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Contribution from the Department of Chemistry,
University of Wisconsin—Madison, Madison, Wisconsin 53706

Synthesis and Characterization of 1-(Cl_2B)B_5H_8 and 1-(Cl_2B)-2-ClB_5H_7: A New Boron-Boron σ Bond

DONALD F. GAINES,* JOSEPH A. HEPPERT, DARRELL E. COONS, and MICHAEL W. JORGENSON[1]

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Two new 1-(dichloroboryl)pentaborane(9) derivatives, 1-(Cl_2B)B_5H_8 and 1-(Cl_2B)-2-ClB_5H_7, have been produced via the reaction of BCl_3 with B_5H_9 and 2-ClB_5H_8, respectively, in the presence of Friedel–Crafts catalysts. These compounds are the first examples of σ bonding between borane cluster atoms and external trigonal boron atoms. The boron–boron bonds undergo cleavage at elevated temperature in the presence of diethyl ether and insert ethylene at ambient temperature to form 1-[2-(dichloroboryl)ethyl]pentaborane(9) derivatives.

Introduction

Boron hydrides containing discrete boron–boron σ bonds are relatively rare. Those known fall into two general groups. The first group contains compounds having boron–boron intercage bonds; examples of this class include the three isomers of $(B_5H_8)_2$.[2,3] Compounds in the second group contain at least two trigonal boron atoms bound to each other primarily via boron–boron σ bonding: The diborane(4) derivative B_2Cl_4 is an example of this group. (For purposes of this discussion we have excluded the tetracoordinated Lewis base adducts of diborane(4) derivatives.) These two types of boron–boron bonds exhibit very different chemical behavior. For example, B_2Cl_4 is prone to cleavage reactions, as is illustrated by its reaction with ethylene (eq 1).[4] Intercage boron–boron bonds,

$$B_2Cl_4 + CH_2CH_2 \xrightarrow{-78\ ^\circ C} Cl_2B\text{–}CH_2\text{–}CH_2\text{–}BCl_2 \quad (1)$$

by contrast, are far less reactive. The cleavage of 1,2′-$(B_5H_8)_2$ under Friedel–Crafts conditions is one of the few known examples of intercage boron-bond cleavage.[5]

$$R\text{–}X + 1,2'\text{-}(B_5H_8)_2 \xrightarrow{AlX_3} 1\text{-}RB_5H_8 + 2\text{-}XB_5H_8 \quad (2)$$
$$R = H, Et$$

Compounds containing a trigonal boron moiety σ-bonded to a boron in a boron hydride cluster have not been previously prepared. In this paper we report the preparation, via Friedel–Crafts syntheses, of 1-(Cl_2B)B_5H_8 (I) and 1-(Cl_2B)-2-ClB_5H_7 (II), the first examples of apical X_2B substitution in pentaborane and the first compounds illustrating a combination of the two classes of discrete boron–boron σ bonding.

Experimental Section

Inert-atmosphere manipulations were performed in nitrogen-filled glovebags and standard high-vacuum systems.[6] All solvents were dried over $LiAlH_4$ and degassed before use. Boron trichloride (technical grade) and ethylene (chemically pure) were used, as obtained from the Matheson Co. The 2-chloropentaborane (2-ClB_5H_8) was prepared by the literature method.[7] Aluminum trichloride was purified by repeated sublimations. Iron trichloride was obtained as the ACS reagent hexahydrate and was dried by the standard method.[8]

Table I. ^{11}B NMR Spectral Data for I and II

compd	B resonance	chem shift, ppm	multiplicity; coupling const, Hz
1-(Cl_2B)B_5H_8 (I)	Cl_2B	75.7	q; $J_{BB} \simeq 124$
	B2–B5	−13.1	d; $J_{BH} = 160.6$
	B1	−51.8	br s
1-(Cl_2B)-2-ClB_5H_7 (II)	Cl_2B	73.0	q; $J_{BB} \simeq 122$
	B2	−1.6	s
	B3, B5	−14.0	d; $J_{BH} = 173.5$
	B4	−23.6	d; $J_{BH} = 173.5$
	B1	−51.6	br s

Table II. ^1H NMR Spectral Data for I and II

compd	H resonance	chem shift, ppm	multiplicity; coupling const, Hz
1-(Cl_2B)B_5H_8 (I)	H2–H5	2.31	q; $J_{BH} = 167$
	H6–H9	−2.74	br s
1-(Cl_2B)-2-ClB_5H_7 (II)	H3, H5	2.25	q; $J_{BH} = 172$
	H4	2.00	q; $J_{BH} = 168$
	H6, H9	−1.05	br s
	H7, H8	−2.79	br s

Phosphorus trichloride was distilled under dry nitrogen and degassed just prior to use. Tri-*n*-butyltin hydride was used as received from Alfa Chemical Co.

