$(CO)_2(SO_2)]$ (isomer A), 87336-15-0; $[Fe(Ph_2(o\text{-}MeC_6H_4O)P)_2(CO)_2(SO_2)]$, 87392-57-2; $[Fe(Ph_2(MeO)P)_2(CO)_2(SO_2)]$, 87336-16-1; $[Fe(Ph_2MeP)_2(CO)_2(SO_2)]$, 87336-17-2; $[Fe(Ph_3P)_2(CO)_2(SO_2)]$, 87336-18-3; $[Fe(P(OC_6H_4Cl\text{-}p)_3)_2(CO)_3]$, 87319-47-9; $[Fe(P(OC_6H_4Cl\text{-}o)_3)_2(CO)_3]$, 87319-48-0; $[Fe(Ph_3P)_2(CO_2)(\eta^2\text{-}CS_2)]$, 86196-40-9; $[Fe((i\text{-}PrO)_3P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 87336-20-7; $[Fe((PhO)_3P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 66808-76-2; $[Fe((o\text{-}MeC_6H_4O)_3P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 72573-16-1; $[Fe((m\text{-}MeC_6H_4O)_3P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 87336-21-8; $[Fe((p\text{-}MeC_6H_4O)_3P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 72557-45-0; $[Fe(Ph(PhO)_2P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 87336-22-9; $[Fe(Ph(o\text{-}MeC_6H_4O)_2P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 87336-23-0; $[Fe(Ph(MeO)_2P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 87336-24-1; $[Fe(Ph(i\text{-}PrO)_2)P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 87336-25-2; $[Fe(Ph_2(PhO)P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 87336-26-3; $[Fe(Ph_2(o\text{-}MeC_6H_4O)P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 87336-27-4; $[Fe(Ph_2(MeO)P)_2(CO)_2(\eta^2\text{-}CS_2)]$, 87336-28-5; $[Fe(Ph_2MeP)_2(CO)_2(\eta^2\text{-}CS_2)]$, 72557-50-7.

Supplementary Material Available: Nonbonding interatomic contact distances (Table VIII), observed and calculated structure factors (Tables IX and X), final atomic anisotropic thermal parameters (Tables XI and XII), atomic parameters for hydrogen atoms (Tables XIII and XIV), and least-squares planes data (Tables XV and XVI) (30 pages). Ordering information is given on any current masthead page.

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Preparation of Thia- and Selenacarborane Derivatives by Carbon Atom Insertion with Isocyanide Derivatives

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Alkyl isocyanides react at room temperature with $B_9H_{11}E$ (E = S or Se) to initially form two isomeric $B_9H_{11}E\cdot CNR$ compounds. One of these isocyanide-complexed intermediates reacted further to form the carborane derivative $B_9H_9ECNH_2R$ in good yield. The second $B_9H_{11}E\cdot CNR$ compound did not undergo further reaction even in refluxing toluene. Treatment of $B_9H_{11}S$ with sodium cyanide formed $Na[B_9H_{11}S\cdot CN]$. This cyano complex was converted to $B_9H_9SCNH_3$ by passing the salt through a column of acid ion-exchange resin.

Introduction

The reaction of $BH_3\cdot O(C_2H_5)_2$ and various alkyl-substituted derivatives with organic compounds containing carbon–carbon double or triple bonds (hydroboration) has been extensively studied.[1,2] Similar reactions of an ether solution of BH_3 with aldehydes, ketones, and azo compounds have been reported.[3] Diborane(6) and alkylboranes add across the carbon–nitrogen multiple bond of alkyl isocyanide derivatives as well.[4-6]

