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Synthesis and Characterization of 2-(Dichloroboryl)pentaborane(9)†

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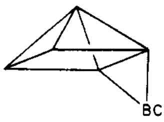
2-(Dichloroboryl)pentaborane(9), 2-$(Cl_2B)B_5H_8$, was synthesized by the treatment of μ-$(Cl_2B)B_5H_8$ with ether (Me_2O, Et_2O, or tetrahydrofuran) followed by the reaction of the resulting 2-$(Cl_2B{\cdot}OR_2)B_5H_8$ with BX_3 (X = Cl or F). The new compound was characterized by its ^{11}B and ^{1}H NMR, mass, and IR spectra. Thus, the syntheses of all three possible isomers of (dichloroboryl)pentaborane(9), μ-, 1-, and 2-isomers, were completed. The new isomer reacted with dimethyl ether, diethyl ether, or tetrahydrofuran to form a 1:1 adduct that was undissociated at room temperature. Ethylene inserted into the terminal B–B bond of the isomer to give 2-$(Cl_2BC_2H_4)B_5H_8$, and bromine cleaved the B–B bond to give 2-BrB_5H_8 and boron trihalides. The compound was inert to hydrogen chloride. The above conversion of μ-$(Cl_2B)B_5H_8$ into the 2-derivative of pentaborane as the result of the ether treatment was compared with the similar conversion of the group 14 element derivatives and was contrasted with the conversion of μ-$[(CH_3)_2B]B_5H_8$ into a hexaborane(10) derivative.

Introduction

Earlier, we reported the synthesis and characterization of μ-(dichloroboryl)pentaborane(9).[1] This compound featured a dichloroboryl (BCl_2) fragment bridging two of the basal boron atoms of the pentaborane framework. (See structure I.) Subsequently, Gaines and co-workers[2] reported the synthesis and characterization of the isomeric compound 1-(dichloroboryl)pentaborane(9) (structure II). This compound was unique in that a trigonal boron moiety was σ-bonded to a boron atom in a boron hydride cluster. Indeed, this compound was the first example of BX_2 substitution at the terminal position of the pentaborane(9) framework. We now report the synthesis and characterization of a third isomer of (dichloroboryl)pentaborane(9), 2-$(Cl_2B)B_5H_8$. This isomer, shown as structure III, contains a similar, discrete boron–boron σ-bond at a basal position of the pentaborane framework. This study thus concludes the isolation of all three possible isomers of (dichloroboryl)pentaborane(9).



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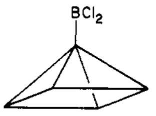

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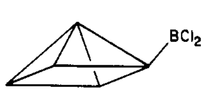

III

Results and Discussion

A. Synthesis of 2-$(Cl_2B)B_5H_8$. 2-(Dichloroboryl)pentaborane(9) was formed by a two-step process starting with μ-(dichloroboryl)pentaborane(9):

$$\mu\text{-}(Cl_2B)B_5H_8 + R_2O \xrightarrow[\text{in } CH_2Cl_2]{-80\ {}^\circ C} 2\text{-}(Cl_2B{\cdot}OR_2)B_5H_8 \quad (1)$$

$$R_2O = Me_2O,\ Et_2O,\text{ or tetrahydrofuran (THF)}$$

$$2\text{-}(Cl_2B{\cdot}OR_2)B_5H_8 + BX_3 \xrightarrow[\text{in } CH_2Cl_2]{\text{low temp}} 2\text{-}(Cl_2B)B_5H_8 + X_3B{\cdot}OR_2 \quad (2)$$