All NMR spectra were obtained on a Bruker WH-270 spectrometer at 270.071 MHz for ^1H and 86.653 MHz for ^{11}B. The ^{11}B NMR spectra were acquired over a 13 000-Hz sweep width and were referenced to $BF_3{\cdot}OEt_2$, while the ^1H spectra were acquired over a 6000-Hz sweep width. Mass spectra were obtained on an AEI MS-9 instrument at 70 eV. Infrared spectra were obtained with a Perkin-Elmer Model 700 spectrophotometer and a 10-cm gas cell. X-ray powder patterns were collected with use of Ni-filtered Cu Kα radiation and a 114.57-mm Debye–Scherrer camera.

Preparation of 1-(Cl_2B)B_5H_8 (I). A 75-mL stainless-steel bomb equipped with a stainless-steel valve was evacuated overnight, filled with dry nitrogen, and charged with 0.1 g of $AlCl_3$. After evacuation, 0.151 g (1.10 mmol) of PCl_3, 0.695 g (11.0 mmol) of B_5H_9, and 2.836 g (24.20 mmol) of BCl_3 were condensed into the bomb. The bomb was sealed, warmed to room temperature, and heated at 110–120 °C for 6 days. The bomb was then opened on the vacuum line, and the mixture was distilled into a −45 °C U-trap followed by a −196 °C U-trap. Compound I condensed in the −45 °C U-trap. Yield: 0.140 g (0.97 mmol), 8.8% based on B_5H_9.

Compound I is a colorless liquid, with a vapor pressure of 11 ± 1 torr at 23 °C. The mass spectrum of I exhibits the parent ion $^{11}B_6{}^1H_8{}^{35}Cl_2$: calculated, *m/e* 144.0561; observed, *m/e* 144.0558. The infrared spectrum of I contains major bands at 2640 m, 995 m, 960 s, and 890 w cm^{-1} (all ±10 cm^{-1}). The ^{11}B and ^1H NMR data for I are listed in Tables I and II.

Preparation of 1-BCl_2-2-ClB_5H_7 (II). In a typical reaction a 100-mL round-bottom reactor equipped with a 12-mm Kontes O-ring stopcock and a Teflon stir bar was evacuated for several hours and then filled with dry nitrogen gas. Anhydrous $FeCl_3$, 0.94 g, was transferred into

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(1) Current address: Union Carbide Corp., Tarrytown Technical Center, Tarrytown, NY 10591.

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the reactor in a nitrogen-filled glovebag. The flask and $FeCl_3$ were evacuated overnight with use of a high-vacuum line. Then 1.50 g (15 mmol) of $2\text{-}ClB_5H_8$ and 1.50 mmol of BCl_3 were condensed into the flask at −196 °C. The flask was sealed, warmed to 45 °C, and stirred for 4 days. As the reaction proceeded, the black $FeCl_3$ catalyst lightened in color, finally becoming cream white.

The reaction mixture was separated by repeated distillations with a −30 °C U-trap followed by a −196 °C U-trap. The material that condensed in the −30 °C U-trap was identified as II. Yield: 0.027 g (0.16 mmol), or 11% based on BCl_3 (the best yield obtained has been 25%). In addition, 1.32 g (88%) of the original $2\text{-}ClB_5H_8$ was recovered by distillation of the remainder of the reaction mixture through a −63 °C trap. About 2.4 mmol of BCl_3 and small amounts of B_5H_9, HCl, and H_2 were also observed.

Compound II, a clear liquid melting near −20 °C, is extremely air and moisture sensitive. It was characterized by its ^{11}B and ^1H NMR spectra (Tables I and II) and by mass spectroscopy. The mass spectrum of II exhibits the parent ion $^{11}B_6{}^1H_7{}^{35}Cl_3$: calculated, *m/e* 178.0177; found, *m/e* 178.0182.

