Earlier studies[10] of $H_3P{\cdot}BF_3$ reported that not only was there a 1:1 adduct produced, *i.e.*, $H_3P{\cdot}BF_3$ but that the species $H_3P{\cdot}2BF_3$ was also produced. Our annealed spectral data did not confirm this in that all of the data are interpretable on the basis of a 1:1 adduct of C_{3v} symmetry. However, in the far-infrared spectrum of nonannealed $H_3P{\cdot}BF_3$ one can clearly see pairs of bands for the BF_3 symmetric deformation (A_1) and the BF_3 rock (E). Upon annealing it is evident that there is only one band for the BF_3 symmetric deformation and two bands for the BF_3 rocking motions. Since the BF_3 rocking is of E symmetry, it is split in the solid as were many of the other E modes of this series of adducts. Thus, it is concluded that this splitting is due to a lower site symmetry in the crystal compared to the molecular symmetry or due to two molecules per primitive cell in the crystal. Therefore, there was no evidence for a species such as $H_3P{\cdot}2BF_3$.

The nuclear magnetic resonance spectra of these phosphine-trihaloborane adducts serve to confirm results obtained by previous investigators.[31,32] The most extensive nmr study of these complexes is that of Rapp and Drake.[32] The failure of PH_3 and BF_3 to form an adduct in solution has been previously noted in a study in which CD_3I was used as a solvent. This failure of $H_3P{\cdot}BF_3$ to form a stable adduct is not surprising in view of the behavior[6,31] of $H_3P{\cdot}BCl_3$ in both C_6D_6 and CD_3I in which a rapid equilibrium exists which results in an averaging of the nmr signals of the adduct and the free species. In contrast to this behavior, $H_3P{\cdot}BBr_3$ appears to be completely stable in C_6D_6 solution with a relatively large phosphorus-boron coupling constant (J_{PB} = 127 Hz) in comparison with other phosphine-borane complexes.[33,34] However, it should be noted that the $Me_3P{\cdot}BX_3$ series (where X = F, Cl, Br) also exhibits[35,36] large J_{PB} values relative to BH_3 complexes. Our values for J_{PH}, J_{PB}, δ_{PH}, and δ_B in $H_3P{\cdot}BBr_3$ agree well with those[31,32] previously reported. The failure to observe experimental nmr parameters for the $H_3P{\cdot}BI_3$ adduct is thought to be simply a consequence of very low solubility in C_6D_6. Nmr parameters have been reported[31,32] for this molecule in CD_3I. The failure to observe a boron-phosphorus coupling constant in $H_3P{\cdot}BF_3$ and $H_3P{\cdot}BCl_3$ unfortunately prevents a meaningful correlation between J_{BP} and the boron-phosphorus stretching force constant in the $H_3P{\cdot}BX_3$ series. Earlier studies have indicated[37] that the B-P force constant is a measure of the stability of the adduct and a comparison of these values to J_{BP} values would be interesting. From the limited data available it appears that the invariance of the B-P stretching force constant is mirrored in the J_{BP} values for $H_3P{\cdot}BBr_3$ and $H_3P{\cdot}BI_3$[32] which are within experimental error of one another.

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Registry No. $H_3P{\cdot}BF_3$, 41593-56-0; $D_3P{\cdot}BF_3$, 52002-92-3; $H_3P{\cdot}BBr_3$, 38822-66-1; $D_3P{\cdot}BBr_3$, 52002-94-5; $H_3P{\cdot}BI_3$, 38822-60-5; $D_3P{\cdot}BI_3$, 52002-93-4.

Supplementary Material Available. Tables IV-IX, showing observed frequencies and calculated fundamentals for $H_3P{\cdot}BX_3$ and $D_3P{\cdot}BX_3$ (X = F, Br, I), will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2729.

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Chemical Studies of the $B_9H_{14}^-$ and $B_9H_{12}S^-$ Ions

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Chemical procedures are outlined for the *in situ* formation of the reactive anions $B_9H_{13}^{2-}$, $B_9H_{11}S^{2-}$, and $B_9H_9S^{2-}$. These compounds are used to produce the new derivatives 6-$PhB_{10}H_{13}$, $(B_9H_{11}S)_2M^{2-}$ (M = Ni, Pd), and $(B_9H_9S)Pd(ligand)_x{}^n$ [ligand = PPh_3 ($x = 2, n = 0$), phen ($x = 1, n = 0$), and $C_2S_2(CN)_2$ ($x = 1, n = 2-$)]. The syntheses of new $B_9H_{11}S{\cdot}$ligand (where the ligand is OH^-, tetrahydrofuran, and PPh_3) compounds are described. The chemical and spectral properties of these compounds are discussed.

