tumor activity. It is difficult to explain this within the present knowledge of the biological properties of these platinum compounds. A great number of factors may determine the activity of the platinum compounds. Among these are toxic side effects, water solubility, lipid solubility, membrane transport, side reactions inside and outside the cell, the reactions with the DNA of the cell (which is known[3] to cause the cytostatic effect in the case of *cis*-$Pt(NH_3)_2Cl_2$), and possible repair mechanisms. An illustration of the difficulties encountered in explaining the wide variation in activity of the different platinum compounds is the question whether or not all platinum–DNA complexes formed with different platinum compounds are the same.[34]

Since NH_2 groups can form hydrogen bonds it seems likely that hydrogen bond formation plays an important role in one or more of the above mentioned factors. For example Marzilli, Bau, and co-workers have shown that hydrogen bonding plays an important role in the interaction of metal ions with nucleic acid constituents.[35] However much work has to be done to verify this idea and to determine the relative importance of the above-mentioned factors. Determination of the pharmacokinetics and distribution in- and outside the cell of different platinum compounds and investigation of the type and number of lesions produced on the DNA by these platinum complexes are very important to obtain more information on the relation between structure and activity.

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Registry No. Pt(DMDAP)(mal), 72968-07-1; Pt(DMDAP)I_2, 72968-08-2; Pt(DMDAP)Br_2, 72968-09-3; Pt(DMDAP)Cl_2, 28866-75-3; Pt(DMDAP)Cl_4, 72968-10-6; Pt(DMDAP)$(OH_2)_2^{2+}$, 72968-11-7; K_2PtCl_4, 10025-99-7.

Supplementary Material Available: A listing of observed and calculated structural factors (10 pages). Ordering information is given on any current masthead page.

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Preparation and Chemistry of the $B_9H_{12}Se^-$ and $B_9H_{12}Te^-$ Ions

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Aqueous polyselenide or polytelluride solutions react with $B_9H_{13}\cdot S(CH_3)_2$ to form the $B_9H_{12}X^-$ (X = Se or Te) anions, which can be isolated as tetramethylammonium salts. Oxidation of these salts with iodine produces the $B_9H_{11}X$ molecules in benzene or the $B_9H_{11}X\cdot CH_3CN$ molecules in the presence of acetonitrile. Reaction of $B_9H_{11}Se\cdot CH_3CN$ with triethylamine produces $B_9H_{11}Se\cdot N(C_2H_5)_3$. Pyrolysis of $B_9H_{11}Se$ produces mixtures of B_9H_9Se and $B_{11}H_{11}Se$. The $B_8H_{10}Se_2$ molecule is formed as a coproduct during the isolation of the $B_9H_{12}Se^-$ ion.

Introduction

The thiaborane anion $B_9H_{12}S^-$ has previously been prepared by a degradation–insertion reaction of decaborane with an aqueous polysulfide solution.[1] Studies of its derivative chemistry[2,3] and the ^{11}B NMR assignment of this anion have been published.[4] Reactions of decaborane with aqueous polyselenide and polytelluride solutions formed mainly the insertion product $B_{10}H_{11}X^-$ (X = Se or Te).[5] We report in this article syntheses of the $B_9H_{12}Se^-$ and $B_9H_{12}Te^-$ anions and some of their derivative chemistry. A preliminary communication has been published concerning the $B_8H_{10}Se_2$ molecule which is produced as a coproduct in the $B_9H_{12}Se^-$ ion synthesis.[6]

Experimental Section

General Procedures and Instrumentation. All reactions were run under an atmosphere of prepurified nitrogen. The organic solvents used as reaction solvents were dried and distilled prior to use. All other reagants were used as received. Melting points were obtained in sealed, evacuated capillaries and are uncorrected.

Boron (^{11}B) NMR spectra at 70.6 MHz were obtained with a Varian HR-220 spectrometer and were externally referenced to $BF_3\cdot O(C_2H_5)_2$. Proton NMR spectra were obtained on a Varian T-60A spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. High-resolution mass spectral data were obtained on an AEI MS-902 spectrometer.[15] Infrared data, contained in Table I, were obtained as KBr disks, or as indicated, on a Perkin-Elmer 283 instrument.