Reaction of I with Diethyl Ether. A 5-mm NMR tube was charged with 0.046 g (0.32 mmol) of I, 0.34 mmol of diethyl-d_{10} ether and about 0.5 mL of C_6H_6 solvent. The tube was sealed and warmed briefly to ambient temperature to mix the reagents, then cooled to −40 °C, and stored for 1 day. The ^{11}B NMR spectrum showed only I. The sample was heated to 50 °C for 2.5 days. Although the ^{11}B NMR spectrum of the sample was similar to that of I, the low-field resonance was broadened and shifted upfield to about 50 ppm. A small sharp resonance also appeared at 11.5 ppm. The sample became gelatinous after further heating at 65–75 °C for 6 days but gave a clear ^{11}B NMR spectrum showing primarily B_5H_9. (It is assumed that $1\text{-}DB_5H_8$ was formed in the initial decomposition reaction and that subsequent interaction of the borane with the ether scrambled the label.) A small amount of I was still present.

Reaction of II with Diethyl Ether. An NMR tube containing equal quantities of compound II and diethyl ether in C_6D_6 was prepared. A similar sample was made containing only II in C_6D_6 solution. The samples were examined by ^{11}B NMR after several hours at room temperature and were found to contain only pure II. After 2 days of heating at 80 °C, no change had occurred in the control sample; in the sample containing ether, however, II had been completely converted to $2\text{-}ClB_5H_8$.[7] Three small singlets were also observed at 25.6, 30.9, and 46.2 ppm; however, unambiguous assignment of their identity was not possible. No solid residues were observed in either tube, and only a slight yellow color appeared in the sample containing ether.

Reaction of II with *n*-Bu_3SnH. In a typical reaction, 3.7 mmol of *n*-Bu_3SnH was placed in a nitrogen-filled reaction vessel. The reactor was cooled to −196 °C and evacuated, and 0.035 g of II was condensed into it. The vessel was sealed, warmed to ambient temperature, and allowed to stand for 1 week. A deep orange color developed as the reaction progressed. On fractionation through a −96 °C trap, one reaction yielded a small amount of white solid melting at about −10 °C. Boron-11 NMR confirmed the identity of this product as $1,2'\text{-}(B_5H_8)_2$.[9] Examination of volatile and nonvolatile products of other reactions by ^{11}B NMR revealed the presence of other pentaborane oligomers that have not as yet been fully characterized.

Reaction of I with Ethylene. A 0.5-mmol sample of I was condensed at −196 °C into a 5-mm thick-walled NMR tube. Sufficient pentane was added to bring the combined liquid height to 3 cm. The solution was frozen at −196 °C, and 0.3 mmol of C_2H_4 was condensed into the tube above the frozen sample. The tube was sealed and allowed to warm from −78 °C to ambient temperature over 1 day.

The progress of the reaction was monitored by ^{11}B NMR for 3 weeks. During this period, a diminution in the intensity of the Cl_2B and B(1) resonances of I was accompanied by the appearance of two singlet resonances at 63.3 and −42.0 ppm. At the end of 3 weeks, the reaction had proceeded to approximately 50% conversion of I based on peak areas, or about 80% conversion based on the C_2H_4 limiting reagent.