Reactions of higher boron hydrides with multiple-bonded functional groups have been studied for nearly 30 years, but on a relatively limited scale. Acetylenes, for example, react with higher boron hydrides to give three distinctly different types of products. The reaction $B_9H_{11}S$ with acetylene forms $B_9H_{10}(CH{=}CH_2)S$ in which the alkenyl groups is exo to the cage framework and is bonded to one of the boron atoms.[7] This is an example of a simple hydroboration. A second type of reaction involves the incorporation of both carbon atoms of the acetylene into the cage framework as illustrated by eq 1.[8,9] The mechanism for this reaction is not understood. The third type of reaction involves incorporation of only one of the acetylene carbon atoms into the cage structure as exemplified by eq 2.[10] This reaction can be viewed as an intramolecular

$$B_{10}H_{12}(SR_2)_2 + HC{\equiv}CH \rightarrow B_{10}H_{10}C_2H_2 + H_2 + 2SR_2 \quad (1)$$

$$B_5H_9 + Li[C{\equiv}CCH_3] \rightarrow \xrightarrow{H^+} B_5H_8CCH_2CH_3 \quad (2)$$

bishydroboration of the acetylide ion.

Table I. Elemental Analyses of the Thia- and Selenacarborane Derivatives

	% calcd		% found	
compd	C	H	C	H
$B_9H_9SCNH_2(t\text{-}C_4H_9)$ (I)	26.87	9.01	26.23	8.85
$B_9H_9SCNH_2(C_6H_{11})$ (II)	33.68	8.84	33.71	8.88
$B_9H_9SCN(CH_3)_2(t\text{-}C_4H_9)$ (III)	33.42	9.61	33.35	9.54
$B_9H_9SeCNH_2(C_6H_{11})$ (V)	28.36	7.48	28.31	7.67

Alkyl isocyanides, which are isoelectronic with the acetylide ion, also undergo a bishydroboration type reaction with decarborane (14) (eq 3).[11] Subsequently i-$B_{18}H_{22}$[12] and $Na[B_{10}H_{13}]$[13] were found to react with alkyl and aryl isocyanides, respectively, to form similar one-carbon carborane derivatives.

$$B_{10}H_{14} + C{\equiv}NCH_3 \rightarrow B_{10}H_{12}CNH_2CH_3 \quad (3)$$

It is quite possible that isocyanide derivatives as well as other polar multiple-bonded reagents will undergo multiple hydroboration reactions with a variety of nido and arachno higher boron hydride derivatives. In this paper we describe our initial studies concerning the reactions of isocyanide derivatives with

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Table II. ^1H NMR Spectral Data[a] for Thia- and Selenacarborane Derivatives

compd	chem shift, ppm	multiplicity	assgnt
$B_9H_9SCNH_2(t\text{-}C_4H_9)$ (I)	1.50	s	$t\text{-}C_4H_9$
	6.25	br, s	NH_2
$B_9H_9SCN(CH_3)_2(t\text{-}C_4H_9)$ (III)	1.60	s	$t\text{-}C_4H_9$
	2.75		$N\text{-}CH_3$
$B_9H_9SeCNH_2(C_6H_{11})$ (V)	3-0.5	complex pattern	cyclohexyl
	6.0	br, s	NH_2
$B_9H_9SCNH_3$ (VII)	7.75	br, s	NH_3
$B_9H_9SCN(CH_3)_3$ (VIII)	3.3	s	$N\text{-}CH_3$

[a] Acetone-d_6 solvent.

$B_9H_{11}E$ (E = S or Se) derivatives, which are isoelectronic and similar in structure to $B_{10}H_{14}$.

Experimental Section

Physical Measurements. Boron (^{11}B) NMR spectra were obtained at 70.6 MHz with a Varian HR-220 spectrometer or at 115.8 MHz with a Nicolet NT-360 instrument and were externally referenced to $BF_3{\cdot}O(C_2H_5)_2$ (positive values downfield). Proton NMR spectra were obtained on either a Varian HR-220 or a Varian T-60A spectrometer and were referenced relative to internal tetramethylsilane (Me_4Si). Infrared spectra were obtained as KBr disks on a Perkin-Elmer 283 spectrometer or a Digilab 15C FTIR spectrometer. Low-resolution mass spectral data were obtained with an Atlas CH-7 spectrometer. Melting points were obtained in sealed, evacuated capillaries and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Materials. All reactions were performed under an atmosphere of prepurified nitrogen. Tetrahydrofuran (THF) and benzene were freshly distilled from sodium benzophenone ketyl. All other commerically available reagents were used as received.