$(CH_3)_4N[B_9H_{12}Se]$ (I) and $B_8H_{10}Se_2$ (II). An aqueous ammonium polyselenide solution was prepared by using the procedure described previously,[5] with 50 mL of ammonia, 0.67 g (29 mmol) of sodium metal, and 4.6 g (58 mmol) of selenium powder in a 100-mL, three-neck flask fitted with a magnetic stirrer, dry ice condenser, and nitrogen inlet. Reduction of sputtering was accomplished by packing dry ice around the reaction flask during the addition of sodium and selenium. The material $B_9H_{13}\cdot S(CH_3)_2$ was prepared by using the literature method described for the synthesis of $B_9H_{13}\cdot S(C_2H_5)_2$.[7] $B_9H_{13}\cdot S(CH_3)_2$, 2.00 g (11.6 mmol), was added rapidly to the reaction flask, and the solution was stirred 12 h. Excess tetramethylammonium chloride in deoxygenated water was added to the reaction mixture, and the resulting air sensitive precipitate was filtered, washed with 2 × 10 mL portions of deoxygenated water, and dried under a nitrogen

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Table I. Infrared Data

compd	absorption, cm^{-1}
I	3020 w, 2520 vs, 2420 m, 2325 w, 1475 s, 1412 w, 1175 m, 1042 m, 995 s, 946 s, 906 m, 860 w, 780 m, 745 m, 710 w, 670 w, 638 w
II	2570 vs, 2550 s, 1036 w, 1010 w, 990 s, 976 sh, 958 w, 950 w, 912 m, 900 m, 863 m, 800 s, 728 w, 712 m
III	3030 w, 2535 vs, 2460 sh, 2540 m, 1476 s, 1410 m, 1172 m, 1045 m, 995 s, 960 s, 950 s, 910 w, 890 m, 870 w, 845 m, 785 m, 745 w, 715 w, 700 w, 675 w, 628 w, 585 m
IV[a]	2580 vs, 1030 m, 1010 m, 982 s, 925 m, 890 m, 860 w, 825 w, 802 w, 750 m, 737 m
VI	2990 w, 2920 m, 2550 vs, 2475 w, 2440 m, 2000 w, 1350 m, 1108 m, 1060 w, 1000 s, 975 w, 940 m, 908 w, 875 w, 790 m, 758 w, 726 m, 687 w, 630 w
VII	2920 w, 2535 vs, 2340 w, 1403 s, br,[b] 1350 w, 1190 m, 1108 s, br, 1060 w, 982 s, 955 w, 942 w, 895 m, 845 m, 790 m, 768 m, 737 m, 696 w, 620 m, 595 m
VIII	2950 w, 2980 w, 2970 m, 2935 w, 2560 s, 2530 s, 2510 s, 2000 w, 1470 m, 1455 m, 1430 w, 1385 s, 1350 w, 1192 m, 1178 w, 1146 m, 1087 w, 1050 w, 1010 s, 995 s, 935 w, 906 m, 880 m, 808 w, 785 m, 759 m, 730 w, 630 w
IX	2590 vs, 2540 vs, 945 s, 895 w, 802 m, 740 w, 682 m, 625 w

[a] Benzene solution. [b] br = broad.

atmosphere. The dry precipitate was then dissolved in acetonitrile and placed on a H^+ ion-exchange column packed with 50 g of Rexyn 101 (H^+) and eluted with 150–200 mL of acetonitrile. Water (50 mL) was added to the eluant, and the acetonitrile was removed by rotary evaporation at 30 °C. The resulting solid was removed from the remaining aqueous solution by filtration in air. Excess tetramethylammonium chloride solution was added to the filtrate, and the resulting white precipitate was recovered by filtration, washed with 2 × 10 mL portions of water, and air-dried. The solid was recrystallized by rotary evaporation from 50 mL of acetonitrile–water (1:1), filtered, and vacuum dried, giving 1.05 g of light yellow crystals of $(CH_3)_4N[B_9H_{12}Se]$; 35% yield based on $B_9H_{13}{\cdot}S(CH_3)_2$. (The yellow color can be removed, but excessive amounts of activated charcoal are necessary.) Compound I decomposed at 335–340 °C without melting. Anal. Calcd for $(CH_3)_4N[B_9H_{12}Se]$: C, 18.30; H, 9.22. Found: C, 17.66; H, 8.84.