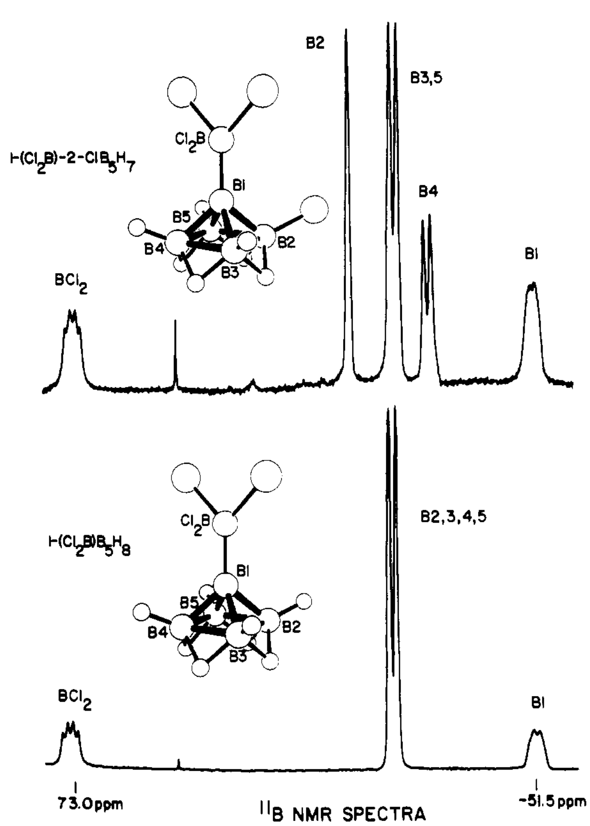

Figure 1. 86.6-MHz ^{11}B NMR spectra of $1\text{-}(Cl_2B)B_5H_8$ (I) and $1\text{-}(Cl_2B)\text{-}2\text{-}ClB_5H_7$ (II).

Subsequently the reaction mixture was distilled through a −30 °C U-trap and was stopped in a −196 °C U-trap. A portion of the material in the −30 °C trap was taken for mass spectroscopic analysis. The mass spectrum of the sample exhibited the parent ion $^{12}C_2{}^{11}B_6{}^1H_{12}{}^{35}Cl_2$: calculated, *m/e* 172.0874; found, *m/e* 172.0874. A large envelope around *m/e* 144 indicated that significant quantities of I were also still present.

Reaction of $1,2'\text{-}(B_5H_8)_2$ with $FeCl_3$. Approximately 1 g of anhydrous $FeCl_3$ was loaded into a small reactor containing a Teflon stir bar. The reactor was evacuated, and 1.5 mmol of $1,2'\text{-}(B_5H_8)_2$ was condensed into it at −196 °C. The reactor was sealed and warmed to 40 °C with stirring for 4 days. On distillation of the volatile portion of the reaction mixture, small amounts of BCl_3, $2\text{-}ClB_5H_8$, B_5H_9, and $1,2'\text{-}(B_5H_8)_2$ were separated and identified by IR spectroscopy. The reaction residues were then extracted with benzene and transferred to a water-cooled sublimator. The benzene was removed under vacuum, and after the contents were warmed to 45 °C, a white crystalline solid sublimed. On the basis of ^{11}B and ^1H NMR spectra the sublimate was tentatively identified as $1'\text{-}Cl\text{-}1,2'\text{-}(B_5H_8)(B_5H_7)$. Mass spectroscopy confirmed the formula, giving a parent ion $^{11}B_{10}{}^1H_{15}{}^{35}Cl_1$ or $^{11}B_8{}^{10}B_2{}^1H_{15}{}^{37}Cl_1$: calculated, *m/e* 160.1793 or 160.1836; found, *m/e* 160.1822.

Results and Discussion

Synthesis and Characterization of I and II. Compound I, $1\text{-}(Cl_2B)B_5H_8$, has been isolated from the reaction of B_5H_9 and BCl_3 (eq 3). No reaction was observed in the absence

$$B_5H_9 + BCl_3 \xrightarrow[100\text{–}120\ °C]{AlCl_3/PCl_3} 1\text{-}(Cl_2B)B_5H_8 + HCl \quad (3)$$

of either or both catalysts.

Compound II, $1\text{-}(Cl_2B)\text{-}2\text{-}ClB_5H_7$, has been prepared by a Friedel–Crafts type reaction between $2\text{-}ClB_5H_8$ and BCl_3 (eq 4). Anhydrous $FeCl_3$ was found to be a specific catalyst for

$$2\text{-}ClB_5H_8 + BCl_3 \xrightarrow[45\ °C]{FeCl_3} 1\text{-}(Cl_2B)\text{-}2\text{-}ClB_5H_7 + HCl \quad (4)$$

this reaction, which requires mild conditions in order to minimize decomposition of the $2\text{-}ClB_5H_8$.

