Inorg. Chem. **1980**, *19*, 458-462

Contribution from the Department of Chemistry† and Molecular Structure Center,
Indiana University, Bloomington, Indiana 47405

Chemistry of Dithia-, Selenathia-, and Diselenaboranes

G. DELBERT FRIESEN, ANTONIO BARRIOLA, PAUL DALUGA, POLLY RAGATZ, JOHN C. HUFFMAN, and LEE J. TODD*

Received July 17, 1979

Treatment of $B_9H_{12}S^-$ with potassium polyselenide formed B_9H_9SSe. Reaction of $B_9H_{12}S^-$ with potassium polysulfide, with a small amount of polyselenide present, generated $B_9H_9S_2$. The ^{11}B NMR spectra suggest that these two molecules have structures very similar to that of the previously reported $B_9H_9Se_2$. Treatment of $B_9H_9Se_2$ (or B_9H_9SSe) with potassium hydroxide followed by reaction of the products with triethylamine, C_5H_6, and $CoCl_2$ formed $B_9H_9Se_2Co(C_5H_5)$ [or $B_9H_9SSeCo(C_5H_5)$]. The X-ray structure of $B_9H_9Se_2Co(C_5H_5)$ shows it to be a 12-vertex nido cage. The closo compound $B_9H_9Se[Co(C_5H_5)]_2$ was also isolated from the reaction with $CoCl_2$. Reaction of B_9H_9SSe with potassium hydroxide and subsequent reaction with aqueous HCl formed B_7H_9SSe.

Introduction

We had reported the formation of $B_9H_9Se_2$ as an unexpected minor product during the synthesis of $B_{10}H_{11}Se^-$.[1] Recently we have discovered that this diselenaborane can be made in good yield by reaction of $B_9H_{14}^-$ with potassium polyselenide.[2] It is probable that during the synthesis of $B_{10}H_{11}Se^-$ from $B_{10}H_{14}$ in strong aqueous base some of the decaborane was converted to $B_9H_{14}^-$ which then reacted with the polyselenide reagent to give $B_9H_9Se_2$. The syntheses of B_9H_9SSe and $B_9H_9S_2$ have also been developed employing $B_9H_{12}S^-$ as the starting material. With a reasonable supply of these nido heteroatom boranes now available, we have studied some reactions of these compounds with strong base. In certain cases the borane degradation products have been incorporated into novel cobalt complexes.

Experimental Section

The boron-11 NMR spectra were obtained at 70.6 MHz with a Varian HR-220 spectrometer and were externally referenced to $BF_3{\cdot}O(C_2H_5)_2$ (with positive values downfield). Proton NMR spectra were obtained by using a Varian T-60-A or a HR-220 spectrometer. Infrared spectra were obtained as KBr disks by using a Perkin-Elmer 283 spectrometer. Ultraviolet-visible spectra were recorded on a Cary 14 instrument. Low-resolution mass spectra were obtained on an Atlas CH-7 instrument. High-resolution mass spectra were obtained on an AEI MS-902 spectrometer.[3] Melting points were obtained in evacuated sealed capillaries and are uncorrected. All reactions were carried out under an atmosphere of prepurified nitrogen. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

$B_9H_9Se_2$. A solution containing the $B_9H_{14}^-$ ion was prepared, according to the literature method,[4] in a two-neck, 50-mL round-bottom flask, fitted with a magnetic stirrer. Twenty milliliters of water, 1.51 g of (12.4 mmol) $B_{10}H_{14}$, and 1.39 g (24.7 mmol) of KOH were added to the reaction flask and stirred until the resulting solution turned colorless (approximately $^1/_2$ h). Concentrated aqueous HCl was added dropwise, causing gas evolution until a neutral solution was formed. Trace amounts of regenerated $B_{10}H_{14}$ were removed from the aqueous solution by extraction with hexanes.

A polyselenide solution was prepared in a two-neck, 250-mL round-bottom flask fitted with a magnetic stirrer and a reflux condenser. Thirty milliliters of water, 3.47 g (61.8 mmol) of KOH, and 4.88 g (61.8 mmol) of powdered selenium were added to the flask, refluxed 20 min, and then cooled to room temperature.

The solution containing the $B_9H_{14}^-$ ion was added as rapidly as possible to the stirred polyselenide solution. An immediate formation of white precipitate occurred. After the reagents were combined, the mixture was stirred at room temperature for 1 h. The reaction mixture was then extracted with several 50-mL portions of hexane until no further solid was observed when a given portion of hexane extract was evaporated to dryness. The combined portions of hexane were rotary evaporated, leaving the crude $B_9H_9Se_2$ which was then sublimed at 60 °C (10^{-2} torr) onto a water-cooled probe. White $B_9H_9Se_2$, 2.81 g (86% yield based on $B_{10}H_{14}$ used), was obtained.