Introduction

It has been previously reported that the $B_9H_{14}^-$ anion exchanges some terminal hydrogens with D_2O under basic conditions.[2] During an nmr study of the $B_9H_{12}S^-$ anion, it was found that D_2O under basic conditions causes H-D exchange involving the two bridge hydrogens and one of the hydrogens on the BH_2 group at the B(9) position.[3] These observations suggested that, if sufficiently strong bases were used, the anions $B_9H_{13}^{2-}$ and $B_9H_{11}S^{2-}$ might be obtained

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and insertion of new atoms into the cage might be accomplished. This paper describes the results of that study.

Experimental Section

^{11}B and ^{1}H nmr spectra were obtained at 70.6 and 220 MHz, respectively, with a Varian Associates HR220 spectrometer. The ^{11}B nmr chemical shifts were measured relative to an external $BF_3 \cdot O(C_2H_5)_2$ reference and ^{1}H nmr chemical shifts relative to internal TMS reference. Positive values for the nmr chemical shifts imply resonances which appear upfield from the reference.

A literature method[4] was used to convert $B_{10}H_{14}$ and 1,2,3,4-$B_{10}D_4H_{10}$ to $CsB_9H_{12}S$ and $CsB_9D_4H_8S$, respectively. The method of Benjamin, *et al.*,[5] was used to prepare CsB_9H_{14}.

6-Phenyldecaborane from $B_9H_{13}^{2-}$. A solution of 0.5 g (2 mmol) of CsB_9H_{14} in 15 ml of tetrahydrofuran was treated with 2 mmol of butyllithium in hexane. The resulting white slurry was stirred for 30 min and then the solvent was removed on the vacuum line. Toluene, 20 ml, was added and the mixture cooled in a Dry Ice bath. A solution of 0.35 ml of phenyldichloroborane in 5 ml of toluene was added dropwise with stirring. The cooling bath was then removed and the mixture was allowed to stir overnight. After this period the mixture was refluxed for 15 min. After cooling to room temperature, the reaction mixture was filtered and the solid phase washed with two 20-ml portions of toluene. The filtrate and washings were combined and evaporated under reduced pressure to give an oily residue which was extracted with 50 ml of boiling hexane. Concentration and cooling of the hexane extract afforded 0.05 g of phenylboronic acid, identified by its infrared spectrum. The mother liquor was evaporated and sublimed (90° (0.025 mm)) onto a water-cooled probe to afford 0.08 g of 6-phenyldecaborane as a colorless, viscous liquid, 40% yield. The mass spectrum contained a peak due to the parent ion at *m/e* 200.2371 (calcd for $^{12}C_6{}^{1}H_{18}{}^{11}B_{10}$, 200.2334).

6-$PhB_{10}H_{11}(PPh_3)_2$. A solution of 0.05 g of 6-phenyldecaborane, 0.2 g of triphenylphosphine, and 10 ml of toluene was refluxed for 14 hr. The solvent was removed under reduced pressure and the residue recrystallized three times from dichloromethane–ethanol to yield 0.03 g of small white crystals. Ir (KBr): 3030 (w), 2500 (s), 1481 (m), 1430 (s), 1260 (w), 1180 (w), 1150 (w), 1100 (s), 1025 (w), 1000 (m), 975 (m), 913 (br, m), 806 (br, m), 743 (w), 711 (m), and 689 (m) cm^{-1}. An analytical sample was purified by thin-layer chromatography (silica gel, chloroform).

$(Ph_3PCH_3)_2[(B_9H_{11}S)_2Pd]$. To a solution of 1.1 g (4 mmol) of $CsB_9H_{12}S$ in 20 ml of tetrahydrofuran was added 2.5 ml of a 1.6 *M* solution of butyllithium in hexane. A thick white precipitate formed as the addition proceeded. To the resulting suspension of $LiCsB_9H_{11}S$ was added 20 ml of acetonitrile. Palladium(II) acetylacetonate, 0.6 g (2 mmol), was added in small portions with a solid addition funnel. The reaction mixture was then stirred overnight and filtered through Celite. The filter pad was washed with tetrahydrofuran. The combined filtrate and washings were evaporated under reduced pressure and the residue was extracted with ethyl acetate. This extract was filtered, evaporated, and taken up in aqueous ethanol. Addition of ethanolic methyltriphenylphosphonium bromide afforded a gummy precipitate which was collected on a filter, washed with ethanol, and air-dried. An initial purification was accomplished by preparative thin-layer chromatography on silica gel developing with 1:1 acetone–chloroform. The fast-moving orange-yellow band was eluted with dichloromethane and subjected to three more cycles of thin-layer chromatography using dichloromethane as the solvent. A final recrystallization from acetonitrile–ethanol gave 0.2 g (12%) of product as deep red-brown needles, mp 207–208° dec. ^{1}H nmr (acetone-d_6): −7.8 (m, 5 H), −3.16 (d, $^{2}J_{PCH}$ = 15 Hz, 1 H). A broad singlet at +1.9 ppm was assigned to the bridge hydrogens. Ir (KBr): strong bands occurred at 2500, 1480, 1430, 1110, 1000, 900, 843, 784, 740, 719, and 709 cm^{-1}. Electronic spectrum (CH_3CN): λ_{max} 261 (ϵ 1.8×10^4), 269 (1.8×10^4), 331 (2.3×10^4), and 428 mμ (1.3×10^4).