$B_9H_9SCNH_2(t\text{-}C_4H_9)$ (I). The thiaborane anion, $B_9H_{12}S^-$, was prepared by the degradation-insertion reaction of decarborane (14) with aqueous polysulfide solution.[14] The thiaborane anion was then converted into $B_9H_{11}S$ as previously reported.[15] In a typical experiment, $B_9H_{11}S$ was prepared from 0.511 g (1.86 mmol) of $CsB_9H_{12}S$ and 0.236 g (0.93 mmol) of iodine in 40 mL of dry benzene. After filtration, 0.2 mL (2.6 mmol) of *tert*-butyl isocyanide was added to the filtrate; the reaction mixture was stirred under nitrogen for 1 h before heating to reflux for another hour and then evaporated to dryness to give a light yellow residue. The residue was dissolved in the minimum amount of CH_2Cl_2 and applied to a 1 × 7 in. silica gel column packed in hexane-1% ether solution. The first 200 mL of eluent was collected and evaporated to give a white solid, which was identified by ^{11}B NMR to be a mixture of $B_9H_{11}S{\cdot}CN(t\text{-}C_4H_9)$ (IX) and I. Further elution with pure diethyl ether and evaporation gave a yellow solid containing I. This solid was washed with small portions of benzene to remove impurities and then crystallized from CH_2Cl_2-hexane to give 0.30 g (72% yield based on $CsB_9H_{12}S$) of I, mp 235-237 °C. The low-resolution mass spectrum of I cutoff at *m/e* 225 corresponding to the $^{12}C_5{}^1H_{20}{}^{11}B_9{}^{32}S^{14}N^+$ parent ion. Elemental analysis and proton NMR data are given in Tables I and II, respectively, for the thia- and selenacarborane derivatives.

The ^{11}B NMR spectrum (CH_2Cl_2) of I is given in Figure 3.

$B_9H_9SCNH_2(C_6H_{11})$ (II). This compound was prepared in the same manner as compound I. The crude product was crystallized from CH_2Cl_2-hexane to give white crystals of II (30% yield), mp 239-240 °C. The ^{11}B NMR spectrum (CH_2Cl_2 solution) is similar to that of compound I with overlapping resonances of area 8 between -6.4 and -18.6 ppm and the doublet of area 1 centered at -41.9 ppm (J_{BH} = 142 Hz).

$B_9H_9SCN(CH_3)_2(t\text{-}C_4H_9)$ (III). Into an "H-shaped" reactor was placed 2 g of NaH as an oil dispersion. Under a stream of nitrogen, the NaH was washed with several portions of hexane and then with several portions of dry THF to remove the oil. Compound I (0.1 g, 0.4 mmol) was added to the THF slurry, and vigorous hydrogen evolution was observed. The reaction mixture was stirred at room temperature for about 1 h and then filtered through the glass frit of the H reactor. Dimethyl sulfate (0.5 mL, 4 mmol) was added to the filtrate, and the mixture was stirred at room temperature overnight. The solvent was taken off under vacuum, and the compound was extracted from the residue with CH_2Cl_2. The compound was crystallized from CH_2Cl_2-hexane to give 0.09 g of III (78% yield); mp 226-228 °C. The low-resolution mass spectrum shows a cutoff at *m/e* 253 corresponding to the $^{12}C_7{}^1H_{24}{}^{11}B_9{}^{32}S^{14}N$ parent ion.

The ^{11}B NMR spectrum is very similar to that of the parent compound I with the complex multiplet of area 8 between -6.1 and -17.7 ppm and the doublet of area 1 at -41.3 ppm (J_{BH} = 149 Hz).