The ^{11}B NMR spectra of I and II are shown in Figure 1; their associated chemical shifts and assignments are tabulated in Table I. The apical B(1) cage-boron resonances, which appear at −51 ppm, are broadened by coupling to the boron

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[9] Gaines, D. F.; Iorns, T. V.; Clevenger, E. N. *Inorg. Chem.* **1971**, *10*, 1096–1097.

atoms of the Cl_2B groups. These couplings are partially resolved in the Cl_2B resonances of I and II at −75 and −73 ppm, respectively. This loss of coupling structure in the high-field resonance of σ-bonded boron atoms is also observed in 1,2′-$(B_5H_8)_2$.[9] The chemical shifts of the B(1) boron atoms of I and II are very similar to the chemical shifts of the apical resonances in their parent boranes (B_5H_9 and 2-ClB_5H_8, respectively[8]), while corresponding resonances in 1,1′-$(B_5H_8)_2$ and 1,2′-$(B_5H_8)_2$ are shifted several ppm upfield.[2,9] It is noteworthy that the Cl_2B resonances in I and II have ^{11}B chemical shifts closer to that of B_2Cl_4 than to the chemical shift ranges for Cl_2B-substituted aryl or alkyl compounds.[10]

The ^1H NMR data for I and II in Table II are consistent with the structure deduced from the ^{11}B NMR spectra. The spectrum of II shows two distinct quartets at 2.25 and 2.00 ppm, representing the two types of basal-terminal hydrogens in the product.

Compound I was initially isolated from the reaction of B_5H_9 and PCl_3 in the presence of $AlCl_3$ at 100 °C. Apparently, a small quantity of BCl_3 is formed under these conditions from the degradation of B_5H_9. Subsequent experiments showed that improved yields of I could be obtained by adding excess BCl_3. Compound I was not produced if a solvent such as benzene or dichloromethane was used for the reaction. Instead, ^{11}B NMR spectra indicated the formation of at least two 1-phosphinopentaborane derivatives.[11]

Compound II was initially isolated in small quantities from an attempted polymerization of 2-ClB_5H_8 using $FeCl_3$ as a Friedel–Crafts catalyst (eq 5). We originally conjectured that

$$2\text{-}ClB_5H_8 + FeCl_3 \xrightarrow{45\ °C} 1\text{-}(Cl_2B)\text{-}2\text{-}ClB_5H_7 \tag{5}$$

II was formed by degradation of a coupled pentaborane species by $FeCl_3$. However, this hypothesis was abandoned when the reaction of $FeCl_3$ with 1,2′-$(B_5H_8)_2$, under similar conditions, produced only the new 1-chloro derivative of the bi(pentaborane) (eq 6). The addition of BCl_3 to the 2-ClB_5H_8/$FeCl_3$

$$1,2'\text{-}(B_5H_8)_2 \xrightarrow[40\ °C]{FeCl_3} 1'\text{-}Cl\text{-}1,2'\text{-}(B_5H_8)(B_5H_7) \tag{6}$$

reaction system increased the yield of II, indicating that its production is properly described by eq 4. The necessary BCl_3 in the reaction shown in eq 5 is presumed a result of in situ degradation of 2-ClB_5H_8 in contact with $FeCl_3$.

The $FeCl_3$ Catalyst System. Anhydrous $FeCl_3$ is a necessary catalyst for the production of II from BCl_3 and 2-ClB_5H_8, as shown in eq 4. When $AlCl_3$ was substituted for $FeCl_3$ in the BCl_3/2-ClB_5H_8 reaction system, no 1-Cl_2B-substituted product was isolated. Conversely, an attempt to synthesize I via catalysis with $FeCl_3$, as shown in eq 7, also failed. These

$$B_5H_9 + BCl_3 \xrightarrow{FeCl_3} 1\text{-}ClB_5H_8 \tag{7}$$

syntheses indicate that $AlCl_3$ and $FeCl_3$ have separate and distinct synthetic applications in these systems.

During the reaction represented by eq 5, the color of the $FeCl_3$ catalyst lightened dramatically. Investigation of the catalyst residue by X-ray powder patterns revealed that, after 4 days of reaction, no anhydrous $FeCl_3$ remained. The observed powder lines did not correspond to $FeCl_2$ and were not identified.

The formation of 1-halopentaborane derivatives is the major identified side reaction of the $FeCl_3$ catalyst system. Examples of this halogenation behavior have been shown in eq 6 and 7. The result observed in the reaction represented by eq 5 can also be attributed to halogenation by $FeCl_3$. Scheme I suggests that 1,2-$Cl_2B_5H_7$ may be formed via the halogenation of 2-ClB_5H_8 with $FeCl_3$. This 1,2-$Cl_2B_5H_7$ species is somewhat unstable at ambient temperature, and its decomposition at elevated temperature is a plausible source of BCl_3. The presence of BCl_3 then gives rise to II through the proposed reaction pathway.