$(Ph_3PCH_3)_2[(B_9H_{11}S)_2Ni]$. This complex was prepared in the same manner as the palladium analog using nickel(II) acetylacetonate which had been vacuum-dried at 90°. The reaction was run at −78° rather than at room temperature. The yield of deep red needles (from acetonitrile–ethanol), mp 226° dec, was 8%. The infrared spectrum is qualitatively like that of the palladium complex. ^{1}H nmr (acetone-d_6): in addition to peaks due to the cation, a broad singlet at +2.1 ppm, assigned to the bridge protons, was observed. Electronic spectrum (CH_3CN): λ_{max} 262 (ϵ 1.3×10^4), 268 (1.4×10^4), 275 (1.1×10^4), 319 (1.1×10^4), 384 mμ (1.4×10^4).

$B_9H_{11}S \cdot C_4H_8O$. A solution of 1.0 g (4 mmol) of iodine in 35 ml of tetrahydrofuran was added dropwise with stirring to 1.1 g (4 mmol) of $CsB_9H_{12}S$ in 30 ml of the same solvent. The iodine color was discharged and 0.8 g of cesium iodide separated. The reaction mixture was filtered under nitrogen and the filtrate was taken to dryness on the vacuum line. The residue was extracted with 20 ml of toluene and the extract filtered. Addition of hexane and cooling to −78° afforded 0.77 g (90%) of white crystalline product. This compound can be sublimed at 70° (0.001 mm) with 30% recovery. It melted with decomposition in the range 90–95°. ^{1}H nmr (C_6D_6): two multiplets at −3.26 and −0.87 ppm, assigned to the THF protons, and a broad singlet at +1.7 ppm, assigned to the bridge protons, were observed. The mass spectrum cut off at *m/e* 214, corresponding to the $^{12}C_4{}^{1}H_{19}{}^{11}B_9{}^{32}S^{16}O$ parent ion.

The tetrahydrofuranate need not be isolated and the toluene solution may be used directly in other reactions. For example, addition of acetonitrile afforded $B_9H_{11}S \cdot CH_3CN$, identified by its ^{11}B nmr and infrared spectra, in 94% yield based on $CsB_9H_{12}S$.

$B_9H_{11}S \cdot PPh_3$. A toluene solution containing 2 mmol of $B_9H_{11}S \cdot THF$ was treated with 0.52 g (2 mmol) of triphenylphosphine. After standing for 24 hr, the toluene was evaporated under reduced pressure and the residue recrystallized from dichloromethane–methyl ethyl ketone to give 0.5 g of product as white flakes, mp 209–210°. ^{1}H nmr ($CDCl_3$): the spectrum contained a complex multiplet centered at −7.5 ppm and a broad singlet due to the bridge protons at +1.6 ppm.

$(C_2H_5)_4N^+HOB_9H_{11}S^-$. To 0.5 g of $B_9H_{11}S \cdot PPh_3$ in 50 ml of acetonitrile was added 10 ml of aqueous tetramethylammonium hydroxide. The solution turned pale yellow but no gas was evolved. The solution was concentrated to a volume of 15 ml on a rotary evaporator without heating. The solids which formed were collected on a filter and washed with benzene. The benzene-insoluble solids were recrystallized from dichloromethane–toluene and then from dichloromethane–ethanol to give 0.12 g (33%) of product as small white crystals, decomposing at 292–294°. ^{1}H nmr (acetone-d_6): cation peaks at −3.41 and −1.35 ppm and a broad singlet due to the bridge protons at +1.6 ppm were observed. Ir (KBr): 3570 (w), 3330 (m, br), 2940 (m), 2530 (s), 1480 (s), 1430 (m), 1390 (s), 1180 (s), 1105 (w), 1005 (s, br), 787 (s), and 754 (w) cm^{-1}.

$(B_9H_9S)Pd(PPh_3)_2$. Solvent was removed on the vacuum line from a toluene solution containing 4 mmol of $B_9H_{11}S \cdot THF$. Tetrahydrofuran, 20 ml, was added. After cooling to −78° (Dry Ice bath), 5 ml of a 1.6 *M* solution of butyllithium in hexane was added slowly with stirring. The turbid yellow solution was stirred for 30 min after which 2.8 g (4 mmol) of $(Ph_3P)_2PdCl_2$ and 1.1 g of triphenylphosphine were added in one portion followed by 25 ml of acetonitrile. The cooling bath was removed and the mixture was stirred overnight. Solvent was then removed under reduced pressure and the residue taken up in benzene. The benzene extract was dissolved in dichloromethane and filtered. Evaporation of the dichloromethane solution afforded the crude product which was recrystallized from dichloromethane–carbon tetrachloride to give 0.75 g (25%) of small yellow needles, mp 201–202°. The melting point is not a good criterion of purity as it varies somewhat with the rate of heating. The ^{1}H nmr spectrum in 1,2-dichloroethane contained a broad multiplet centered at −7.4 ppm assigned to the phenyl protons. Ir (KBr): strong bands occurred at 2530, 1470, 1430, 1090, 1010, and 689 cm^{-1}. Electronic spectrum (1,2-$C_2H_4Cl_2$): λ_{max} 235 (ϵ 4.2×10^4) amd 316 mμ (1.8×10^3).