Intermediate from Reaction of $B_9H_9Se_2$ with Hydroxide Ion (I). Absolute ethanol, 70 mL, and 430 mg (7.76 mmol) of KOH were added to a two-neck, 250-mL round-bottom flask fitted with a magnetic stirrer. The mixture was stirred until the KOH completely dissolved. Then 1.00 g (3.88 mmol) of $B_9H_9Se_2$ was added, and the resulting mixture was stirred for an additional 4 h. Saturated aqueous tetramethylammonium chloride was added to the reaction mixture until no further precipitation was observed. The resulting orange precipitate was removed by filtration in air, washed with two 10-mL portions of water, and air-dried on the filter. The precipitate was dissolved in acetone and crystallized by rotary evaporation from acetone/benzene. The excess benzene was removed by filtration. The resulting small red-orange crystals were redissolved in 25 mL of acetone, 25 mL of absolute ethanol was added, and the resulting solution was slowly rotary evaporated. The excess ethanol was removed by filtration and the solid was air-dried, resulting in 740 mg of red crystalline material (I). In a sealed capillary this material decolorizes at approximately 220 °C and melts with decomposition at 240-243 °C. Anal. Calcd for $C_4H_{22}NB_9Se_2O$: C, 13.51; H, 6.24. Found: C, 13.70; H, 6.47. Proton NMR spectrum (acetone-d_6 solvent): 3.45 ppm ($N(CH_3)_4$ group). The trimethylammonium salt was made by the same reaction. Anal. Calcd for $C_3H_{20}NB_9Se_2O$: C, 10.55; H, 5.91; B, 28.50. Found: C, 10.33; H, 6.15; B, 28.43.

$B_9H_9Se_2(C_5H_5)$ (II) and $B_9H_9Se[Co(C_5H_5)]_2$ (III). Twenty milliliters of dry tetrahydrofuran, 2 mL of triethylamine, 0.7 mL of freshly cracked cyclopentadiene, and 200 mg of compound I were added to a 100-mL, two-neck flask and stirred magnetically for a few minutes before 400 mg of anhydrous $CoCl_2$ was added. The resulting mixture was stirred 4 h and then opened to the air and stirred an additional 0.5 h. The reaction mixture was rotary evaporated to dryness and the resulting solid placed on a short silica gel column and eluted with CH_2Cl_2. The resulting dark band was collected, a small amount of silica gel added, the solvent removed by rotary evaporation, and then the residue vacuum-dried. The coated silica gel was placed on a 1 × 7 in. silica gel column and eluted with benzene. A small unidentified yellow band preceded a dark green band and then a dark red band.

The dark green fraction was rotary evaporated and the resulting solid was recrystallized from CH_2Cl_2/hexane, resulting in 13 mg of green plates of $B_9H_9Se_2Co(C_5H_5)$ (II). The low-resolution mass spectrum shows a cutoff at m/e 392 corresponding to the $^{12}C_5{}^1H_{14}{}^{11}B_9{}^{59}Co^{80}Se_2{}^+$ ion. No melting point was observed up to 500 °C. Proton NMR spectrum (acetone-d_6 solvent): 5.9 ppm (br, cyclopentadienyl group). UV-visible spectrum (CH_3CN solvent) [λ_{max}, nm (ϵ)]: 450 (1.28×10^3), 279 (2.26×10^4), 257 sh (1.97×10^4). A suitable crystal for X-ray structure analysis (vide infra) was obtained by dissolving the plates in a small amount of acetone, carefully placing a layer of *n*-heptane over the acetone solution, and then allowing slow diffusion of the two layers.

The dark red chromatography fraction was isolated in a similar manner, resulting in 16 mg of red plates, mp 286-288 °C dec. The

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† Contribution No. 3369.

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(2) Friesen, G. D.; Barriola, A.; Todd, L. J. *Chem. Ind.* (*London*) **1978**, 631.
(3) The authors are indebted to Dr. Donald F. Gaines, Chemistry Department, University of Wisconsin, and Dr. Sheldon Shore, Chemistry Department, The Ohio State University, for obtaining the high-resolution mass spectra.
(4) Benjamin, L. E.; Stafiej, S. F.; Takacs, E. A. *J. Am. Chem. Soc.* **1963**, *85*, 2674.

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Table I. Crystal and Diffractometer Data[a]

temp: −118 ± 5 °C
space group: $P2_1/n$
$a = 11.340$ (2) Å
$b = 14.177$ (3) Å
$c = 7.861$ (3) Å
$\beta = 94.40$ (1)°
$Z = 4$
$D_{calcd} = 2.05$ g/cm³
cryst dimensions: 001, 0.200 mm; −1,0,0, 0.164 mm; 110, 0.164 mm; 1,0,−1, 0.176 mm; −1,0,1, 0.176 mm; −1,1,0, 0.128 mm; 1,−1,0, 0.128 mm
max and min abs cor ($\mu = 70.4$ cm^{-1}): 0.281, 0.128
Mo K$\bar{\alpha}$ radiation: λ 0.709 300
source to sample: 23.5 cm
sample to detector: 22.5 cm
receiving aperture: 2.5 × 4.0 mm
scan speed: 3.0°/min
scan width: 2.0° + dispersion due to Kα_1–Kα_2 separation
bkgd: 10 s at extremes of scan
ignorance factor: 0.07
collection limits: 3° ⩽ 2ϕ ⩽ 55°

[a] Cell parameters were based on refinement of angular data of 15 reflections centered at −118 ± 5 °C.