$B_9H_9SCN(CH_3)_2(C_6H_{11})$ (IV). Compound II (0.1 g, 0.4 mmol) was reacted with NaH as described for III but was left stirring overnight at room temperature. The solution was then filtered under nitrogen and the filtrate treated with dimethyl sulfate (0.5 mL, 4 mmol) for 10 min. The reaction mixture was worked up as described for III. The crude product was crystallized from CH_2Cl_2-hexane to give 0.09 g (81% yield) of IV, mp 256-258 °C.

The ^{11}B NMR spectrum is similar to that of III with the overlapping resonances of area 8 between -6.5 and -17.7 ppm and the doublet of area 1 at -41.0 ppm (J_{BH} = 147 Hz).

$B_9H_9SeCNH_2(C_6H_{11})$ (V). A solution containing $B_9H_{11}Se$ was prepared as described previously[16] by using 0.467 g (1.78 mmol) of $(CH_3)_4N[B_9H_{12}Se]$ and 0.225 g (0.89 mmol) of iodine in 15 mL of dry benzene. The volume of solvent was then reduced to 7 mL under vacuum, back-filled with nitrogen, and 0.4 mL (5.3 mmol) of cyclohexyl isocyanide was added. The reaction mixture was stirred 1 h before heating to reflux for 15 min. The solution was then allowed to cool, and the solvent was removed under vacuum. The resulting solids were extracted with 3 × 10 mL portions of methylene chloride. The combined extracts were rotary evaporated, leaving a gummy solid that was placed on a 5 × 1 in. silica column eluted with chloroform, giving an initial yellow fraction containing an unidentified mixture of compounds. The column was then eluted with methylene chloride to give a second light yellow fraction. The solvent was removed from the second fraction, and the resulting solid was crystallized from a diethyl ether-hexanes mixture by slow rotary evaporation to give 0.195 g of off-white crystals of $B_9H_9SeCNH_2(C_6H_{11})$: mp 221-222.5 °C; 35% yield based on starting $(CH_4)_4N[B_9H_{12}Se]$.

$N(CH_3)_4[B_9H_{11}X{\cdot}CN]$ (VI). The thiaborane salt, $CsB_9H_{12}S$ (3.06 g, 11.2 mmol), was converted to 6-$B_9H_{11}S$ as described above for compound I. The benzene solvent used in the synthesis of 6-$B_9H_{11}S$ was removed by evaporation and replaced with 30 mL of dry THF. A solution of 0.6 g (12.2 mmol) of NaCN in 20 mL of THF was added to the thiaborane and stirred at room temperature overnight. The solvent was evaporated under vacuum and the residue dissolved in a minimum amount of water. Addition of a solution of tetramethylammonium bromide to the aqueous product mixture gave a precipitate of VI, which was crystallized from acetone-water to give 0.81 g (34% yield) of pure $N(CH_3)_4[B_9H_{11}S{\cdot}CN]$. The ^{11}B NMR spectrum of VI (acetone solvent) contained five doublets with relative areas of 1:3:1:2:2, respectively, as follows in ppm (J_{BH}, Hz): 9.2 (137), -6.1, -18.7 (117), -29.9 (147), -33.3 (142).

$B_9H_9SCNH_3$ (VII). This compound was prepared either by using trimethylsilyl bromide or by employing a hydrogen ion exchange resin.

a. Trimethylsilyl Bromide Method. To a solution of $Na[B_9H_{11}S{\cdot}CN]$ (prepared from 3.06 g (11.16 mmol) of $CsB_9H_{12}S$ as described above) was added 2 mL (13 mmol) of trimethylsilyl bromide. The mixture was refluxed with stirring under nitrogen for 15 h. The white solid (NaBr) was removed by filtration. The THF filtrate was evaporated to dryness under vacuum and then treated with 50 mL of 20% NaOH for 5 h at 50 °C. The resulting solution was acidified to pH 6 and evaporated to dryness. The solid residue was extracted with ether and crystallized from methylene chloride-hexane to give 0.074 g of $B_9H_9SCNH_3$ (4% yield based on $CsB_9H_{12}S$). This compound does not melt below 400 °C but darkens around 270 °C. The ^{11}B NMR spectrum (acetone-d_6) shows a cluster of overlapping doublets between -6.0 and -18.7 ppm of area 8 and a doublet of area 1 at -41.9 ppm (J_{BH} = 144 Hz).