The solid formed during the rotary evaporation of the eluant from the H^+ ion-exchange column was recrystallized by dissolving the solid in a minimum of methylene chloride, an equal quantity of acetonitrile was added, and the mixture was slowly rotary evaporated. The resulting solid was isolated by filtration and air-dried, giving 0.730 g of white crystalline $B_8H_{10}Se$: mp 197–199 °C dec; 25% yield based on $B_9H_{13}{\cdot}S(CH_3)_2$. The high-resolution mass spectrum contains a parent ion peak at *m/e* 257.9834, corresponding to the $^{11}B_8{}^1H_{10}{}^{80}Se_2{}^+$ ion (calcd 257.9857).

$(CH_3)_4N[B_9H_{12}Te]$ (III). A polytelluride solution was prepared by using 0.60 g (26 mmol) of sodium metal and 7.8 g (61 mmol) of tellurium metal in a system similar to that used for the preparation of I. The $B_9H_{13}{\cdot}S(CH_3)_2$, 1.50 g (8.70 mmol), was added to the reaction mixture, and the solution was stirred for 12 h. Excess tetramethylammonium chloride solution was added, and the resulting precipitate was filtered, washed with 2 × 10 mL portions of water, and air-dried. The solid was dissolved in dry acetone, the solution was filtered, and the precipitate was recrystallized by rotary evaporation from a slightly air sensitive acetone–methanol mixture. The solid was recovered by filtration and vacuum dried, giving 1.91 g of slightly yellowish crystals of $(CH_3)_4N[B_9H_{12}Te]$ [70% yield based on $B_9H_{13}{\cdot}S(CH_3)_2$].

Anal. Calcd for $(CH_3)_4N[B_9H_{12}Te]$: C, 15.44; H, 7.72. Found: C, 15.83; H, 8.04.

$B_9H_{11}Se$ (IV) and $B_9H_{11}Te$ (V). A 100-mL, two-neck flask was fitted with a magnetic stirrer and a nitrogen inlet. Benzene (15 mL) was added to the flask, followed by 0.193 g (0.76 mmol) of I_2 and 0.4 g (1.52 mmol) of $(CH_3)_4N[B_9H_{12}Se]$. The mixture was stirred for 20 min or until gas evolution ceased. The solvent was removed under vacuum. The volatile solid was sublimed at 40 °C onto a water-cooled probe under a static vacuum (10^{-2} torr). The material on the probe was removed under an inert atmosphere, giving 0.182 g of yellowish solid $B_9H_{11}Se$, mp 84–85 °C (64% yield). The low-resolution mass spectrum exhibited a cutoff at *m/e* 192 corresponding to the $^{11}B_9{}^1H_{11}{}^{82}Se^+$ parent ion. The high-resolution mass spectrum contained a peak at *m/e* 190.0867 corresponding to the $^{11}B_9{}^1H_{11}{}^{80}Se^+$ ion (calcd 190.0863).

$B_9H_{11}Te$ was prepared in a similar manner by the reaction of 40 mg (0.16 mmol) of I_2 and 0.10 g (0.32 mmol) of $(CH_3)_4N[B_9H_{12}Te]$ with the exception that the iodine was added slowly to a slurry of the starting telluraborane and benzene. The product was not isolated due to thermal instability.

Table II. ^1H NMR

compd	shift, ppm	compd	shift, ppm
I[a]	3.43	VII[b]	2.0 (s), 2.6 (s)
III[a]	3.42	VIII[b]	3.07 (q), 1.15 (t)
VI[a]	2.97 (s), 2.93 (s)		

[a] Solvent acetone-d_6. [b] Solvent chloroform-*d*.

$B_9H_{11}Se{\cdot}CH_3CN$ (VI). The $B_9H_{11}Se$ was prepared in situ by reaction of $(CH_3)_4N[B_9H_{12}Se]$, 0.190 g (0.92 mmol), with iodine, 0.10 g (0.78 mmol), in 4 mL of benzene by using the procedure described above. After the mixture was stirred for 15 min, 2 mL of acetonitrile was added and the solution stirred an additional 5 min. The reaction mixture was evaporated to dryness, and the solid residue was extracted with 3 × 15 mL portions of methylene chloride which were combined and rotary evaporated. The resulting red solid was chromatographed on a 7 in. × 1 in. silica gel column eluted with methylene chloride. The initial colorless band eluted before an unidentified green band was collected. The colorless material was evaporated to dryness. The crude product was crystallized from methylene chloride–hexane to give 0.10 g of off-white $B_9H_{11}Se{\cdot}CH_3CN$, mp 175–176 °C dec, in 48% yield.