Table II. Atomic Coordinates and Isotropic Thermal Parameters

atom	$10^4x/a$	$10^4y/b$	$10^4z/c$	$10B_{iso}$, Å^2
Co(7)	2542 (0)	4049 (0)	1019 (1)	12[a]
Se(8)	3851 (0)	3045 (0)	−500 (1)	15
Se(12)	1916 (0)	2618 (0)	2248 (1)	16
B(1)	1450 (4)	3379 (4)	−2902 (6)	16
B(2)	1188 (4)	4054 (3)	−1095 (6)	14
B(3)	2622 (4)	3999 (4)	−1848 (6)	16
B(4)	2815 (4)	2791 (4)	−2789 (6)	16
B(5)	1526 (4)	2163 (3)	−2251 (7)	16
B(6)	488 (4)	2936 (4)	−1448 (7)	18
B(9)	2788 (5)	1924 (4)	−997 (7)	20
B(10)	1248 (4)	2061 (4)	−87 (7)	18
B(11)	747 (3)	3335 (3)	706 (6)	14
C(1)	3521 (5)	5270 (4)	1123 (7)	26
C(2)	3896 (4)	4679 (3)	2542 (6)	21
C(3)	2913 (5)	4552 (4)	3477 (6)	23
C(4)	1936 (4)	5038 (4)	2632 (8)	30
C(5)	2343 (5)	5478 (4)	1203 (8)	30
H(1)	1099 (35)	3588 (34)	−4399 (52)	7 (8)
H(2)	679 (50)	4749 (40)	−1295 (72)	22 (11)
H(3)	3044 (38)	4525 (36)	−2364 (56)	8 (8)
H(4)	3235 (47)	2726 (37)	−3756 (69)	17 (10)
H(5)	1246 (48)	1495 (42)	−2802 (68)	21 (11)
H(6)	−403 (53)	2877 (44)	−1841 (76)	25 (12)
H(7)	3186 (36)	1277 (33)	−863 (54)	6 (8)
H(8)	774 (43)	1544 (38)	−52 (62)	15 (10)
H(9)	−211 (33)	3507 (29)	1238 (50)	0 (7)
H(10)	3846 (54)	5385 (44)	420 (78)	23 (13)
H(11)	4730 (59)	4362 (51)	2924 (82)	39 (14)
H(12)	3236 (43)	4203 (37)	4454 (66)	11 (9)
H(13)	1143 (80)	5096 (69)	2899 (117)	69 (23)
H(14)	1953 (62)	5838 (51)	540 (89)	38 (16)

[a] The isotropic equivalent of those atoms refined anisotropically are given.

low-resolution mass spectrum shows a cutoff at m/e 436 corresponding to the $^{12}C_{10}{}^{1}H_{19}{}^{11}B_9{}^{59}Co_2{}^{80}Se^+$ ion. The high-resoluion mass determination of this peak gave a value of m/e 436.0135 (calcd 436.0154). Proton NMR spectrum (acetone-d_6 solvent): 5.44 ppm (cyclopentadienyl group). UV–visible spectrum (CH_3CN solvent) [λ_{max}, nm (ϵ)]: 423 (1.15 × 10³), 299 (2.95 × 10⁴), 258 (1.31 × 10⁴).

Crystallography of $B_9H_9Se_2Co(C_5H_5)$. Crystal and diffractometer data are given in Table I. The diffractometer used was a Picker four-circle goniostat equipped with a Furnas monochromator (graphite crystal, 0.02 plane) and controlled by a locally designed and constructed interface to a TI 980B minicomputer. The sample was cooled to −118 ± 5 °C by using a liquid-nitrogen boiloff cooling system of local construction.[10]

A total of 3039 unique structure amplitudes with $+h,+k,\pm l$ were collected, of which 2789 had intensities greater than their estimated standard deviations based on counting statistics, and the latter were used in the refinement. A partially redundant set of data with $-h,+k,\pm l$ was collected to check the validation of the absorption correction, but the latter were not used in the final data.

Direct methods located the two selenium atoms and the cobalt atom, and their positions were confirmed by Patterson techniques. A Fourier[11] map based on the phases of these atoms was used to locate all remaining nonhydrogen atoms. Anisotropic refinement rapidly converged to $R(F)^{12} = 0.062$ and $R_w(F) = 0.082$. A difference Fourier map located all hydrogen atoms, and the latter were included in the final refinement. Final residuals were $R(F) = 0.037$ and $R_w(F) = 0.055$. The goodness of fit for the last cycle was 1.44, and an isotropic extinction parameter which was included in the refinement converged to 4.6 (8) × 10⁻⁷. A final difference Fourier map was essentially featureless with the largest peak less than 0.5 e/Å³.

Final positional parameters are given in Table II.

$B_9H_9S_2$ (IV). Selenium (0.79 g, 0.01 mol) and a solution of KOH (22.4 g, 0.4 mol) in 65 mL of H_2O were introduced into a 200-mL round-bottom flask fitted with a water-cooled condenser, a nitrogen inlet, and a magnetic stirrer. The solution was heated with a heating mantle, while stirring, and refluxed for 15 min, producing a red dilute polyselenide solution. Sulfur (12.8 g, 0.4 mol) was next added to the hot, dilute polyselenide solution. The solution was allowed to reflux an additional 15 min, resulting in a reddish brown solution which was cooled to room temperature. Forty milliliters (0.04 mol) of a previously prepared 1 M $K^+B_9H_{12}S^-$ solution[9] was added to the reaction mixture dropwise via a pressure-compensated addition funnel. No immediate reaction was apparent so the reaction mixture was allowed to stir overnight (∼11 h). The reaction mixture was then extracted with 3 × 30 mL of hexane in order to remove the neutral species from the aqueous medium. Reduction of the hexanes on a rotary evaporator yielded 365 mg of a white, acrid-smelling solid, which was determined to be a mixture of $B_9H_9S_2$ and B_9H_9SSe by ^{11}B NMR. Purification of this crude product was achieved by means of preparatory scale gas chromatography. A Varian Associates Model 2700 gas chromatograph fitted with a ³/₈ in. × 6 ft OV 17 preparatory scale column, isothermal at 200 °C, afforded a good separation of the crude products as evidenced by two distinct peaks at retention times of 2 and 4 min. Twelve 100-μL injections of a saturated CH_2Cl_2 solution (120 mg/mL) yielded 60 mg of pure white, crystalline $B_9H_9S_2$ from the first peak (mp 275–276 °C dec). The low-resolution mass spectrum cutoff at m/e 172 corresponded to $^{11}B_9{}^{1}H_9{}^{32}S_2$. The high-resolution mass spectral determination contained a peak at m/e 172.0989 (calcd for $^{11}B_9{}^{1}H_9{}^{32}S_2$ 172.0983).