b. H^+ Ion Exchange Method. The $Na[B_9H_{11}S{\cdot}CN]$ was prepared from 3.06 g (11.16 mmol) of $CsB_9H_{12}S$ as described above. The THF solvent was removed under vacuum, and the residue was dissolved

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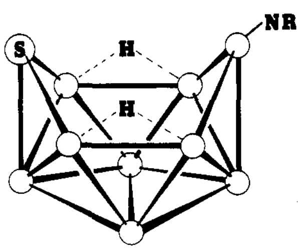

Figure 1. Structure of $B_9H_{11}SN(C_2H_5)_3$. Terminal hydrogen atoms have been omitted for clarity.

in water and applied to an Amberlite IR 120, 20–50 mesh H^+ ion exchange column. The collected eluent was evaporated to give a white residue, which was extracted with ether and crystallized from methylene chloride–hexane to give 0.12 g of $B_9H_9SCNH_3$ (6.5% yield based on $CsB_9H_{12}S$).

$B_9H_9SCN(CH_3)_3$ (VIII). The aqueous eluent from the preparation of $B_9H_9SCNH_3$ by the H^+ ion exchange method described above was placed in a 1-L three-necked flask fitted with a nitrogen inlet and two self-compensating dropping funnels. The funnels were charged with 100 mL of 10% NaOH solution and 15 mL of dimethyl sulfate. Each of these reagents was added in three portions: first one portion of base and then one portion of dimethyl sulfate. Each portion of base was added in a 10-min period, and each portion of dimethyl sulfate was added dropwise over a 30-min period. After addition of all the reagents, the solution was stirred overnight at room temperature. The white precipitate was filtered and crystallized from methylene chloride–hexane to give 0.35 (15% yield based on starting $CsB_9H_{12}S$) of $B_9H_9SCN(CH_3)_3$, mp 334–336 °C. The ^{11}B NMR (acetone solvent) contains a cluster of overlapping resonances of area 8 ranging from −5.8 to −19.5 ppm and a doublet of area 1 at −41.8 ppm (J_{BH} = 147 Hz).

Results and Discussion

The thiaborane $B_9H_{11}S$ and its selenium analogue are known to complex with Lewis bases to form 1:1 adducts as illustrated in Figure 1. The X-ray structure of $B\,H_{11}S{\cdot}N(C_2H_5)_3$ has been determined.[17] During the reaction of $B_9H_{11}S$ with *tert*-butyl isocyanide in refluxing benzene, $B_9H_{11}S{\cdot}CN(t\text{-}C_4H_9)$ (IX) was formed in low yield and the major product (in 72% yield) was $B_9H_9SCNH_2(t\text{-}C_4H_9)$ (I). The infrared spectrum of I contained absorption bands at 3198 and 1450 cm^{-1}, which are attributed to the NH stretch and NH_2 deformation modes, respectively. The proton NMR spectrum of I contained a broad singlet of area 2 at 6.25 ppm assigned to the NH_2 group as well as a sharp singlet of area 9 at 1.5 ppm attributed to the *tert*-butyl group. The existence of an NH_2 group in I was further confirmed by deprotonation with aqueous sodium hydroxide and methylation with dimethyl sulfate to form $B_9H_9SCN(CH_3)_2(t\text{-}C_4H_9)$ (III). Similar insertion reactions were accomplished with cyclohexyl isocyanide and $B_9H_{11}S$ or the selenium analogue to form $B_9H_9SCNH_2(C_6H_{11})$ (II) and $B_9H_9SeCNH_2(C_6H_{11})$ (V), respectively.