Anal. Calcd for $B_9H_{11}Se{\cdot}CH_3CN$: C, 10.52; H, 6.18. Found: C, 10.43; H, 6.17.

$B_9H_{11}Te{\cdot}CH_3CN$ (VII). A solution of 50 mg (0.16 mmol) of $(CH_3)_4N[B_9H_{12}Te]$ in 10 mL of acetonitrile was placed in a 50-mL round-bottom flask fitted with a nitrogen inlet. The flask was cooled to 0 °C and stirred magnetically while 20 mg (0.08 mmol) of I_2 was slowly added. Stirring was continued until the iodine color disappeared. The solvent was removed under vacuum. The resulting solid was extracted with methylene chloride. The solvent was removed from the slightly air-sensitive extract under vacuum resulting in 0.021 g of solid $B_9H_{11}Te{\cdot}CH_3CN$ (47% yield). The compound decomposed without melting at 38 °C.

Anal. Calcd for $B_9H_{11}Te{\cdot}CH_3CN$: C, 8.68; H, 5.06. Found: C, 8.85; H, 5.30.

$B_9H_{11}Se{\cdot}N(C_2H_5)_3$ (VIII). Triethylamine (20 mL) was vacuum distilled into a 50-mL, two-neck flask and then back-filled with nitrogen. $B_9H_{11}Se{\cdot}CH_3CN$, 500 mg (2.19 mmol), was added to the reaction vessel and stirred magnetically for 15 min. The volatiles were removed under vacuum, and the resulting solid was extracted with 2 × 20 mL portions of CH_2Cl_2. The extract was evaporated to dryness and then crystallized from a methylene chloride–methanol mixture by slow rotary evaporation, giving 0.318 g (50% yield) of slightly yellow crystals of $B_9H_{11}Se{\cdot}N(C_2H_5)_3$, mp 138–139 °C.

Anal. Calcd for $B_9H_{11}Se{\cdot}N(C_2H_5)_3$: C, 24.98; H, 9.08. Found: C, 25.06; H, 8.95.

B_9H_9Se (IX). A 10 mm × 1 m glass tube with a test tube end was evacuated and back-filled with nitrogen. The unsealed end was introduced into a nitrogen-filled glovebag, 0.093 g of $B_9H_{11}Se$ (0.49 mmol) was placed into the tube, and a glass wool plug was used to force the solid to the closed end of the tube. A second glass wool plug was placed one-half the distance down the tube. The tube was connected to a U-tube trap. The pyrolysis tube was placed into a 90 cm long tube furnace, preheated to 380 °C, with the test tube end outside the hot zone. The system was continuously evacuated through the U-tube trap which was placed in a liquid-nitrogen bath. The closed

