution. [c] Acetone solution.

the following absorptions [λ_{max}, nm (ϵ)]: 462 (338), 318 (8380), and 255 (11 600).

Results and Discussion

One antimony atom was added to $B_{10}H_{12}As^-$ to give 1,2-$B_{10}H_{10}AsSb$ (I) when $SbCl_3$ reacted with it in the presence

$$B_{10}H_{12}As^- + 2(C_2H_5)_3N + SbCl_3 \rightarrow 3Cl^- + 2(C_2H_5)_3\,NH^+ + 1,2\text{-}B_{10}H_{10}AsSb$$

of triethylamine. I is the first known mixed heteroatom group 5 borane and has one of the highest melting points of any heteroatom borane (>500 °C).

I was characterized by its low-resolution mass spectrum and ^{11}B NMR spectrum (Table III). The low-resolution mass spectrum cut off at *m/e* 318, corresponding to the $^{11}B_{10}{}^1H_{10}{}^{75}As^{123}Sb^+$ parent ion. The ^{11}B NMR spectrum is in a 1:1:2:2:2:2 pattern characteristic of C_s symmetry.

Two antimony atoms are inserted into decaborane by a reaction similar to that used to synthesize[13] $B_{10}H_{12}As^-$ and 1,2-$B_{10}H_{10}As_2$. Triethylamine is the base, zinc dust the reductant, and antimony trichloride the source of antimony. No $B_{10}H_{12}Sb^-$ was found in the reaction mixture. However, if $B_{10}H_{14}$ is added to a slurry of excess NaH in diethyl ether and then a dilute ether solution of $SbCl_3$ is added, impure $B_{10}H_{12}Sb^-$ can be obtained by slow hydrolysis of the ether solution and precipitation with tetramethylammonium chloride solution. The impure salt (characterized by IR) was found to be quite unstable in most polar organic solvents and therefore has not been obtained in the pure state.

1,2-$B_{10}H_{10}Sb_2$ (II) was obtained with difficulty and in low yield from the Zn–triethylamine–$SbCl_3$ reaction. It began to blacken below its melting point, as is the case for the related stibacarborane[9] 1,2-$B_{10}H_{10}CHSb$.

The low-resolution mass spectrum of II cut off at *m/e* 366, corresponding to the $^{11}B_{10}{}^1H_{10}{}^{123}Sb_2{}^+$ parent ion. The ^{11}B NMR spectrum shows a 2:2:4:2 pattern, interpretable as C_{2v} molecular symmetry with two pairs of borons accidentally degenerate. Assignment of the two low-field doublets of relative area 1 in the spectrum of I can be carried out by comparing the low-field doublets of area 2 each in the spectra of II and 1,2-$B_{10}H_{10}As_2$.[13] The doublets in the spectrum of I occur at 14.2 and 12.3 ppm, while the lowest field doublet for II is at 13.9 ppm and for 1,2-$B_{10}H_{10}As_2$ is at 15.5 ppm. Thus As shows a tendency to shift the boron para to it to lower field than Sb. Therefore, the resonance in the spectrum of I at 14.2 ppm can be assigned to the boron para to As, while the resonance at 12.3 ppm can be assigned to the boron para to Sb.

We wondered whether Sb could be inserted into $B_{11}H_{14}^-$ under the same conditions as for insertion into $B_{10}H_{12}As^-$ (see above). When triethylamine as base, THF as solvent, and $SbCl_3$ as the source of antimony were used, a low yield of $(CH_3)_4NB_{11}H_{11}Sb$ (III) was obtained upon hydrolysis of the product mixture and precipitation with $(CH_3)_4NCl$ solution.

Resonances in the ^{11}B NMR spectrum appeared in a 1:5:5 pattern. The low-field doublet is assigned to the boron para to antimony, while the resonances of relative area 5 each are assigned to the two five-membered rings.

Attempts to quaternize the antimony in III resulted in cage destruction, as is the case[13] also for $B_{11}H_{11}As^-$.

For most known neutral icosahedral heteroboranes, reaction with strong base (KOH or piperidine) removes a boron adjacent to the heteroatom or heteroatoms. Reacting I or II with piperidine at 50–70 °C gave products that were precipitated from aqueous solutions when $(CH_3)_4NCl$ solution was added. On attempted purifications, the salts slowly decomposed. Both impure salts showed a doublet at quite high field, as has been noted for the similar ion $B_9H_{10}As_2^-$.

In order to stabilize the 11-particle fragments, attempts were made to quaternize As or Sb with methyl iodide in THF. The ion[13] $B_9H_{10}As_2^-$ yields $B_9H_{10}AsAsCH_3$ when stirred with methyl iodide in THF at room temperature.[16] However, the products from reaction of piperidine and I or II did not react with methyl iodide.

Not having been able to purify or stabilize the 11-particle icoshedral fragments, we tried tying them up as part of a cyclopentadienylcobalt(III) complex. Reacting I or II, $CoCl_2$, and freshly cracked C_5H_6 in piperidine at 60–75 °C gave low yields of $C_5H_5CoB_9H_9AsSb$ (IV) and $C_5H_5CoB_9H_9Sb_2$ (V), respectively.