This carbon-insertion reaction probably occurs at the open face of the thia- or selenaborane. The reaction is accomplished under mild (benzene reflux) conditions. Therefore, no cage rearrangement is expected. As illustrated in Figure 2, we propose that the thia- or selenacarborane products have a nido 11-atom structure with the carbon and sulfur (or selenium) atoms in adjacent positions on the open face of the cage structure. The ^{11}B NMR spectra for all thia- and selenacarborane derivatives exhibit a complex overlapped pattern similar to that illustrated in Figure 3 for $B_9H_9SCNH_2(t\text{-}C_4H_9)$. Almost all nido 11-atom borane derivatives known at present contain a ^{11}B signal of unit area at relatively high field, which is attributed to the boron atom on the opposite side of the cage structure from the open face.[18] The ^{11}B NMR spectra of these compounds also contain one doublet that is unusually narrow. This resonance is attributed to the one boron atom in the cage that is adjacent to both the sulfur and carbon atoms. This boron nucleus should experience less ^{11}B–^{11}B coupling and therefore be a narrower signal.

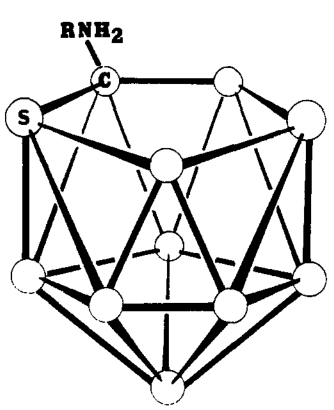

Figure 2. Proposed structure of the $B_9H_9SCNH_2R$ derivatives.

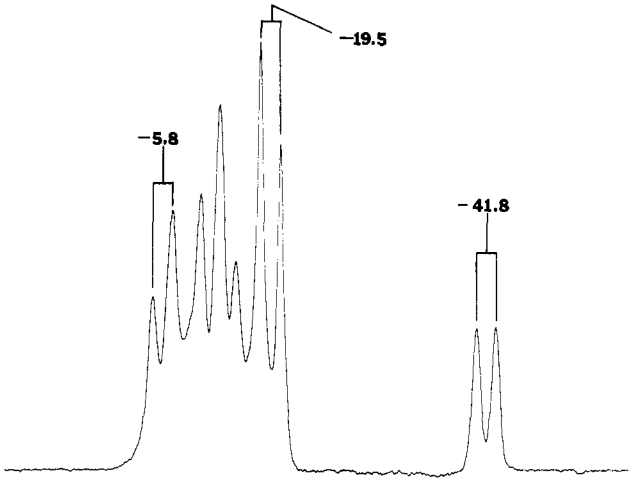

Figure 3. 70.6-MHz ^{11}B NMR spectrum of $B_9H_9SCNH_2(t\text{-}C_4H_9)$ in CH_2Cl_2 solution ($BF_3{\cdot}O(C_2H_5)_2$ at 0 ppm).

Reaction of $B_{10}H_{14}$ with alkyl isocyanide generates $B_{10}H_{12}CNH_2R$. Alternate synthetic routes to these one-carbon carboranes involve the protonation, alkylation, or silylation of the cyano-substituted anion $B_{10}H_{13}CN^{2-}$.[19] Similar chemistry was also found to be possible with the $B_9H_{11}S$ system. Treatment of $B_9H_{11}S$ with NaCN in THF solution formed $Na[B_9H_{11}S{\cdot}CN]$ in good yield. The ^{11}B NMR spectrum of this cyano derivative is very similar to the spectra of other known $B_9H_{11}S$·ligand derivatives such as compound IX.[20] An aqueous solution of $B_9H_{11}S{\cdot}CN^-$ was passed through an acid ion-exchange column to form $B_9H_9SCNH_3$. Alternately, the cyano anion was reacted with $(CH_3)_3SiBr$, which initially formed $B_9H_{11}S{\cdot}CNSi(CH_3)_3$ detected by its characteristic ^{11}B NMR spectrum. This intermediate was not isolated but was converted to $B_9H_9SCNH_2Si(CH_3)_3$, which was subsequently hydrolyzed with aqueous base to form $B_9H_9SCNH_3$. Thus, we find striking parallels in the isocyanide insertion chemistry of $B_{10}H_{14}$ and $B_9H_{11}S$.