B_9H_9SSe (V). The polyselenide reagent was prepared as described for compound IV from 3.9 g of selenium and 2.8 g of KOH in 25 mL of water. An aqueous solution of $K(B_9H_{12}S)$ was prepared according to the literature procedure.[5] Fifty milliliters of 0.1 M $K(B_9H_{12}S)$ was placed in a 250-mL flask having a nitrogen inlet and magnetic stirring. The polyselenide reagent was then added in one portion with rapid stirring. After 10 min, white solid B_9H_9SSe began to precipitate from solution and gas evolution was observed. The mixture was stirred at room temperature for 3 h until gas evolution ceased. The reaction mixture was extracted with 25 × 4 mL of hexane to remove the B_9H_9SSe from aqueous solution. The hexane extracts were evaporated, leaving the crude B_9H_9SSe which was then sublimed at 60 °C (10⁻² torr) onto a water-cooled probe. White B_9H_9SSe (V), 1.6 g (17% yield), was obtained (mp 313–315 °C). Anal. Calcd for B_9H_9SSe: B, 44.77. Found: B, 44.31. The high-resolution mass spectrum contained a parent ion peak at m/e 220.0411 corresponding to the $^{11}B_9{}^{1}H_9{}^{32}S^{80}Se^+$ ion (calcd 220.0429).

$B_9H_9SSeCo(C_5H_5)$ (VI). Potassium hydroxide, 0.13 g, was dissolved in 15 mL of methanol in a flask fitted with a nitrogen inlet and magnetic stirring bar. To this solution B_9H_9SSe (0.4 g, 0.0018 mol) was added and the mixture stirred at room temperature for 20 min. The methanol was removed under vacuum, and then 20 mL of THF and 1.5 mL of triethylamine were added. This mixture was stirred for 1 h at room temperature and then 0.5 mL of freshly cracked cyclopentadiene and cobalt(II) chloride (0.3 g, 0.0023 mol) were added. This mixture was stirred for 20 h under nitrogen, and then the solution was opened to the air and stirring continued for 3 h more. The mixture was evaporated to dryness. The solid residue was dissolved in benzene

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Table III. ^{11}B NMR Spectra

compd (area ratios)	shift, ppm (J_{BH}, Hz)
I[a,b] (2:1:2:2:1:1)	−0.9 (150), −2.5 (150), −3.5 (145), −10.6 (162), −44.5 (140), −46.6 (150)
II[c] (1:2:2:1:1:2)	27.8 (161), 14.0 (166), ~0.0, ~2.1, ~−4.5, −22.4 (158)
III[c] (2:3:1:2:1)	25.7 (134), ~13.4, (~150), ~11.1, 0.1 (149), −8.0 (139)
IV (7:1:1)	~−2.5, −11.4 (176), −37.1 (156)
V (3:4:1:1)	−1.1, −2.6, −10.5 (176), −36.2 (152)
VI[d] (1:2:3:1:1:1)	25.4 (176), 10.4 (161), −1.3 (146), −3.9 (155), −20.3 (163), −24.6 (156)
VII[e] (1:1:1:1:1:1:1)	5.8, 4.6, −1.0 (166), −16.2 (176), −21.7 (185), −34.3 (171), −48.9 (152)

[a] CH_3CN solvent. [b] Shifts and coupling constants obtained from partially relaxed spectra. [c] Acetone-d_6 solvent. [d] CH_2Cl_2 solvent. [e] Hexane solvent.

Table IV. Infrared Spectra

compd[a]	absorption, cm^{-1}
I	3010 w, 2512 vs, 1475 s, 1410 w, 1280 w, 1256 w, 1000 m, br, 942 m, 810 w, br, 720 w, br, 665 w, br, 500 w, br
II	3098 m, 2580 s, 2550 s, 2505 s, 1420 m, 1410 m, 1058 w, 995 s, 940 w, 880 w, 841 m, 776 w, 720 w, 678 w, 495 w
III	3097 m, 2495 vs, 1420 m, 1410 m, 1057 w, 1010 m, 980 s, 921 w, 858 m, 832 s, 821 s, 670 w, 500 w, 450 w, 420 m
IV	2600 vs, 2560 vs, 1004 s, 982 m, 902 w, 885 w, 795 w, 790 w, 760 m, 732 w, 684 w, 630 w
V	2600 s, 2560 s, 1260 m, 1000 m, 980 m, 905 m, 888 m, 795 m, 765 m

[a] Obtained as KBr disks.

and chromatographed on a 18 cm × 2 cm Florisil column with benzene as eluant. A dark green band was eluted. This fraction was evaporated to dryness and the resulting solid crystallized from CH_2Cl_2/hexane to give 0.05 g (7% yield) of $B_9H_9SSeCo(C_5H_5)$ (VI). The air-stable green crystals exhibited a parent ion peak in the mass spectrum at *m/e* 344.0125 corresponding to the $^{12}C_5{}^1H_{14}{}^{11}B_9{}^{32}S^{80}Se^{59}Co^+$ ion (calcd 344.0152).