$$BX_3 = BF_3 \text{ or } BCl_3$$

In eq 1, the BCl_2 group migrated from its original bridge position to a basal terminal position upon the reaction with ether. Characterization of 2-$(Cl_2B{\cdot}OR_2)B_5H_8$ is described in part D of this section. Treatment of the ether complex of 2-(dichloroboryl)pentaborane(9) with an excess of BX_3 in dichloromethane liberated 2-$(Cl_2B)B_5H_8$, which was recovered in a 65–70% yield based on the original amount of μ-$(Cl_2B)B_5H_8$ used. For ease of isolation of 2-$(Cl_2B)B_5H_8$, BCl_3 was the preferred choice of Lewis acid to BF_3, because of the lower volatility of its ether adducts relative to that of the BF_3 etherates. The compound 2-$(Cl_2B)B_5H_8$ was isolated as a volatile, colorless liquid that yellowed on standing at room temperature in vacuo. It was extremely sensitive to water and air and required exhaustive flame-drying of the high-vacuum apparatus to prevent immediate formation of B_5H_9 and a nonvolatile white solid. Although it appeared reasonably stable at room temperature up to 1 week in dilute dichloromethane solutions, most solutions of this compound slowly turned yellow upon long standing at room temperature and B_5H_9 was detected in the ^{11}B NMR spectra of these solutions.

B. Characterization of 2-$(Cl_2B)B_5H_8$. Mass Spectrum. The mass spectrum of 2-$(Cl_2B)B_5H_8$ displayed a cluster of peaks around *m/z* 143, with the highest mass cutoff at *m/z* 148, which corresponded to the formula $^{11}B_6{}^{1}H_8{}^{37}Cl_2$. Other significant peak clusters in the spectrum included *m/z* 58–63 and 80–85, corresponding to $B_5H_n^+$ and BCl_2^+, respectively. Thus, it appeared that the facile dissociation of the boryl group in the spectrometer was similar to the case of the μ-$(Cl_2B)B_5H_8$ isomer.[1]

NMR Spectra. The ^{11}B and ^{1}H NMR data for 2-$(Cl_2B)B_5H_8$ are listed in Table I along with those for other new, related compounds, and the ^{11}B spectra are shown in Figure 1. The doublet signal at −50.3 ppm can be assigned to the apex B(1) atom, and the two doublets at −11.8 and −7.8 ppm in an approximately 2:1 intensity ratio are assigned to the B(3,5) and B(4) atoms, respectively. The signal of the trigonal boron atom in the $-BCl_2$ moiety appears at +67.5 ppm with a $J_{^{11}B^{11}B}$ value of 106 Hz. The signal of the B(2) atom, which is expected to be a broad quartet also, is overlapped by the B(3,5) signal, and only its high-field end is discernible in the ^{1}H-spin-decoupled spectrum (see Figure 1). The ^{11}B-spin-decoupled ^{1}H NMR spectrum shows the presence of two signals in a 1:1 intensity ratio in the bridge hydrogen region. Thus, the NMR data are consistent with the structure of 2-$(Cl_2B)B_5H_8$, which is schematically indicated in the figure. It is noted that, although the terminal ^{11}B–^{11}B coupling constant (106 Hz) is in the range (79–151 Hz) that has been found for the other compounds,[3] the Kroner and Wrackmeyer correlation predicts[3,4] a value of 86.2 Hz for the ^{11}B–^{11}B coupling constant. The assumptions made for the calculation were that the $-BCl_2$ moiety is hybridized sp^2 and the hybridization of the B(2) atom in 2-$(Cl_2B)B_5H_8$ is the same as that in 2,2′-$(B_5H_8)_2$, which is deduced from the observed B(2)–B(2′) coupling constant 79.4 Hz.[3] The disagreement between the observed and calculated values is considerable. It has been shown[3] that the same treatment for the terminal ^{11}B–^{11}B coupling constant for 1-$(Cl_2B)B_5H_8$, with the assumptions similar to the above, gives 118.8 Hz, which is in good agreement with the observed value 124 Hz. The cause of this discrepancy between the two systems is not immediately obvious.

[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(1) Nelson, M. A.; Kameda, M.; Snow, S. A.; Kodama, G. *Inorg. Chem.* **1982**, *21*, 2898.
(2) Gaines, D. F.; Heppert, J. A.; Coons, D. E.; Jorgenson, M. W. *Inorg. Chem.* **1982**, *21*, 3662.
(3) Anderson, J. A.; Astheimer, R. J.; Odom, J. D.; Sneddon, L. G. *J. Am. Chem. Soc.* **1984**, *106*, 2275 and references therein.
(4) Kroner, J.; Wrackmeyer, B. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 2283.