When $B_9H_{11}S$ was reached with *tert*-butyl isocyanide at room temperature, two compounds were formed rapidly in a 4:1 ratio as indicated by both ^1H and ^{11}B NMR. The minor product was identified as the adduct $B_9H_{11}S{\cdot}CN(t\text{-}C_4H_9)$ (IX), previously isolated in the reaction at higher temperature. The ^{11}B NMR spectrum of IX (CH_2Cl_2 solvent) contained six doublets with relative areas of 1:1:2:2:1:2, respectively, as

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follows in ppm (J_{BH}, Hz): 9.2 (147), -4.2 (153), -9.1 (152), -29.9 (149), -34.0 (126), -36.0 (147 Hz). The ^{11}B NMR spectrum of the major compound (CH_2Cl_2 solvent) contained five doublets with relative areas of 1:1:2:3:2, respectively, as follows in ppm (J_{BH}, Hz): 11.4 (144), -2.3 (172), -5.9 (155), -27.8 (134), -32.4 (148 Hz). The ^{11}B NMR spectrum of the major compound was different from but still quite similar to that of compound IX. An analysis of the ^{11}B NMR spectra of $B_9H_{11}E$·ligand (where E = S, Se, or Te) compounds has been reported previously.[16] Both the major and minor compounds have ^{11}B NMR spectra very similar to those of other known $B_9H_{11}S$·ligand derivatives. After stirring of the mixture at room temperature for 2 h, nearly complete conversion of this major compound to the thiacarborane I was observed. the quantity of IX did not change during this prolonged reaction at room temperature. Even an attempt to convert IX to I by reflux in toluene for 48 h was not successful.

We interpret this result to mean that there are two isomeric $B_9H_{11}S·CN(t\text{-}C_4H_9)$ adducts initially formed. One isomer, IX, is stable and cannot easily be converted to the thiacarborane, but the second adduct is more reactive and readily converts to I. The structures of these two adducts are of great interest and are presently under study. It is possible that IX has the structure given in Figure 1 and that the less stable isomer has the alkyl isocyanide ligand coordinated to the same boron atom but extending over the open face of the $B_9H_{11}S$ unit.

The presence of isomeric adducts of $B_9H_{11}S·NCCH_3$ was previously suggested by the observation in the ^1H NMR spectrum of two singlet resonances attributed to the methyl group.[14] A similar finding was observed for $B_9H_{11}E·NCCH_3$ (E = Se or Te) as well.[16]

There are a few previous reports of the synthesis of thia- and selenacarboranes. Reaction of $K[7,8\text{-}B_9C_2H_{12}]$ with $K_2S_2O_5$ at 100 °C formed *nido*-$SC_2B_8H_{10}$.[21,22] Treatment of $Na[C_2B_{10}H_{13}]$ with HCl and $KHSO_3$ formed *arachno*-$SCH_2B_7H_9$ (a $B_7C_2H_{13}$ analogue).[22] A low yield of $B_7C_2H_{11}Se$ was produced by reaction of $B_7C_2H_{13}$ with polyselenide ion in aqueous base and subsequent acidification of the mixture.[23] The nido derivative $B_9H_9SeCN(CH_3)_3$ was prepared by reaction of $B_9H_{11}CN(CH_3)_3$ with the polyselenide ion.[24] The thia- and selenacarboranes reported previously were each obtained in low yield. The synthetic route described in this paper gives for the first time thia- and selenacarboranes in sufficiently high yields so that futher chemical studies of this type of molecule can be made and such studies are under way at present.