B_7H_9SSe (VII). Potassium hydroxide, 0.17 g, was dissolved in 15 mL of methanol in a flask fitted with a nitrogen inlet and magnetic stirring bar. Solid B_9H_9SSe (0.3 g, 0.0015 mol) was added and the mixture stirred at room temperature for 0.5 h. The solvent was removed under vacuum and 20 mL of degassed water added to the yellow residue. Five milliliters of 5 M HCl was added to the solution, and then the mixture was extracted with 3 × 25 mL of hexane. The hexane extract was evaporated to dryness and the yellow solid sublimed at 0 °C (10^{-2} torr) to give B_7H_9SSe (0.06 g, 20% yield), mp 115–120 °C dec. The low-resolution mass spectrum contains an ion at *m/e* 197 corresponding to $^{11}B_7{}^1H_8{}^{32}S^{80}Se^+$.

Results and Discussion

Addition of an aqueous solution of KB_9H_{14} to a solution of potassium polyselenide formed $B_9H_9Se_2$ in good yield. The availability of usable quantities of this selenaborane has allowed us to study some of the chemical properties of this neutral nido molecule.

Ethanolic KOH reacted with $B_9H_9Se_2$ to form an anionic product (I) which was obtained in crystalline form as a tetramethylammonium salt. Elemental analyses for two different salts suggested that I has the composition $M^+(B_9H_{10}Se_2O^-)$. The ^{11}B NMR spectrum contains six doublets in a 2:1:2:2:1:1 area ratio. Since there are no singlets in this spectrum, the oxygen function may be attached to a selenium atom or a BH (oxygen group) may be present. The infrared spectrum does not show the presence of a hydroxyl group (see Table IV). Since the position of attachment of the oxygen group is uncertain, an X-ray structure of I is planned. Treatment of I with triethylamine, cyclopentadiene monomer, and $CoCl_2$ formed two cobalt-containing complexes each in low yield. The mass spectrum of the green complex (II) cutoff at *m/e* 392 corresponding to the formulation $B_9H_9Se_2Co(C_5H_5)$. The valence electron count for this molecule suggests that it should be a nido 12-atom structure. This was confirmed by a single-crystal X-ray diffraction study which revealed the structure given in Figure 1. The bond distances and angles are given in Tables V and VI. The overall geometry is that of a 13-vertex closo polyhedron with a vertex removed to form a distorted *five-membered* open-face. This structure is unique but related to that found previously for $(C_5H_5)Fe(CH_3)_4C_4B_7H_8$[5] and $[(C_5H_5)Co]_2C_4B_6H_{10}$[6] in which a *six-membered* open-face is formed upon removal of a vertex from the 13-vertex closo polyhedron. The nido structure of II fits the electron-counting rules for a 12-vertex, 28-skeletal-bonding-electron system.[7] It should be kept in mind as previously indicated[8] that several other 12-vertex, 28-electron systems have different nido structures than those described above. It appears that for large polyhedral cages that the local bonding requirements of different types of cage units play an important part in determining the overall geometry of a given molecule. The ^{11}B NMR spectrum obtained at room temperature has apparent symmetry not observed in the solid-state structure. This can be explained by accidental overlap of certain resonances in the spectrum or by a fluxional process which might be operating in solution at room temperature.

Table V. Important Distances in $B_9H_9Se_2Co(C_5H_5)$ (Å)

A	B	dist	A	B	dist
Se(8)	Co(7)	2.435 (1)	B(2)	B(6)	1.784 (7)
Se(8)	B(3)	2.160 (5)	B(2)	B(11)	1.845 (7)
Se(8)	B(4)	2.103 (5)	B(3)	B(4)	1.885 (7)
Se(8)	B(9)	2.015 (5)	B(4)	B(5)	1.789 (7)
Se(12)	Co(7)	2.378 (1)	B(4)	B(9)	1.872 (8)
Se(12)	B(10)	2.087 (5)	B(5)	B(6)	1.760 (7)
Se(12)	B(11)	2.004 (5)	B(5)	B(9)	1.708 (7)
Co(7)	C(1)	2.056 (5)	B(5)	B(10)	1.759 (7)
Co(7)	C(2)	2.076 (4)	B(6)	B(10)	1.812 (7)
Co(7)	C(3)	2.072 (5)	B(6)	B(11)	1.788 (7)
Co(7)	C(4)	2.045 (5)	B(9)	B(10)	1.948 (8)
Co(7)	C(5)	2.045 (5)	B(10)	B(11)	2.007 (7)
Co(7)	B(2)	2.175 (4)	C(1)	H(10)	0.71 (6)
Co(7)	B(3)	2.264 (5)	C(2)	H(11)	1.07 (7)
Co(7)	B(11)	2.270 (4)	C(3)	H(12)	0.96 (5)
C(1)	C(2)	1.434 (7)	C(4)	H(13)	0.94 (9)
C(1)	C(5)	1.373 (8)	C(5)	H(14)	0.83 (7)
C(2)	C(3)	1.393 (7)	B(1)	H(1)	1.25 (4)
C(3)	C(4)	1.425 (8)	B(2)	H(2)	1.15 (6)
C(4)	C(5)	1.394 (9)	B(3)	H(3)	0.99 (5)
B(1)	B(2)	1.757 (7)	B(4)	H(4)	0.93 (6)
B(1)	B(3)	1.748 (7)	B(5)	H(5)	1.08 (6)
B(1)	B(4)	1.753 (6)	B(6)	H(6)	1.04 (6)
B(1)	B(5)	1.798 (7)	B(9)	H(7)	1.02 (5)
B(1)	B(6)	1.756 (7)	B(10)	H(8)	0.91 (5)
B(2)	B(3)	1.775 (6)	B(11)	H(9)	1.22 (4)