Table III. ^{11}B NMR

compd	area ratio	shift, ppm (J_{B-H}, Hz)
$(CH_3)_4N[B_9H_{12}Se]$ (I)^a	1:3:1:2:2	5.5 (137), ~7.7,^{b} −13.6 (115),^{c} −33.7 (139), −36.3 (141)
$B_8H_{10}Se_2$ (II)^d	2:4:2	14.9 (178), −16.9 (160),^{e} −30.7 (155)
$(CH_3)_4N[B_9H_{12}Te]$ (III)^a	1:4:2:2	7.3 (137), ~−10.8,^{f} −25.3 (137), −35.5 (139)
$B_9H_{11}Se$ (IV)^g	2:1:2:2:1:1	28.9 (172), 16.7 (161), 6.2 (157), −9.6 (159),^{h} −21.5 (167), −29.9 (174)
$B_9H_{11}Te$ (V)^g	2:1:2:2:1:1	31.3 (170), 15.7 (158), 7.5 (146), −7.4 (144), −21.4 (149), −31.0 (177)
$B_9H_{11}Se{\cdot}CH_3CN$ (VI)^i	1:1:2:1:2:2	7.6 (135), ~−6.4, −8.8 (160), −19.5 (130), −27.9 (142),^{j} −36.9 (149)
$B_9H_{11}Te{\cdot}CH_3CN$ (VII)^i	1:1:3:2:2	8.7 (137), −6.9 (159), ~−14.9,^{b} −23.3 (129), −36.2 (149)
$B_9H_{11}Se{\cdot}N(C_2H_5)_3$ (VIII)^i	1:1:3:2:2	2.6 (130), −4.0 (130), −8.8,^{b} −29.8 (130),^{k} −38.1 (146)
B_9H_9Se (IX)^i	1:4:4	73.3 (180), −5.4 (176), −19.9 (156)
$(CH_3)_4N[B_9H_{12}S]^a$	1:2:1:1:2:2	3.8 (132), −8.1 (149), −11.6 (~180), −15.0 (112),^{c} −33.7 (139), −36.8 (151)
$B_9H_{11}S$[10]	2:1:2:2:1:1	24.9 (170), 17.3 (170), 6.8 (150), −10.1 (145), −21.5 (160), −30.7 (180)
$B_9H_{11}S{\cdot}CH_3CN^i$	1:3:1:2:2	6.3 (139), −9.1,^{b} −21.0 (122), −31.1 (130), −37.5 (147)

^{a} Solvent CH_3CN. ^{b} Unsymmetrical doublet. ^{c} Triplet. ^{d} Solvent $CHCl_3$. ^{e} $J_{B-\mu-H} = 35$ Hz, line narrowed. ^{f} Unsymmetrical multiplet. ^{g} Solvent C_6H_6. ^{h} $J_{B-\mu-H} = 37$ Hz, line narrowed. ^{i} Solvent CH_2Cl_2. ^{j} $J_{B-\mu-H} = 43$ Hz, line narrowed. ^{k} $J_{B-\mu-H} = 40$ Hz, line narrowed.

end of the tube was gradually pulled into the furnace until solid was observed condensing in two bands on the vacuum side of the pyrolysis tube. After 1 h, the tube was allowed to cool and the system was opened to the air. The band furthest from the hot zone and the material which had collected in the U-tube trap were dissolved in acetonitrile. The solvent was removed under vacuum, and the resulting solid was extracted with hexanes. Evaporation of the hexanes followed by sublimation at 40 °C (10^{-2} torr) onto a water-cooled probe gave 0.055 g (60% yield) of white crystalline B_9H_9Se, mp 260–261.5 °C dec. The low-resolution mass spectrum exibited a cutoff at *m/e* 190 corresponding to the $^{11}B_9{}^1H_9{}^{82}Se^+$ ion. The high-resolution mass spectrum contains a peak at *m/e* 188.0710 corresponding to the $^{11}B_9{}^1H_9{}^{80}Se^+$ ion (calcd 188.0707).

Pyrolysis $B_9H_{11}Se{\cdot}N(C_2H_5)_3$. A sample of $B_9H_{11}Se{\cdot}N(C_2H_5)_3$, 50 mg (0.17 mmol), was sealed into a 10 mm (i.d.) × 20 cm pyrolysis tube under vacuum. The entire tube was placed in a tube furnace at 300 °C for 15 min. The tube was then cooled, and the pyrolysis product was extracted with 5 mL of methylene chloride. The only material observed in the ^{11}B NMR spectrum of the extract was $B_{11}H_{11}Se$ which was identified by comparison with the spectrum of an authentic sample.

Results and Discussion

Isolation of $B_9H_{12}X^-$ Ions (X = Se or Te). Reaction of decaborane with polyselenide and polytelluride solutions, unlike polysulfide solutions, formed ten-boron heteroatom boranes. Attempts to prepare the $B_9H_{12}X^-$ ions by the reaction of the $B_9H_{14}^-$ ion with polyselenide (Se_x^{2-}) or polytelluride (Te_x^{2-}) solutions failed. In the selenium case, rapid mixing of $B_9H_{14}^-$ and Se_x^{2-} solutions produced $B_9H_9Se_2$ in high yield.[8] Slow addition of Se_x^{2-} to $B_9H_{14}^-$ produced an inseparable mixture similar to that described for the $B_9H_{12}S^-$–$B_9H_{14}^-$ mixture.[1] In the analogous tellurium reaction only starting materials were isolated.