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Table I. ^{11}B and ^{1}H NMR Data for $2\text{-}(Cl_2B)B_5H_8$ and Related Compounds

^{11}B Shifts (ppm) and Coupling Constants (Hz)

	B(1)		B(2)		B(3,5)		B(4)		B(6)	
compd	shift	J_{BH}	shift	J_{BH}	shift	J_{BH}	shift	J_{BH}	shift	J_{BB}
$2\text{-}(Cl_2B)B_5H_8$	−50.3	178	−13.3		−11.8	160	−7.8	165	+67.5	106
$2\text{-}[Cl_2B{\cdot}O(CH_3)_2]B_5H_8$	−51.7	171	−5.9		−13.6	158	(−13.6)[a]	(158)	+11.3	*b*
$2\text{-}[Cl_2B{\cdot}O(C_2H_5)_2]B_5H_8$	−52.3	165	−4.4		−14.3	159	(−14.3)[a]	(159)	+7.2	*b*
$2\text{-}(Cl_2B{\cdot}OC_4H_8)B_5H_8$	−51.2	169	−3.1		−12.9	159	(−12.9)[a]	(159)	+8.4	*b*
$2\text{-}(Cl_2BC_2H_4)B_5H_8$	−52.5	172	+1.9		−13.8	156	−18.2	156	+62.0	
$2\text{-}[Cl_2B(OC_4H_8)C_2H_4]B_5H_8$	−52.9	171	+3.8		−14.6	160	−19.7	157	+14.1	
$\mu\text{-}(Cl_2B)B_5H_8$[c]	−34.2	185	−4.5	185 [for B(2,3) and B(4,5)]					+74.8	
$1\text{-}(Cl_2B)B_5H_8$[d]	−51.8		−13.1	160.6 [for B(2,3,4,5)]					+75.7	124

^{1}H Shifts (ppm)

compd	H(1)	H(3,4,5)[e]	H(μ)	compd	H(1)	H(3,4,5)[e]	H(μ)
$2\text{-}(Cl_2B)B_5H_8$	+0.66	+2.78	−1.65, −1.88	$2\text{-}(Cl_2BC_2H_4)B_5H_8$[g]	+0.49	+2.44	−1.51, −2.21
$2\text{-}[Cl_2B{\cdot}O(C_2H_5)_2]B_5H_8$[f]	+0.31	+2.43	−1.82, −2.20				

[a] The B(3,5) and B(4) signals are overlapped, and the shifts are almost identical. [b] The expected quartet structure could not be observed due to the broadness of the signal. [c] Reference 1. [d] Reference 2. [e] The signals of H(3,5) and H(4) could not be resolved unequivocally due to the broadness of the signals. [f] The signals of the CH_3 and CH_2 protons in $(C_2H_5)_2O$ appeared at 1.39 and 4.14 ppm, respectively. [g] The signals of C_2H_4 protons are located in the range from 1.0 to 1.6 ppm as overlapped peaks of a second-order coupling pattern.

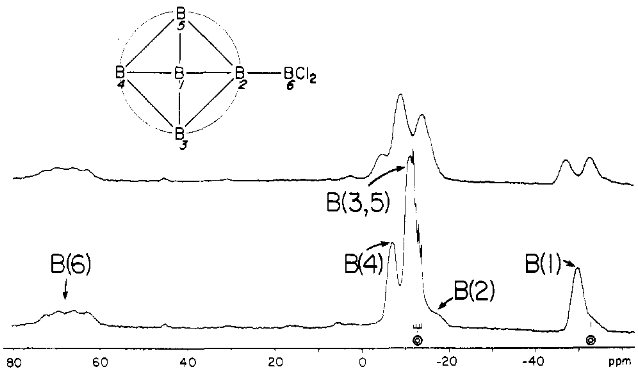

Figure 1. ^{11}B NMR spectra of $2\text{-}(BCl_2)B_5H_8$ in CH_2Cl_2 at ambient temperature: upper, normal spectrum; lower, proton-spin-decoupled spectrum; circles, signals of B_5H_9.