Pyrolysis of $(B_9H_9S)Pd(PPh_3)_2$. A suspension of 0.1 g of $(B_9H_9S)Pd(PPh_3)_2$ in 10 ml of sodium-dried mesitylene was refluxed under nitrogen for 12 hr during which time the color changed from yellow to orange-brown. The solvent was removed on the vacuum line. The residue was chromatographed on a 10 × 1 in. column of silica gel, eluting with chloroform. The fast-moving orange-brown band was collected. The product was recrystallized from dichloromethane–ethanol and then washed with cold acetone to give 0.03 g of orange-brown crystals, mp 282–285° dec. Ir (KBr): 3220 (w), 2550 (s), 1560 (w), 1470 (s), 1420 (s), 1165 (s), 1080 (s), and 1010 cm^{-1}.

$(B_9H_9S)Pd(C_{10}H_8N_2)$. Phenanthroline monohydrate, 0.17 g (1 mmol), was added to a solution of 0.15 g (0.19 mmol) of $(B_9H_9S)Pd(PPh_3)_2$ in 5 ml of 1,2-dichloroethane. After 24 hr, the yellow needles which had separated were collected on a filter, washed with dichloroethane, and vacuum-dried. The yield was 0.064 g (80%). The compound melted with decomposition at 260°. Ir (KBr):

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Table I. Elemental Analyses of Borane and Thiaborane Derivatives

	%									
	C		H		Metal		S		N	
Compd	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$6\text{-PhB}_{10}H_{11}(PPh_3)_2$	61.46	61.07	5.60	5.34						
$(Ph_3PCH_3)_2[(B_9H_{11}S)_2Pd]$	48.45	48.22	6.20	6.27	11.29	11.66	6.80	6.58		
$(Ph_3PCH_3)_2[(B_9H_{11}S)_2Ni]$	51.04	50.86	6.53	6.42	6.56	6.17	7.17	7.43		
$(Ph_3P)_2Pd(B_9H_9S)$ (yellow isomer)	56.25	56.22	5.08	5.75	13.80	14.27	4.17	3.60		
$B_9H_{11}S\cdot PPh_3$	53.73	53.75	6.47	6.65						
$(C_2H_5)_4N(HOB_9H_{11}S)$	33.45	33.63	11.15	10.73			11.15	10.88		
$(C_{10}H_8N_2)Pd(B_9H_9S)$	30.00	29.67	4.24	4.38					7.00	7.24
$(Ph_4As)_2\{[C_2S_2(CN)_2]Pd(B_9H_9S)\}$	54.26	54.32	4.26	4.56	9.22	9.35	8.35	8.46		
$(Ph_3P)_2Pd(B_9H_9S)$ (orange-brown isomer)	56.25	56.19	5.08	4.86						
$(Ph_3P)_2Pt(B_9H_9S)$	50.41	50.14	4.55	4.77	22.75	22.35	3.73	3.60		

strong bands occurred at 2530, 1500, 1410, 1025, 1010, 840, and 722 cm^{-1}. The complex was too insoluble in nonreactive solvents for nmr spectra to be obtained.

$(Ph_4As)_2(B_9H_9S)Pd[C_2S_2(CN)_2]$. A solution of 0.1 g of $(B_9H_9S)Pd(PPh_3)_2$ and 0.02 g of $Na_2C_2S_2(CN)_2$ in 25 ml of 1:1 dichloroethane–acetonitrile was stirred at room temperature for 36 hr. The solution was filtered and evaporated under reduced pressure. The residue was dissolved in aqueous ethanol containing a few drops of acetone and filtered to recover 0.02 g of $(B_9H_9S)Pd(PPh_3)_2$. The filtrate was treated with excess ethanolic tetraphenylarsonium chloride and then concentrated under a nitrogen jet to afford yellow needles of the product. Further purification was accomplished by three recrystallizations from ethanol–acetone, mp 192–193° dec. Electronic spectrum (CH_3CN): λ_{max} 235 (ϵ 6.6 × 10^4), 245 (sh), 260 (sh), 270 (2.8 × 10^4), 297 (2.6 × 10^4), 324 (sh), 404 mμ (8.0 × 10^3). Ir (KBr): B–H stretch at 2500 cm^{-1}, C≡N stretch at 2175 cm^{-1}, and additional bands at 1694 (w), 1587 (w), 1470 (s), 1430 (s), 1190 (s), 1140 (s), 1110 (s), 1080 (s), 1020 (s), 1000 (s), 740 (s), and 684 cm^{-1}.