The borane–ligand complex $B_9H_{13}{\cdot}S(CH_3)_2$, however, reacts with Se_x^{2-} and Te_x^{2-} solutions to produce the desired $B_9H_{12}X^-$ ions. The tellurium derivative can be isolated from the reaction mixture by precipitation with aqueous tetramethylammonium chloride solution to give the impure $(CH_3)_4N[B_9H_{12}Te]$ (III) in 70% yield. The isolation of the $B_9H_{12}Se^-$ ion was complicated by the presence of an additional air-sensitive selenaborane anion which coprecipitates when aqueous tetramethylammonium chloride solution is added to the reaction mixture. These two materials can be separated by passing the mixed precipitate through an H^+ ion-exchange column by using acetonitrile as the solvent. In this process, the air-sensitive salt is converted to $B_8H_{10}Se_2$ (II). This compound precipitates when the eluant is mixed with water and then rotary evaporated to remove the acetonitrile. The $B_9H_{12}Se^-$ ion remains in solution as the hydronium salt and can be isolated as $(CH_3)_4N[B_9H_{12}Se]$ (I) by precipitation with aqueous tetramethylammonium chloride solution.

Both I and III appear to have limited stability, as shown by the difficulty in obtaining good elemental analyses from samples which give clean ^{11}B and ^{1}H NMR spectra. The identity of these compounds is confirmed by their subsequent chemistry and the similarity of their ^{11}B NMR spectra with that of the $B_9H_{12}S^-$ ion (described below).

The chemistry of $B_8H_{10}Se_2$ (II), which is a coproduct in the synthesis of I, will be discussed in a subsequent paper.

Chemistry of the $B_9H_{12}X^-$ Ions. The chemistry of I and III appears to parallel that of the $B_9H_{12}S^-$ ion.[9,10] Reaction of I and III with one equivalent of iodine, in a neutral solvent such as benzene, produces the hygroscopic molecules $B_9H_{11}Se$ (IV) and $B_9H_{11}Te$ (V), respectively. Compound IV was sublimed from the reaction mixture after removal of the solvent and then isolated under dry atmosphere conditions. Attempts to isolate V failed due to its thermal instability, but its identity was established by the similarity of the area ratio pattern and coupling constants in its ^{11}B NMR spectrum relative to IV and $B_9H_{11}S$.

Molecules IV and V are acidic (in the Lewis sense) and will form acid–base adducts when reacted with basic solvents. The compounds $B_9H_{11}Se{\cdot}CH_3CN$ (VI) and $B_9H_{11}Te{\cdot}CH_3CN$ (VII) were obtained by oxidation of the salts I and III, respectively, with iodine in the presence of CH_3CN. Reaction of VI with triethylamine formed $B_9H_{11}Se{\cdot}N(C_2H_5)_3$ (VIII) in a rapid ligand displacement reaction. The ^{1}H NMR spectra of VI and VII (see Table II) contain two solvent-dependent singlet resonances in the spectral region where one methyl group signal was expected. A similar finding was observed previously for $B_9H_{11}S{\cdot}CH_3CN$.[1] This observation is still not understood.

The formation of *closo*-B_9H_9Se (IX) by pyrolysis (380 °C) of IV in a flow-through reactor system also parallels that of known thiaborane chemistry;[9,10] however, the presence of cage coupled products was not observed by mass spectral or GLC experiments. Compound IX was purified by sublimation at 40 °C under vacuum because minor amounts of $B_{11}H_{11}Se$ (identified by mass spectral analysis and comparison of its ^{11}B NMR with that of an authentic sample) were also obtained during the pyrolysis. The pyrolysis of the triethylamine adduct, compound VIII, as an alternative method for the formation of B_9H_9Se was studied. The only borane isolated from this pyrolysis was $B_{11}H_{11}Se$ in 10–15% yield. A possible reaction sequence in this pyrolysis may be the initial formation of triethylamine–borane, by partial degradation of some of the starting material, which could then insert B–H units into the remaining $H_9H_{11}Se$ to form the observed product. The effectiveness of trialkylamine–borane as a B–H insertion reagant