C. Reactions of $2\text{-}(Cl_2B)B_5H_8$. With Diethyl Ether. Treatment of $2\text{-}(Cl_2B)B_5H_8$ with diethyl ether at −80 °C resulted in the immediate formation of the ether adduct, which was stable in a diethyl ether solution at room temperature up to 3 h. This behavior was significantly different from that observed for $1\text{-}(Cl_2B)B_5H_8$, which did not appear to form an ether complex until it was heated to 50 °C.[2] It is known that on the pentaborane framework the apical position carries the greatest negative charge.[5] This higher charge density would decrease the acidity of the apically substituted BCl_2 moiety through an inductive effect. It is notable that there is a significantly large difference in the terminal ^{11}B–^{11}B coupling constants of the 1- and 2-isomers (*124 Hz* for $1\text{-}(Cl_2B)B_5H_8$[2] vs. *106 Hz* for $2\text{-}(Cl_2B)B_5H_8$). This would imply that the B–B bond in the apical isomer is stronger and therefore more resistant to the bond deformation. It may be this high energy of reorganization that requires the heating of the mixture for the 1-isomer adduct formation. The considerable difference in the observed behavior of these two isomers toward diethyl ether, however, is not completely understood. Further study, both experimental and theoretical, is needed to elucidate this different behavior.

With Bromine. Bromine reacted with $2\text{-}(Cl_2B)B_5H_8$ at a moderate rate in a dilute dichloromethane solution at room temperature, and $2\text{-}BrB_5H_8$ and boron trihalides were produced:

$$2\text{-}(Cl_2B)B_5H_8 + Br_2 \rightarrow 2\text{-}BrB_5H_8 + \text{“}BCl_2Br\text{”}$$

The mixed halide of boron in the product underwent a disproportionation reaction to produce BCl_3 and BBr_3. This reaction can be compared with the cleavage of B_2Cl_4 with Br_2 that occurs at −23 °C to form a mixture of BCl_3 and BBr_3 as the final products.[6]

With Hydrogen Chloride. No evidence for the reaction between HCl and $2\text{-}(Cl_2B)B_5H_8$ was detected when the reactants were mixed in dichloromethane and kept standing for 1 h at room temperature. This contrasted with the reactivity of the B–B bond in $B_2H_4{\cdot}2P(CH_3)_3$, which was cleaved readily by hydrogen chloride at −80 °C to give $(CH_3)_3P{\cdot}BH_3$ and $(CH_3)_3P{\cdot}BH_2Cl$.[7] Diboron tetrachloride, however, appeared to be inert to hydrogen chloride.[8]

With Ethylene. Ethylene inserted into the B–B bond of $2\text{-}(Cl_2B)B_5H_8$ to give $2\text{-}(Cl_2BC_2H_4)B_5H_8$. The reaction was slow at room temperature even in the presence of excess ethylene, requiring up to 2 weeks for the formation of a sufficient amount of the product. Thus, the rate of this reaction appeared to be comparable with that of $1\text{-}(Cl_2B)B_5H_8$ with ethylene.[2] Insertion of ethylene into the B–B bond in B_2Cl_4 proceeds readily at −80 °C.[9] In contrast, ethylene does not react with $B_2H_4{\cdot}2P(CH_3)_3$, even at room temperature.[10]

The ethylene insertion product, $2\text{-}(Cl_2BC_2H_4)B_5H_8$, was isolated as a colorless liquid, which was stable at room temperature, and was characterized by its ^{11}B and ^{1}H NMR spectra (Table I). The B(4) signal is shifted upfield 10 ppm from that of $2\text{-}(Cl_2B)B_5H_8$, and the B(2) signal is shifted downfield by 11 ppm. Thus, the appearance of the ^{11}B NMR spectrum resembles a superposition of the $2\text{-}CH_3B_5H_8$ and CH_3BCl_2 spectra.[11] The compound formed an adduct with tetrahydrofuran at the BCl_2 site, as indicated by the large upfield shift of the BCl_2 signal from +62.0 to +14.1 ppm.