Scheme I

$$2\text{-}ClB_5H_8 + FeCl_3 \xrightarrow{40\ °C} 1,2\text{-}Cl_2B_5H_7$$

$$1,2\text{-}Cl_2B_5H_7 \xrightarrow{40\ °C} BCl_3$$

Anhydrous $FeBr_3$ showed no catalytic activity in 1-X_2B substitution reactions. The reaction of Ph_2BCl and B_5H_9 in the presence of $FeCl_3$ produced (on the basis of ^{11}B NMR evidence) a boron–boron σ-bonded species (eq 8). The compound was never fully characterized, as we were unable to separate it from the Ph_2BCl starting material. In contrast, when a similar reaction using $FeBr_3$ and Ph_2BBr was attempted, 1-BrB_5H_8 was the only product. Small amounts of bromide ion in $FeCl_3$ catalyst samples were invariably found to interfere by producing 1-BrB_5H_8. Consequently, it is clear that $FeCl_3$ used as a catalyst in these syntheses must be free of bromide ion.

$$Ph_2BCl + B_5H_9 \xrightarrow{FeCl_3} 1\text{-}(Ph_2B)B_5H_8 \tag{8}$$

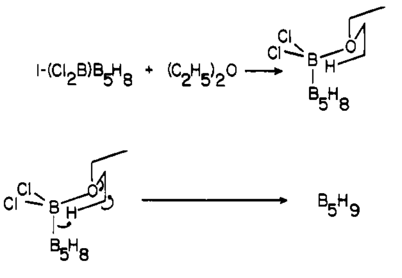
The Chemistry of I and II

Reaction of I and II with Diethyl Ether. Boron-11 NMR evidence indicates that I and II react at elevated temperatures with diethyl ether and that the two derivatives produce similar products. When I is heated to 50 °C in the presence of an equimolar amount of ether, the Cl_2B-group resonance is broadened and shifted upfield by 25 ppm. This observation is consistent with the formation of a four-coordinate complex between the ether and the Cl_2B group of I (eq 9). Subsequent heating of the sample to 70 °C causes decomposition of the complex and the formation of B_5H_9. Similarly, heating II to 80 °C in the presence of ether produces 2-ClB_5H_8. No other boron-containing products were observed in NMR spectra of the reaction mixtures. This suggests that the Cl_2B portion of the starting material and any other borane residues are incorporated either in high molecular weight compounds or in solids coating the interior surface of the NMR tubes.

$$1\text{-}(Cl_2B)B_5H_8 + Et_2O \xrightarrow{50\ °C} 1\text{-}[Cl_2B{\cdot}OEt_2]B_5H_8 \tag{9}$$

A proposed mechanism for the formation of B_5H_9 from I is shown in Scheme II. The proposal involves the formation of a four-coordinate intermediate, as observed by NMR spectroscopy, and subsequent intramolecular hydrogen transfer with the intermediate in a six-membered chair conformation. The mechanism implies that the borane and two byproduct molecules are formed in a quantitative conversion based on pentaborane product.

Scheme II



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(10) Noth, H.; Wrackmeyer, B. *NMR: Basic Princ. Prog.* **1978**, *14*, 129–131, 257.

(11) The $^{11}B\{^1H\}$ NMR spectra exhibited singlets at −8.8 and −10.6 ppm (basal borons) and two doublets at −41.4 and −52.1 ppm (apical borons; J_{BP} = 270 and 220 Hz, respectively).

(12) Urry, G.; Wartik, T.; Moore, R. E.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1954**, *76*, 5293–5298.

In contrast with the behavior of I and II, B_2Cl_4 reacts rapidly with diethyl ether at low temperatures (eq 10).[13]

$$B_2Cl_4{\cdot}OEt_2 \xrightarrow{-78\ ^\circ\text{C–room temp}} \text{“}BOCl_2\text{”} + 2EtCl \qquad (10)$$

Ethyl chloride was the only identified product of the reaction.