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Registry No. I, 87639-05-2; II, 87639-06-3; III, 87616-12-4; IV, 87616-13-5; V, 87639-07-4; VI, 87616-15-7; VII, 87639-08-5; VIII, 87616-16-8; IX, 87616-17-9; $B_9H_{11}S$, 12447-77-7; $CsB_9H_{12}S$, 11092-86-7; $B_9H_{11}Se$, 72985-65-0; $(CH_3)_4[B_9H_{12}Se]$, 73116-65-1; *tert*-butyl isocyanide, 7188-38-7; iodine, 7553-56-2; cyclohexyl isocyanide, 931-53-3; sodium cyanide, 143-33-9; trimethylsilyl bromide, 2857-97-8.

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Acid Hydrolysis of Organonitriles Coordinated to Ruthenium(III)

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Previous reports have demonstrated that the base hydrolysis of organonitriles is catalyzed by a factor of about 10^8 on coordination to pentaammineruthenium(III) and by about 10^6 on coordination to Co(III) and Rh(III). Although not previously reported, there is a base-independent hydrolysis path as well. The reported specific rates of base hydrolysis at 25 °C for acetonitrile and benzonitrile coordinated to Ru(III) are 2.2×10^2 and 2.0×10^3 M^{-1} s^{-1}, respectively. The rates of acid hydrolysis for acetonitrile, benzonitrile, and 1-adamantylcarbonitrile complexes at 25 °C are 1.2×10^{-5}, 3.4×10^{-5} and 7.2×10^{-6} s^{-1}, respectively. In acid aqueous solution, the hydrolysis reaction rate constant is independent of acid concentration and ionic strength, indicating that the attacking nucleophile is a water molecule. The activation parameters for the acid hydrolysis of pentaammineruthenium(III) complexes of acetonitrile, benzonitrile, and 1-adamantylcarbonitrile ($\Delta H^\ddagger = 20.0 \pm 0.2$ kcal mol^{-1}, $\Delta S^\ddagger = -13.9 \pm 0.5$ eu, $\Delta G^\ddagger = 24.1$ kcal mol^{-1}; $\Delta H^\ddagger = 19.0 \pm 0.2$ kcal/mol^{-1}, $\Delta S^\ddagger = -15.3 \pm 0.5$ eu, $\Delta G^\ddagger = 23.5$ kcal/mol^{-1}; $\Delta H^\ddagger = 21.2 \pm 0.3$ kcal/mol^{-1}, $\Delta S^\ddagger = -10.8 \pm 1.0$ eu, $\Delta G^\ddagger = 24.4$ kcal mol^{-1}, respectively) are very similar, which is consistent with postulation of a similar mechanism for each reaction.

Introduction

In 1973 Buckingham, Keene, and Sargeson reported that the hydrolysis of acetonitrile in basic aqueous solution is catalyzed by a factor of 2×10^6 on coordination to $Co(NH_3)_5^{3+}$.[1] More recently, Zanella and Ford reported that the effect of coordination to $Rh(NH_3)_5^{3+}$ was similar to that of $Co(NH_3)_5^{3+}$ and that $Ru(NH_3)_5^{3+}$ was an even more effective catalyst by 2 orders of magnitude.[2] In both cases, there was no evidence for a base-independent hydrolysis path. We have synthesized bimetallic complexes with Co(III) and Ru(III) ammines bound to nitrile groups for the study of intramolecular electron-transfer reactions.[3] When such complexes are dissolved in acidic aqueous solution, spectral changes consistent with hydrolysis of the nitrile group bound to Ru(III) occur slowly. To understand the nature of this reaction and to determine how well the reaction rate can be predicted for given conditions, we undertook the study of the acid hydrolysis of organonitriles bound to Ru(III) reported herein.

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