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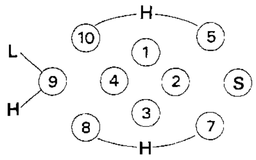

Figure 1. Structure and numbering system for $B_9H_{11}S{\cdot}L$ (L = H^- or $(C_2H_5)_3N$).

has been shown in its reaction with $B_{10}H_{12}Se$ to form $B_{11}H_{11}Se$ in refluxing xylenes.[11]

^{11}B NMR Spectra. The ^{11}B NMR spectrum of $CsB_9H_{12}S$ has been assigned as B(4), B(5,7), B(2), B(9), B(8,10), and B(1,3) reading upfield (see Figure 1 for numbering system).[4] The spectra of $(CH_3)_4N[B_9H_{12}X]$ (X = S, Se, and Te) in acetonitrile solution (see Table III) show a low-field doublet of area 1 and two doublets of area 2 at high field, one of which shows additional bridge hydrogen coupling. The triplet resonance in the −10 to −15 ppm region seen for the sulfur and selenium compounds is not observed in the tellurium compound probably due to the combined shift to lower field of the triplet and upfield shift of an area 2 resonance. With allowances made for the overlap of the area 2 and area 1 resonances in the −7 to −10 ppm range, a similar ^{11}B NMR assignment to that of $B_9H_{12}S^-$ for the $B_9H_{12}Se^-$ and $B_9H_{12}Te^-$ ions is reasonable.

With this presumed assignment, a decrease in shielding S > Se > Te is seen for the B(4) [Δ = 3.5 ppm],[12] B(9) [Δ = 5 ppm], B(8,10) [Δ = 8 ppm], and B(1,3) [Δ = 1 ppm] resonances of the $B_9H_{12}X^-$ compounds. The resonance due to B(5,7) and B(2), which are adjacant to the heteroatom, shows an upfield shift in the case of the $B_9H_{12}Te^-$ ion. This may be due to a diamagnetic contribution to the shielding from the larger tellurium atom.[16]

There are similarities in the ^{11}B NMR spectra of the $B_9H_{12}X^-$ ions relative to that of the $B_9H_{11}X{\cdot}L$ (L = Lewis base) molecules. These observations might be expected due to the fact that X-ray crystal studies of $CsB_9H_{12}S$[13] and $B_9H_{11}S{\cdot}N(C_2H_5)_3$[14] reveal similar structures for both compounds. The ^{11}B NMR spectrum of $B_9H_{11}S{\cdot}HCON(CH_3)_2$ contains resonances at 2.2, −0.1, −7.8 (145), −15.3 (165), −33.1 (140), and −38.4 ppm (J_{BH} = 145 Hz) with relative areas 1:1:2:1:2:2, respectively. With use of proton decoupling and a specifically deuterium-labeled derivative, the spectrum has been assigned as B(4), B(9), B(5,7), B(2), B(8,10), B(1,3), respectively, reading upfield.[17] From comparison of these results with the assignment found for $CsB_9H_{12}S$, it is clear that the B(9) and B(2) resonances experience large changes in shielding and actually exchange relative positions in the spectrum. The chemical shift variations of these two signals among different $B_9H_{11}X{\cdot}L$ derivatives is not known at present. However, the shielding variations for B(4), B(5,7), B(8,10), and B(1,3) appear to be consistent. The same trends in shielding of these later four resonances of $B_9H_{11}X{\cdot}CH_3CN$ are observed as were found for the $B_9H_{12}X^-$ ions described above.

For the $B_9H_{11}X$ (X = S, Se, or Te) class of molecules bridge hydrogen coupling to an area 1 resonance in the 15–18 ppm region and to an area 2 resonance in the −7 to −11 ppm region[3] allows assignment of these two resonances to B(9) and B(8,10), respectively (the same numbering given in Figure 1 is used here). With these limited assignments it appears that the shielding trends for various boron positions in $B_9H_{12}X^-$ and $B_9H_{11}X{\cdot}CH_3CN$ will not coincide with the shielding trends observed for $B_9H_{11}X$. This is not surprising since *arachno*-$B_9H_{12}X^-$ and *nido*-$B_9H_{11}X$ have different electronic structures.

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