The sharp resonance at τ 4.40 in the ^1H NMR spectra of I and II identified the cyclopentadienyl groups. The low-resolution mass spectra cut off at *m/e* 430 and 478, for the $^{11}B_{10}{}^1H_{14}{}^{12}C_5{}^{75}As^{123}Sb^{59}Co^+$ and $^{11}B_9{}^1H_{14}{}^{12}C_5{}^{123}Sb_2{}^{59}Co^+$ parent ions, respectively.

^{11}B NMR spectra (Table III) are badly overlapped but readily interpreted in terms of C_s cage symmetry.

Thus the number of accessible stibaboranes and their chemistry appear to be quite limited when synthesis starts with $SbCl_3$. Use of Sb_2O_3 as a source of antimony (cf. As_2O_3 to synthesize an arsacarborane[17]) offers some promise, however.

Acknowledgment. The authors thank Dr. L. J. Todd and Mr. G. Delbert Friesen for the boron NMR spectra and the Research Corp. and the University of Mississippi Committee on Faculty Research for support.

Registry No. I, 69531-86-8; II, 69531-87-9; III, 69668-66-2; IV, 69576-60-9; V, 69576-61-0; $(CH_3)_4NB_{10}H_{12}As$, 51292-89-8; $B_{10}H_{14}$, 17702-41-9; $(C_2H_5)_3NH^+B_{11}H_{14}^-$, 12106-44-4; $SbCl_3$, 10025-91-9; $CoCl_2$, 7646-79-9.

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Magnetic Studies of Chromium(II) and Chromium(III) Metallocarboranes

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Received April 6, 1978

Temperature-dependent magnetic susceptibility data for $[(C_2H_5)_4N]_2[Cr^{II}(C_2B_{10}H_{12})_2]$ have been collected in the range 1.4–80 K. The magnetic data may be fit to the Curie–Weiss law $\chi = C/(T - \Theta)$ with $g = 2.00$ and $\Theta = -1.7$ K. Magnetic data for $Cs[Cr^{III}(C_2B_9H_{11})_2]$ yield $g = 1.98$ and $\Theta = -1.5$ K, in excellent agreement with results from EPR studies. The deviations from the Curie law, as indicated by the Θ values, are thought to arise from single-ion effects.

Introduction

The mode of bonding and the degree of electron delocalization in metal sandwich complexes have been the subjects of a number of investigations.[1,2] Sandwich complexes include the metallocenes and metallocarboranes, with the latter series offering more opportunity for subtle structural and chemical variety. Much of the work on paramagnetic metallocarboranes has involved analysis of the NMR shifts that have been observed. Recently Warren[3-5] has derived expressions for the magnetic properties of sandwich complexes and has noted some discrepancies between the reported results and the predictions from his models. The d^4 case is of particular interest since the ground state depends on the ligand field strength, and the differences in ground-state properties may be seen in the magnetic studies. With use of the notation for $C_{\infty v}$ symmetry, a $^3\Delta$ ground state is expected for the ligand field strengths usually observed in sandwich complexes with d^4 electronic configurations, and substantial orbital contributions to the magnetic moment are expected. The data for chromocene[6] yield a magnetic moment of 3.2 ± 0.16 μ_B between 90 and 295 K, a value which is significantly greater than the spin-only value of 2.83 μ_B and which is consistent with a $^3\Delta$ ground state. For the isoelectronic bis(mesitylene)vanadium(I) cation,[7] the observed moment of 2.80 ± 0.17 μ_B (88–193 K) suggests a $^3\Sigma^-$ ground state. The air-stable complex $[(C_2H_5)_4N]_2[Cr^{II}(C_2B_{10}H_{12})_2]$ has recently been prepared. It was of interest to determine the magnetic properties of this compound and to compare the results with the data for the two other sandwich compounds with d^4 electronic configurations. The results of magnetic susceptibility investigations between 1.8 and 90 K of the chromium(II) complex and of $Cs[Cr^{III}(1,2\text{-}C_2B_9H_{11})_2]$ are reported here.

Experimental Section

The Cr complexes were prepared according to the literature methods.[8] Anal. Calcd for $CrB_{20}C_{20}H_{64}N_2$: C, 39.97; H, 10.73; N, 4.66; B, 35.98; Cr, 8.65. Found: C, 39.89; H, 10.65; N, 4.50; B, 36.03; Cr, 8.57.

The magnetic susceptibilities were measured as described elsewhere.[9]

Results

The magnetic data for the unusual air-stable chromium(II) compound $[(C_2H_5)_4N]_2[Cr(C_2B_{10}H_{12})_2]$ are shown in Figure 1 as inverse susceptibility vs. temperature. The best least-squares fit to the Curie–Weiss law, $\chi = C/(T - \Theta)$, yielded $g = 2.00 \pm 0.01$ and $\Theta = -1.7 \pm 0.1$ K, where the g value was calculated from the expression

$$g = \left[\frac{3kC}{N\beta^2 S(S + 1)}\right]^{1/2}$$

In this expression, C is the Curie constant, S is the spin and is equal to 1, and the other symbols have their usual meanings. The g value obtained from the Curie–Weiss fit is very nearly equal to the free electron g value; this indicates that the orbital angular momentum is almost completely quenched. The small Θ value may be assumed to arise primarily from single-ion effects since there is little chance for magnetic exchange through carborane ligands. NMR evidence has shown that the metal electron density is not delocalized throughout the ligand cage.[1]

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0020-1669/79/1318-1600$01.00/0