The above described reactions indicate that the reactivity of $2\text{-}(Cl_2B)B_5H_8$ is similar to that of the 1-isomer except for the acid behavior toward diethyl ether. These BCl_2 derivatives of pentaborane(9), however, are less reactive than B_2Cl_4, or “$(Cl_2B)_2$”. The reactivity pattern of another B–B-bonded compound, $B_2H_4{\cdot}2P(CH_3)_3$, did not parallel that of the dichloroboryl compounds due to the entirely different environment of the boron atoms.

D. Reactions of $\mu\text{-}(Cl_2B)B_5H_8$ with Ethers ($(CH_3)_2O$, $(C_2H_5)_2O$, $(CH_2)_4O$). The reaction of $\mu\text{-}(Cl_2B)B_5H_8$ with dimethyl ether,

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(5) See, for example: Lipscomb, W. N. In "Boron Hydride Chemistry"; Muetterties, E. L., Ed.; Academic Press: New York, 1975; p 54.

(6) Apple, E. F.; Wartik, T. *J. Am. Chem. Soc.* **1958**, *80*, 6153.

(7) Kameda, M.; Kodama, G. *Inorg. Chem.* **1980**, *19*, 2288.

(8) Urry, G. In "The Chemistry of Boron and Its Compounds"; Muetterties, E. L., Ed.; Wiley: New York, 1967; Chapter 6, p 351.

(9) Urry, G.; Kerigan, J.; Parsons, T. D.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1954**, *76*, 5299.

(10) Kameda, M.; Kodama, G., unpublished observation.

(11) ^{11}B NMR shift values in ppm: for $2\text{-}CH_3B_5H_8$, B(1) −50.4, B(2) +2.2, B(3,5) −12.7, B(4) −18.1; for CH_3BCl_2, −62.3 (taken from: Eaton, G. R.; Lipscomb, W. N. "NMR Studies of Boron Hydrides and Related Compounds"; W. A. Benjamin: New York, 1969; pp 112, 449).

diethyl ether, or tetrahydrofuran was very rapid at −80 °C in the ether itself as solvent or in dichloromethane. As the reaction was monitored by ^{11}B NMR spectroscopy, the signals of μ-$(Cl_2B)B_5H_8$ immediately disappeared and were replaced by the signals of 2-$(Cl_2B{\cdot}OR_2)B_5H_8$, which are listed in Table I. No other signals of possible intermediates could be detected. As one visualizes from the shift values in Table I, the ^{11}B NMR spectra of the etherates have a general feature that is common to that of B_5H_9; i.e., two distinct doublets around −52 and −13 ppm stand our conspicuously. Two major differences between the ^{11}B NMR spectra of μ-$(Cl_2B)B_5H_8$ and 2-$(Cl_2B{\cdot}OR_2)B_5H_8$, however, help to identify the ether adduct. First, the resonance of the BCl_2 boron atom has been shifted upfield more than 60 ppm. This is consistent with the conversion of a trigonally coordinated boron atom into a tetrahedrally coordinated boron atom. The second difference between the two spectra is the broadness of the two signals that are assigned to the $Cl_2B{\cdot}OR_2$ boron atom and to the B(2) atom of the pentaborane framework. This wide breadth ($\nu_{1/2} \simeq 350$ Hz) is consistent with the presence of the B–B single bond between the two boron atoms. The ^{11}B-spin-decoupled ^1H NMR spectra showed two signals in the region of bridge hydrogen resonances in a 1:1 intensity ratio. This is also consistent with the 2-isomer structure of the adduct, but not with the μ-isomer structure.