$(B_9H_9S)Pt(PPh_3)_2$. This complex was prepared in the same manner as the palladium analog using $(Ph_3P)_2PtCl_2$ as the starting metal reagent. The reaction mixture was filtered and the filtrate evaporated under reduced pressure. The residue was dissolved in dichloromethane, diluted with ethanol, and concentrated on a rotary evaporator without heating until yellow needle crystals separate. Acetone was added dropwise to the mixture to complete the crystallization of the yellow compound. This compound contains no B–H band in its infrared spectrum and is probably $(Ph_3PS)_2PtCl_2$. The filtrate from the isolation of the boron-free compound was evaporated under reduced pressure and the residue crystallized three times from dichloromethane–ethanol to give yellow crystalline $(B_9H_9S)Pt(PPh_3)_2$ in 40% yield. Ir (KBr): 2531 (s), 2439 (sh), 1587 (m), 1428 (s), 1092 (s), 1030 (s), 1015 (s), 1000 (s), 757 (s), 740 (s), and 689 cm^{-1}. Electronic spectrum (CH_2Cl_2): λ_{max} 236 (ϵ 3.8 × 10^4), 282 (sh, 2.2 × 10^4), and 300 mμ (sh, 1.9 × 10^4). The ^{1}H nmr spectrum (acetone-d_6) contained a complex multiplet at −7.3 ppm assigned to the phenyl protons.

Results and Discussion

Chemistry of the $B_9H_{14}^-$ Ion. Addition of 1 equiv of butyllithium to a tetrahydrofuran solution of CsB_9H_{14} produced a thick white precipitate, presumably of $LiCsB_9H_{13}$. This compound was extremely reactive toward water and ignited when exposed to air. Controlled hydrolysis with aqueous tetrahydrofuran regenerated $B_9H_{14}^-$ in nearly quantitative yield. This high reactivity frustrated further efforts at direct chemical or spectroscopic characterization of this dianion, but derivatives could be prepared.

Boron insertion into $B_9H_{13}^{2-}$ was accomplished by reaction with phenyldichloroborane to give 6-phenyldecaborane. Substitution at the B(6) position was indicated by the ^{11}B nmr spectrum (see Table II) which was quite similar to that of 6-benzyldecaborane prepared by the alkylation of $NaB_{10}H_{13}$ with benzyl bromide.[6] Further characterization was achieved by reaction of the phenyldecaborane with excess triphenylphosphine in refluxing toluene to form $6\text{-PhB}_{10}H_{11}(PPh_3)_2$. The elemental analysis of this compound is given in Table I. $LiCsB_9H_{13}$ proved to be a strong reducing agent and converted $BrMn(CO)_5$ and $C_5H_5Fe(CO)_2I$ to $Mn_2(CO)_{10}$ and $[C_5H_5Fe(CO)_2]_2$, respectively.

Metal Derivatives of the $B_9H_{11}S^{2-}$ Ion. Treatment of a tetrahydrofuran solution of $CsB_9H_{12}S$ with butyllithium afforded a white solid which is presumably $LiCsB_9H_{11}S$ or a tetrahydrofuran solvate. This solid was pyrophoric and extremely moisture sensitive. Hydrolysis regenerated $B_9H_{12}S^-$ in good yield.

Reaction of $LiCsB_9H_{11}S$ with nickel or palladium acetylacetonate produced metallothiaboranes of the type $[(B_9H_{11}S)_2M]^{2-}$ (M = Ni, orange; M = Pd, yellow-brown). These anions were isolated as the methyltriphenylphosphonium salts which facilitate their purification by chromatography. Efforts to prepare the analogous Pt(II) complex led to reduction of the metal salt. Compared to $B_{10}H_{12}^{2-}$, $B_9H_{11}S^{2-}$ appears to be a more reactive ligand and displaces both triphenylphosphine and tri-*n*-butylphosphine from $(R_3P)_2NiCl_2$ and triphenylphosphine and benzonitrile from $(PPh_3)_2PdCl_2$ and $(PhCN)_2PdCl_2$, respectively, to form the metalloboranes described above.