The 1,2'- and 2,2'-bi(pentaborane) isomers, on the other hand, are relatively inert in ether solutions. Neither isomer shows evidence of reaction or isomerization at 100 °C in diethyl ether.[13]

It is interesting to note that I and II show no evidence for isomerization in the presence of diethyl ether. Were isomerization observed in these derivatives, one might expect the formation of hexaborane derivatives, as is observed with $(\mu\text{-}Me_2B)B_5H_8$ (eq 11).[14]

$$(\mu\text{-}Me_2B)B_5H_8 \xrightarrow{Et_2O} 4,5\text{-}Me_2B_6H_8 \qquad (11)$$

While it has been inferred that such boron insertion reactions occur from the bridging position, the actual intermediate operating in the insertion may contain a terminal R_2B unit. It is evident that for I and II the activation energy for isomerization is greater than the activation energy for cleavage of the boron–boron σ bond. A study of the chemistry of various trigonal boron derivatives of pentaborane may lead to a better understanding of the mechanistic pathway for the production of hexaboranes from B_5H_9.

Reaction of II with Bu_3SnH. Tri-*n*-butyltin hydride is an effective dehalogenation agent for 1- and 2-halopentaboranes.[15] Compound II was reacted with *n*-Bu_3SnH in an effort to replace some or all of its chlorine atoms with hydrogen atoms. The only isolated products of this reaction were coupled boranes (eq 12).

$$1\text{-}(Cl_2B)\text{-}2\text{-}ClB_5H_7 + Bu_3SnH \xrightarrow[\text{1 week}]{\text{ambient}} 1,2'\text{-}(B_5H_8)_2 + \text{other nonvolatile oligomers} \qquad (12)$$

The mechanism of formation of the 1,2'-interpentaborane bonds in the products is unclear. The $1,2'\text{-}(B_5H_8)_2$ species has been independently synthesized via Friedel–Crafts catalyzed coupling (eq 13).[3]

$$B_5H_9 + 2\text{-}BrB_5H_8 \xrightarrow{AlBr_3} 1,2'\text{-}(B_5H_8)_2 + HBr \qquad (13)$$

Such a mechanism may also be operating here in the presence of a tetravalent tin Lewis acid.

Reaction of I and II with Ethylene. Both I and II react with ethylene at room temperature to form $1\text{-}[2\text{-}(Cl_2B)C_2H_4]$ pentaborane derivatives (eq 14).

$$1\text{-}(Cl_2B)B_5H_8 + C_2H_4 \xrightarrow[\text{pentane}]{\text{room temp}} 1\text{-}[2\text{-}(Cl_2B)C_2H_4]B_5H_8 \qquad (14)$$

The chemical properties of the $1\text{-}(Cl_2B)$ pentaborane derivatives again appear to parallel the reactivity of B_2Cl_4 (eq 1). The reactions between ethylene and I and II form only insertion products in aliphatic solvents but produce significant quantities of ethylbenzene-d_6 when conducted in benzene-d_6 solution.

The chemistry of the new $1\text{-}(Cl_2B)$ derivatives of pentaborane appears to parallel the reactivity of B_2Cl_4 more closely than the reactivity of intercage boron–boron σ bonds. The cleavage reactions of I and II observed in the presence of ether and the insertion of ethylene into the boron–boron σ bond of I and II are, superficially, very similar to the corresponding reactions of B_2Cl_4. Insufficient mechanistic data are currently available to conclude that the processes are actually identical. The formation of oligomers from II in the presence of *n*-Bu_3SnH suggests that the boron–boron σ bond may be a site for electrophilic attack, much like the boron–boron σ bond of $1,2'\text{-}(B_5H_8)_2$.

Acknowledgment. This work was supported in part by grants, including departmental instrument grants, from the National Science Foundation.

Registry No. I, 82544-57-8; II, 82554-82-3; B_5H_9, 19624-22-7; BCl_3, 10294-34-5; $2\text{-}ClB_5H_8$, 19469-14-8; Et_2O, 60-29-7; *n*-Bu_3SnH, 688-73-3; $1,2'\text{-}(B_5H_8)_2$, 31831-99-9; $H_2C{=}CH_2$, 74-85-1; $1\text{-}[2\text{-}(Cl_2B)C_2H_4]B_5H_8$, 82544-58-9; $FeCl_3$, 7705-08-0; $1'\text{-}Cl\text{-}1,2'\text{-}(B_5H_8)(B_5H_7)$, 82544-59-0.

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