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Table VI. Important Angles in $B_9H_9Se_2Co(C_5H_5)$ (Deg)

A	B	C	angle
Co(7)	Se(8)	B(3)	58.7 (1)
Co(7)	Se(8)	B(4)	101.4 (1)
Co(7)	Se(8)	B(9)	100.3 (2)
B(3)	Se(8)	B(4)	52.5 (2)
B(3)	Se(8)	B(9)	92.6 (2)
B(4)	Se(8)	B(9)	54.0 (2)
Co(7)	Se(12)	B(10)	93.7 (1)
Co(7)	Se(12)	B(11)	61.7 (1)
B(10)	Se(12)	B(11)	58.7 (2)
Se(8)	Co(7)	Se(12)	85.0 (0)
Se(8)	Co(7)	C(1)	99.5 (2)
Se(8)	Co(7)	C(2)	94.7 (1)
Se(8)	Co(7)	C(3)	124.8 (2)
Se(8)	Co(7)	C(4)	162.1 (1)
Se(8)	Co(7)	C(5)	133.5 (2)
Se(8)	Co(7)	B(2)	92.8 (1)
Se(8)	Co(7)	B(3)	54.6 (1)
Se(8)	Co(7)	B(11)	105.2 (1)
Se(12)	Co(7)	C(1)	151.6 (1)
Se(12)	Co(7)	C(2)	111.3 (1)
Se(12)	Co(7)	C(3)	87.7 (1)
Se(12)	Co(7)	C(4)	102.0 (2)
Se(12)	Co(7)	C(5)	141.1 (2)
Se(12)	Co(7)	B(2)	95.6 (1)
Se(12)	Co(7)	B(3)	114.5 (1)
Se(12)	Co(7)	B(11)	51.0 (1)
C(1)	Co(7)	B(2)	112.0 (2)
C(1)	Co(7)	B(3)	90.2 (2)
C(1)	Co(7)	B(11)	149.0 (2)
C(2)	Co(7)	B(2)	152.5 (2)
C(2)	Co(7)	B(3)	120.2 (2)
C(2)	Co(7)	B(11)	150.7 (2)
C(3)	Co(7)	B(2)	142.4 (2)
C(3)	Co(7)	B(3)	156.7 (2)
C(3)	Co(7)	B(11)	111.8 (2)
C(4)	Co(7)	B(2)	102.8 (2)
C(4)	Co(7)	B(3)	132.8 (2)
C(4)	Co(7)	B(11)	91.8 (2)
C(5)	Co(7)	B(2)	88.6 (2)
C(5)	Co(7)	B(3)	96.6 (2)
C(5)	Co(7)	B(11)	110.3 (2)
B(2)	Co(7)	B(3)	47.1 (2)
B(2)	Co(7)	B(11)	49.0 (2)
B(3)	Co(7)	B(11)	89.0 (2)
Co(7)	C(1)	C(2)	70.5 (3)
Co(7)	C(1)	C(5)	70.0 (3)
C(2)	C(1)	C(5)	108.8 (5)
Co(7)	C(2)	C(1)	68.9 (2)
Co(7)	C(2)	C(3)	70.2 (3)
C(1)	C(2)	C(3)	106.5 (4)
Co(7)	C(3)	C(2)	70.5 (3)
Co(7)	C(3)	C(4)	68.7 (3)
C(2)	C(3)	C(4)	108.5 (4)
Co(7)	C(4)	C(3)	70.8 (3)
Co(7)	C(4)	C(5)	70.1 (3)
C(3)	C(4)	C(5)	107.4 (4)
Co(7)	C(5)	C(1)	70.8 (3)
Co(7)	C(5)	C(4)	70.1 (3)
C(1)	C(5)	C(4)	108.9 (5)
B(2)	B(1)	B(3)	60.8 (3)
B(2)	B(1)	B(4)	114.9 (3)
B(2)	B(1)	B(5)	107.4 (3)
B(2)	B(1)	B(6)	61.1 (3)
B(3)	B(1)	B(4)	65.1 (3)
B(3)	B(1)	B(5)	109.2 (3)
B(3)	B(1)	B(6)	111.0 (3)
B(4)	B(1)	B(5)	60.5 (3)
B(4)	B(1)	B(6)	112.8 (4)
B(5)	B(1)	B(6)	59.4 (3)
Co(7)	B(2)	B(1)	117.6 (3)
Co(7)	B(2)	B(3)	69.1 (2)
Co(7)	B(2)	B(6)	113.3 (3)
Co(7)	B(2)	B(11)	68.2 (2)
B(1)	B(2)	B(3)	59.3 (3)
B(1)	B(2)	B(6)	59.5 (3)
B(1)	B(2)	B(11)	113.1 (3)
B(3)	B(2)	B(6)	108.5 (3)
B(3)	B(2)	B(11)	122.8 (3)
B(6)	B(2)	B(11)	59.0 (3)
Se(8)	B(3)	CO(7)	66.7 (1)
Se(8)	B(3)	B(1)	110.8 (3)
Se(8)	B(3)	B(2)	115.9 (3)
Se(8)	B(3)	B(4)	62.2 (2)
Co(7)	B(3)	B(1)	113.6 (3)
Co(7)	B(3)	B(2)	63.8 (2)
Co(7)	B(3)	B(4)	115.7 (3)
B(1)	B(3)	B(2)	59.8 (3)
B(1)	B(3)	B(4)	57.6 (3)
B(2)	B(3)	B(4)	107.9 (3)
Se(8)	B(4)	B(1)	113.2 (3)
Se(8)	B(4)	B(3)	65.3 (2)
Se(8)	B(4)	B(5)	107.2 (3)
Se(8)	B(4)	B(9)	60.6 (2)
B(1)	B(4)	B(3)	57.3 (3)
B(1)	B(4)	B(5)	61.0 (3)
B(1)	B(4)	B(9)	106.6 (3)
B(3)	B(4)	B(5)	103.7 (3)
B(3)	B(4)	B(9)	107.0 (3)
B(5)	B(4)	B(9)	55.6 (3)
B(1)	B(5)	B(4)	58.5 (3)
B(1)	B(5)	B(6)	59.2 (3)
B(1)	B(5)	B(9)	112.0 (3)
B(1)	B(5)	B(10)	110.3 (4)
B(4)	B(5)	B(6)	110.9 (3)
B(4)	B(5)	B(9)	64.7 (3)
B(4)	B(5)	B(10)	118.7 (3)
B(6)	B(5)	B(9)	118.1 (4)
B(6)	B(5)	B(10)	62.0 (3)
B(9)	B(5)	B(10)	68.3 (3)
B(1)	B(6)	B(2)	59.5 (3)
B(1)	B(6)	B(5)	61.5 (3)
B(1)	B(6)	B(10)	109.7 (3)
B(1)	B(6)	B(11)	116.0 (3)
B(2)	B(6)	B(5)	107.8 (3)
B(2)	B(6)	B(10)	109.3 (3)
B(2)	B(6)	B(11)	62.2 (3)
B(5)	B(6)	B(10)	59.0 (3)
B(5)	B(6)	B(11)	118.1 (3)
B(10)	B(6)	B(11)	67.8 (3)
Se(8)	B(9)	B(4)	65.4 (2)
Se(8)	B(9)	B(5)	114.6 (3)
Se(8)	B(9)	B(10)	112.9 (3)
B(4)	B(9)	B(5)	59.8 (3)
B(4)	B(9)	B(10)	106.1 (3)
B(5)	B(9)	B(10)	57.1 (3)
Se(12)	B(10)	B(5)	137.7 (3)
Se(12)	B(10)	B(6)	112.6 (3)
Se(12)	B(10)	B(9)	94.9 (3)
Se(12)	B(10)	B(11)	58.6 (2)
B(5)	B(10)	B(6)	59.0 (3)
B(5)	B(10)	B(9)	54.6 (3)
B(5)	B(10)	B(11)	107.6 (3)
B(6)	B(10)	B(9)	104.5 (3)
B(6)	B(10)	B(11)	55.5 (3)
B(9)	B(10)	B(11)	119.2 (3)
Se(12)	B(11)	Co(7)	67.3 (1)
Se(12)	B(11)	B(2)	122.6 (2)
Se(12)	B(11)	B(6)	117.7 (3)
Se(12)	B(11)	B(10)	62.7 (2)
Co(7)	B(11)	B(2)	62.8 (2)
Co(7)	B(11)	B(6)	108.9 (2)
Co(7)	B(11)	B(10)	99.3 (2)
B(2)	B(11)	B(6)	58.8 (3)
B(2)	B(11)	B(10)	99.1 (3)
B(6)	B(11)	B(10)	56.7 (3)