The structure proposed for $[(B_9H_{11}S)_2M]^{2-}$ complexes, Figure 1, is similar to that of $[(B_{10}H_{12})_2Ni]^{2-}$ [7] except that a B–S–M interaction is present in the metallothiaboranes. It is proposed that the coordination about the transition metal is essentially square planar. The ^{11}B nmr spectrum of $(Ph_3PCH_3)_2[(B_9H_{11}S)_2Pd]$ in acetone (Figure 2) shows at least eight doublets indicating that the B_9SPd framework does not possess a mirror plane of symmetry. The infrared spectra of both the Ni and Pd compounds contain a single, sharp band in the BH stretching region, suggesting the absence of BH_2 groups. The ^{1}H nmr spectra reveal broad singlets upfield of tetramethylsilane, attributable to bridge hydrogens bonded to two boron atoms. The spectroscopic data point strongly to a $B_9H_{11}S^{2-}$ formulation for the ligand. The ^{11}B nmr spectra are very different from $B_9H_9S^{2-}$ complexes and metal derivatives of $B_9H_{13}S^{2-}$ are unlikely as it would require hydrogen transfer to the ligand. These complexes are also isomeric with $(B_9H_{10}S)Pt(H)(PPh_3)_2$ prepared previously[8] by the reaction

$$CsB_9H_{12}S + (PPh_3)_2PtHCl \rightarrow CsCl + H_2 + (B_9H_{10}S)Pt(H)(PPh_3)_2$$

It was thought that the following equilibrium might be operative

$$(B_9H_{11}S)_2M \rightleftarrows (B_9H_{10}S)M(H)(B_9H_{11}S)$$

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Table II. 70.6-MHz ^{11}B Nmr Spectra of Borane and Thiaborane Derivatives

Compd	Chem shift[a] (rel intens) [*J*(B–H), Hz][b]	Solvent
6-$PhB_{10}H_{13}$	−23.1[c] (1), −10.5 (3), −1.3 (2) [150], +4.1 (2) [155], +31.9 (1) [155], +37.7 (1) [150]	CS_2
6-$PhCH_2B_{10}H_{13}$	−25.2[c] (1), −10.6 (3), −1.3 (2) [150], +1.1 (2) [150], +33.3 (1) [155], +37.7 (1) [155]	CS_2
$(B_9H_9S)Pd(PPh_3)_2$ (yellow isomer)	−42.4, −5.7, +5.7, +22.7 [130]	CH_2ClCH_2Cl
$(B_9H_9S)Pd(PPh_3)_2$ (orange-brown isomer)	−46.4, +2.8, +21.8	CH_2Cl_2
$B_9H_{11}S\cdot THF$	−2.3 (1) [140], +7.8 (3), +13.1 (1) [145], +33.4 (2) [140], +38.6 (2) [145]	CH_2Cl_2
$(C_2H_5)_4N(HOB_9H_{11}S)$	−9.1 (1) [145], +4.4 (3), +24.4 (1) [150], +33.5 (2) [140], +38.4 (2) [140]	Acetone
$B_9H_{11}S\cdot PPh_3$	−7.2 [145], +7.4, +24.4, +38.3 [140], +35.6 [155]	CH_2Cl_2
$B_9H_{11}S\cdot DMF$	−2.6 (1), +1.4 (1), +7.8 (2) [145], +16.3 (1) [145], +33.1 (2) [140], +34.4 (2) [145]	CH_3CN
$(Ph_3PCH_3)_2[(B_9H_{11}S)_2Ni]$	−11.9, −4.8, +0.2, +16.2, +25.7	CH_2Cl_2

[a] Ppm *vs.* $BF_3\cdot O(C_2H_5)_2$. [b] Due to overlap of signals, measurement of some coupling constants is not possible. [c] This resonance is a singlet. All other signals are doublets.

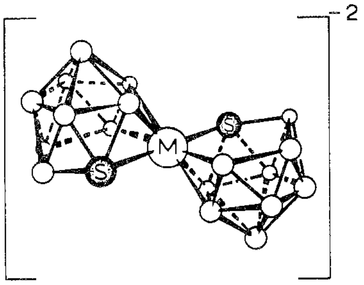


Figure 1. Proposed structure of $(B_9H_{11}S)_2M^{2-}$ (M = Ni or Pd).

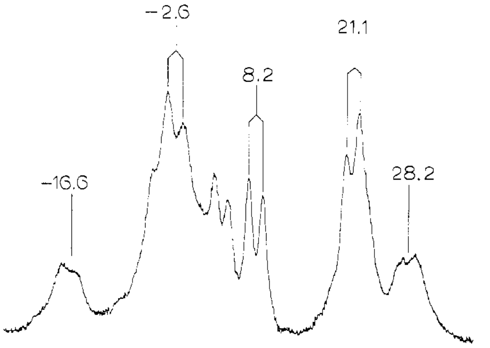
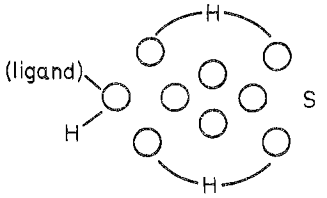


Figure 2. The 70.6-MHz ^{11}B nmr spectrum of $(Ph_3PCH_3)_2[(B_9H_{11}S)_2Pd]$ in acetone solution.

The infrared spectrum of the palladium compound was examined carefully in search of a Pd-H stretching band but this was not observed. This equilibrium would interconvert B-H-B and Pd-H environments. However the single observed resonance above TMS is at +1.9 ppm which is the usual region for B-H-B groups in boranes and carboranes.

$B_9H_{11}S$·ligand Derivatives. Iodine oxidation of CsB_9H_{12} in tetrahydrofuran affords white crystalline $B_9H_{11}S\cdot THF$ in good yield. Like the known compound $B_9H_{11}S\cdot S(CH_3)_2$,[4] the THF adduct was very moisture sensitive and was characterized by its ^{1}H and ^{11}B nmr spectra. The ^{11}B nmr spectrum of $B_9H_{11}S\cdot THF$ was quite similar to the spectrum of $B_9H_{11}S\cdot(CH_3)_2NCHO$ (see Table II) which had been reported previously.[4] Treatment of $B_9H_{11}S\cdot THF$ with acetonitrile or triphenylphosphine easily generated $B_9H_{11}S\cdot CH_3CN$ and $B_9H_{11}S\cdot PPh_3$ in good yield. Reaction of $B_9H_{11}S\cdot PPh_3$ with tetraethylammonium hydroxide in aqueous acetonitrile formed $(C_2H_5)_4N[HOB_9H_{11}S]$ in moderate yield. The pattern of the ^{11}B nmr spectrum of this hydroxy derivative is very similar to the spectrum of $B_9H_{11}S\cdot(CH_3)_2NCHO$. This suggests that $HOB_9H_{11}S^-$ is a member of the $B_9H_{11}S$·ligand class of compounds with the ligand being OH^-. We have previously studied the 70.6-MHz ^{11}B nmr spectra of $B_9H_{12}S^-$ and its labeled derivatives.[3] Comparison of the boron spectra suggests that $B_9H_{12}S^-$ is also a member of the $B_9H_{11}S$·ligand class in which H^- is the ligand.

Thus it is seen that the ^{11}B nmr spectra of $B_9H_{12}S^-$, $HOB_9H_{11}S^-$, and $B_9H_{11}S$·ligand are very similar. In each spectrum it is observed that the resonance of area 2 at +33 ppm is rather broad suggesting secondary bridge hydrogen coupling. In the case of $Cs[B_9H_{12}S]$ this bridge hydrogen coupling was demonstrated by observation of the sharpening of the ^{11}B nmr signal while simultaneously irradiating the bridge proton frequency.[3] This information strongly suggests that the structures of these different derivatives are related as suggested in the structure



where ligand = H^-, OH^-, CH_3CN, DMF, $(CH_3)_2S$, THF, and PPh_3.

Metal Derivatives of the $B_9H_9S^{2-}$ Ion. The reaction of $B_9H_{11}S\cdot THF$ with 2 equiv of butyllithium in THF at −78° afforded a pale yellow solution presumably containing $Li_2B_9H_9S$. Addition of 1 equiv of $(PPh_3)_2PdCl_2$ to this solution gave a 25% yield of yellow $(B_9H_9S)Pd(PPh_3)_2$. The ^{11}B nmr spectrum of this complex was very poorly resolved as is the case with many other triphenylphosphine-containing metalloborane complexes. The phosphine ligands were displaced by 1,10-phenanthroline and disodium maleonitriledithiolate to give $(B_9H_9S)Pd(C_{10}H_8N_2)$ and $Na_2\{(B_9H_9S)Pd[C_2S_2(CN)_2]\}$, respectively. The ^{11}B nmr spectrum of the latter compound, isolated as the tetraphenylarsonium salt, is shown in Figure 3. The spectrum is well resolved and is interpretable in terms of the structure shown in Figure 4. The doublet of area 3 at +27.2 ppm presumably arises from an accidental degeneracy of the chemical shifts of two doublets having areas 1 and 2. Such overlap is a common feature in the ^{11}B nmr spectra of complex boron hydride derivatives. The 1:1:2:2:3 pattern of this spectrum suggests that the palladium is located on a mirror plane of symmetry in the B_9S framework. It should be noted that the resonance of unit area at −4.2 ppm in Figure 3 is noticeably broadened. This may be due to the quadrupolar interaction with ^{105}Pd [22.2% natural abundance, $I = ^5/_2$]. This is also consistent with the empirical observation[9] that closo metalloboranes having a low-coordinate boron atom adjacent to a metal have a low-field resonance in the ^{11}B nmr spectrum. Another

(9) W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 95, 4565 (1973).