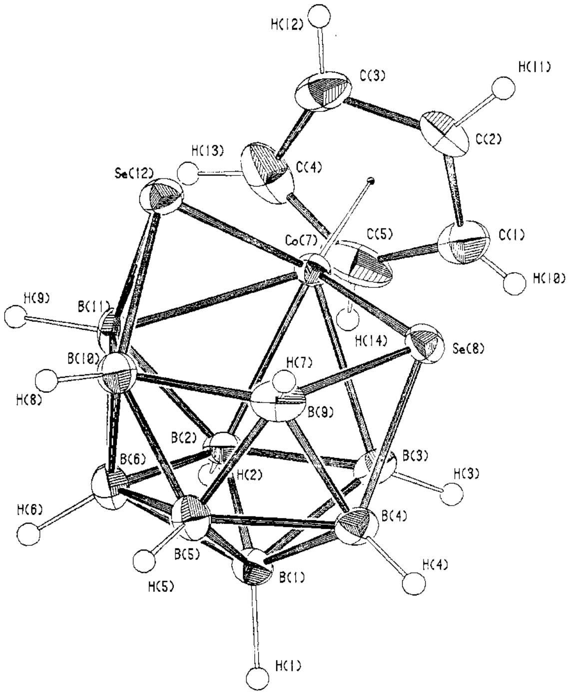

Figure 1. The structure of $B_9H_9Se_2Co(C_5H_5)$. The terminal hydrogen atoms have been omitted for clarity.

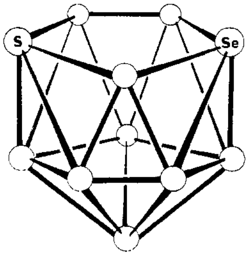

Figure 2. Proposed structure of B_9H_9SSe.