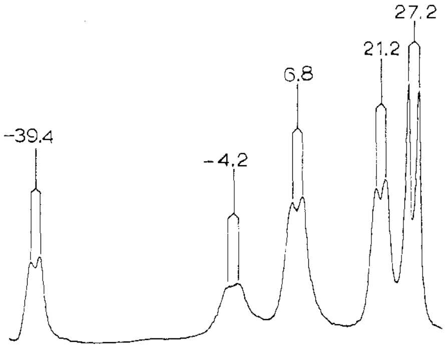


Figure 3. The 70.6-MHz ^{11}B nmr spectrum of $(Ph_4As)_2\{(B_6H_9S)Pd[C_2S_2(CN)_2]\}$ in acetone solution.

conspicuous feature of this spectrum is the very low-field resonance at −39.4 ppm. A similar low-field resonance (−74.5 ppm) was reported recently for the unique apex boron atom in B_9H_9S.[10] By analogy to this and other results on phosphacarboranes,[11] the −39.4-ppm peak in the palladium complex may be due to the unique boron atom which is in an antipodal (transoid) relationship to the sulfur atom in the proposed structure (Figure 4). The ^1H nmr spectrum of $[Ph_4As]_2\{(B_9H_9S)Pd[C_2S_2(CN)_2]\}$ contains peaks in the aromatic region due to the cation but no high-field signals attributable to B-H-B or Pd-H-B protons.

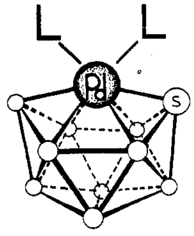


Figure 4. Proposed structure of $(B_9H_9S)Pd(ligand)_2$ compounds.

In many cases 11-atom closo heteroatom-borane compounds readily undergo rearrangement to isomeric closo derivatives. Heating $(B_9H_9S)Pd(PPh_3)_2$ at reflux in mesitylene causes a color change from yellow to orange-brown. The purified product has the correct elemental analysis for $(B_9H_9S)Pd(PPh_3)_2$ but a distinctly different melting point, infrared spectrum, and ^{11}B nmr spectrum. This information suggests that a polyhedral rearrangement has occurred. Further structural studies are in progress to confirm this finding.

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Registry No. 6-$PhB_{10}H_{13}$, 38998-69-5; 6-$PhB_{10}H_{11}(PPh_3)_2$, 52628-73-6; $(Ph_3PCH_3)_2[(B_9H_{11}S)_2Pd]$, 52760-66-4; $(Ph_3PCH_3)_2[(B_9H_{11}S)_2Ni]$, 52760-67-5; $B_9H_{11}S{\cdot}C_4H_8O$, 52628-75-8; $B_9H_{11}S{\cdot}PPh_3$, 52628-76-9; $(C_2H_5)_4N^+HOB_9H_{11}S^-$, 52760-68-6; $(B_9H_9S)Pd(PPh_3)_2$(yellow isomer), 52628-77-0; $(B_9H_9S)Pd(PPh_3)_2$(orange-brown isomer), 52555-13-2; $(B_9H_9S)Pd(C_{10}H_8N_2)$, 52628-78-1; $(Ph_4As)_2(B_9H_9S)Pd[C_2S_2(CN)_2]$, 52628-80-5; $(B_9H_9S)Pt(PPh_3)_2$, 52628-81-6; 6-$PhCH_2B_{10}H_{13}$, 52628-82-7; $B_9H_{11}S{\cdot}DMF$, 52628-83-8; $C_5B_9H_{14}$, 52555-14-3; $C_5B_9H_{12}S$, 52555-12-1; $(Ph_3P)_2PdCl_2$, 13965-03-2; phenanthroline, 66-71-7.

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Substituent Effects on the Redox Behavior of a Series of Chromium-Phenanthroline Complexes

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The formal redox potentials of the couples CrL_3^{3+}-CrL_3^{2+} and CrL_3^{2+}-CrL_3^{+}, where L is 1,10-phenanthroline or substituted 1,10-phenanthroline, were evaluated using dc and ac polarography and cyclic voltammetry. The results indicate that the degree of metal–ligand interaction in these complexes increases markedly as the oxidation state of the central metal atom decreases and/or the electron-acceptor ability of the ligand increases. The effect of the ligand substituents is especially great for the Cr(I) oxidation state. A chemical reaction coupled to the CrL_3^{3+}-CrL_3^{2+} electron transfer was observed and measured for several of the complexes. The interference of the coupled chemical reaction on the measured redox potenials could be eliminated using ac polarography and cyclic voltammetry.

In recent years there have been a number of reports concerning the complexes of chromium(II) with the chelating imine ligands 1,10-phenanthroline, 2,2′-bipyridine, and 2,2′,2″-terpyridine. Farina and Wilkins[2] have reported the spectrum of $Cr(terpy)_2^{2+}$, and Herzog and Aul[3] have reported the preparation and magnetic moments of $Cr(terpy)_2I_2$. Lutz[4] has detailed the preparation, magnetic properties, and spectra of several bis(terpyridine)chromium(II) complexes. We have previously reported the dc and ac polarographic behavior of $Cr(terpy)_2^{2+}$.[5] A number of studies of the dc and ac polarography of $Cr(bipy)_3^{2+}$ have been reported.[6-10]

The preparation and properties of tris(phenanthroline)chromium(II) complexes have been reported by several authors.[11-16] More recently, La Mar and Van Hecke[17-22] have

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