The dark red complex (III) obtained from the reaction described above had the formulation $B_9H_9Se[Co(C_5H_5)]_2$ as indicated by the high-resolution mass spectral study. Valence electron count suggests that III is probably a closo icosahedral molecule. The 2:3:1:2:1 resonance pattern in the ^{11}B NMR spectrum of III suggests the possibility of some symmetry for this molecule. However, we do not know the relative positions of the cobalt and selenium atoms in the cage structure. The formation of a monoselenium complex suggests that OH^- attack on $B_9H_9Se_2$ may be at selenium.

Previously we had reported that the polyselenide ion was a useful reagent for insertion of selenium into the molecules $B_9H_{14}^-$, $B_9H_{13}(SMe_2)$, and $B_7C_2H_{13}$ to form $B_9H_9Se_2$, $B_8H_{10}Se_2$, and $B_7C_2H_{11}Se$, respectively.[2] We have found that the polyselenide reagent will react with $B_9H_{12}S^-$ to form B_9H_9SSe (V) in low yield. The composition of this thiaselenaborane was determined by elemental analysis and a high-resolution mass spectral determination. The ^{11}B NMR spectrum of V is very similar to that of $B_9H_9Se_2$. The area one doublet at −10.5 ppm is unusually sharp. This feature may be due to reduced ^{11}B–^{11}B spin coupling of a boron atom on the open-face of the 11-atom nido structure which is situated between the sulfur and selenium atoms. On this basis we propose the structure given in Figure 2 for B_9H_9SSe. An X-ray structure determination of V was attempted, but the crystals were disordered.

Treatment of $B_9H_{12}S^-$ with potassium polysulfide alone did not lead to the formation of $B_9H_9S_2$. However, when a small amount of polyselenide ion was mixed with the polysulfide reagent and then reacted with $B_9H_{12}S^-$, a mixture of B_9H_9SSe and $B_9H_9S_2$ (IV) was formed. The role of selenium in the formation of IV is not understood at present. The new dithiaborane was purified by GLC. The composition was determined by a high-resolution mass spectral study. The ^{11}B NMR spectrum of IV has the characteristic pattern observed for $B_9H_9Se_2$[1] and B_9H_9SSe (see Table IV for NMR data).

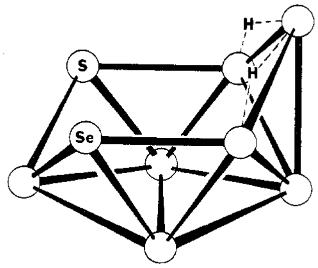

Figure 3. Proposed structure of B_7H_9SSe.

Treatment of V with potassium hydroxide in methanol at room temperature and subsequent reaction with triethylamine, cyclopentadiene, and cobalt(II) chloride formed green $B_9H_9SSeCo(C_5H_5)$ (VI) in low yield. The composition of this complex was determined by a high-resolution mass spectral study. The ^{11}B NMR spectrum of this thiaselena compound was quite similar to the spectrum of II. On this basis we suggest that VI has a similar structure to that determined for II.

Reaction of V with excess potassium hydroxide in methanol followed by removal of the solvent under vacuum gave a solid product residue. This was dissolved in water and a hexane layer placed over the aqueous mixture. Acidification of the mixture liberated a borane into the hexane layer. The solid obtained by evaporation of the hexane extract was further purified by sublimation to given B_7H_9SSe in low yield. Recently $B_7H_9S_2$ was prepared by reaction of $B_9H_{12}S^-$ with potassium hydrogen sulfite in aqueous acid.[9] The 70.6-MHz ^{11}B NMR spectrum of B_7H_9SSe exhibits seven doublets suggesting the absence of symmetry in the molecule. However, the chemical shift positions and line width characteristics of this spectrum are very similar to those reported for $B_7H_9S_2$.[9] A doublet of unit area with unusually narrow peaks at half-height is centered at −1.0 ppm. This is probably due to the boron atom on the open-face situated between the sulfur and selenium atoms. In this case ^{11}B–^{11}B coupling would be reduced. On this basis we propose the structure given in Figure 3 for the B_7H_9SSe molecule. This is the structure which is known for the *C,C′*-dimethyl derivative of $B_7C_2H_{13}$[13] and which has been proposed for $B_7H_9S_2$.[9] The "CH_2" units of $B_7C_2H_{13}$ are formally replaced with the isoelectronic "S" units in $B_7H_9S_2$.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE 78-08719.

Registry No. I, 72403-01-1; II, 72207-08-0; IV, 72207-43-3; V, 72207-44-4; VI, 72207-09-1; VII, 72214-09-6; $B_9H_9Se_2$, 61618-06-2; $B_{10}H_{14}$, 17702-41-9; $[HN(CH_3)_3][B_9H_{10}Se_2O]$, 72268-93-0; $K(B_9H_{12}S)$, 63105-95-3; potassium polyselenide, 50864-79-4; potassium polysulfide, 37199-66-9; KOH, 1310-58-3.

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(11) All computations were performed on a CYBER 172-CDC 6600 multiframe system using the IUMSC XTEL program library. The latter are interactive programs based in part on a code obtained from J. A. Ibers (Northwestern University) and A. C. Larson (Los Alamos Scientific Laboratory), as well as a local code.

(12) $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w(F) = [\sum w(||F_o| - |F||)^2/\sum w|F_o|^2]^{1/2}$ where $w = 1/\sigma(F)$.

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