The above described migration of a boron atom from the bridge to the 2-position of the pentaborane(9) framework is new for group 13 element derivatives, but is reminiscent of the ether-catalyzed isomerization of group 14 element derivatives of pentaborane(9),[12] e.g.

$$\mu\text{-}(ER_3)B_5H_8 \xrightarrow{\text{ether}} 2\text{-}(ER_3)B_5H_8 \quad (E = Si, Ge)$$

Among the group 14 elements, carbon is unique in that the carbon-bridging derivatives of pentaborane(9) are unknown, whereas several 2-(alkyl)B_5H_8 species are known.[13] Gaines and Jorgenson suggested,[14] on the basis of their observation on the reactions of $B_5H_8^-$ with allyl iodide and with benzyl bromide both in the absence of a Lewis base, that the carbon-bridging derivatives were thermodynamically unstable with respect to the corresponding 2-isomers and that the μ-derivatives isomerized to 2-derivatives at rates comparable to the rate of formation of the μ-derivatives. In our boron atom migration, the actual migrating group, $-BCl_2{\cdot}OR_2$, behaved as a "quasi-alkyl" moiety and migrated rapidly to the 2-position in a manner similar to that of the alkyl analogue. The formation of 2,2′-$(B_5H_8)_2$ in the reaction of $K^+B_5H_8^-$ with 2-BrB_5H_8[15] can be interpreted as the result of the quasi-alkyl behavior of the basal boron atom, which may have entered first at the bridging position of the pentaborane anion framework.

While the above similarity is apparent, a striking difference is noted between μ-$(Cl_2B)B_5H_8$ and μ-$[(CH_3)_2B]B_5H_8$ in the results of their interactions with ether; the latter converts into 4,5-dimethylhexaborane(10) in the presence of diethyl ether.[16] It is important to clarify the factors involved in these two different processes since they would be responsible for determining the route to the cage expansion or to the exocage substitution after a borane species has been placed in a bridge position of a boron hydride cluster.

Experimental Section

General Data. Conventional vacuum-line techniques were used for the handling of volatile compounds. For quantitative manipulation of (dichloroboryl)pentaborane(9) derivatives it was essential to have Teflon stopcocks fitted with Viton O-rings and removable joints with O-ring seal because of these compounds' high affinity for Apiezon M or N high-vacuum grease. Air- and moisture-sensitive solids were handled in glovebags filled with dry nitrogen gas. Boron trichloride, boron trifluoride, dimethyl ether, ethylene (Matheson Gas Products), and bromine (Mallinckrodt Chemicals) were purified by fractional condensation on the vacuum line. Commercially obtained reagent grade diethyl ether and tetrahydrofuran were stored over $LiAlH_4$, and dichloromethane was stored over molecular sieves. These liquids were distilled directly into reaction vessels on the vacuum line.

The ^{11}B and ^1H NMR spectra were recorded either on a Varian XL-100-15 spectrometer or on a Varian FT-80A spectrometer, both of which were operating in the FT mode. For the Varian XL-100-15, spectra were obtained at 32.1 and 100.1 MHz (^{11}B and ^1H, respectively), or for the FT-80A, ^{11}B spectra were acquired at 25.5 MHz. Chemical shifts were expressed with respect to $BF_3{\cdot}O(C_2H_5)_2$ and tetramethylsilane. The mass spectra were obtained from a VG Micromass 7070 double-focusing high-resolution mass spectrometer with VG data System 2000. Infrared spectra were acquired on a Beckman IR-20 infrared spectrometer.

Reactions of μ-$(Cl_2B)B_5H_8$ with Ethers (Me_2O, Et_2O, THF). Samples of μ-$(Cl_2B)B_5H_8$ were prepared by the literature method.[1] Reactions with ethers were performed in 9-mm-o.d. Pyrex tubes that were fitted with stopcocks. A weighed sample of the μ-isomer was condensed at the bottom of the reaction tube and was dissolved in about 2 mL of CH_2Cl_2. Then a measured amount of the ether sample was condensed into the tube. The mixture was allowed to melt and was agitated briefly at −80 °C. Then the tube was placed into the probe of the NMR spectrometer (−80 °C) for the spectrum recording. The reaction of μ-$(Cl_2B)B_5H_8$ with the ether was rapid and essentially complete at this temperature. In any mixture where the ratio of ether to μ-$(Cl_2B)B_5H_8$ was greater than 1, the ^{11}B NMR spectrum showed complete conversion of μ-$(Cl_2B)B_5H_8$ into 2-$(Cl_2B{\cdot}OR_2)B_5H_8$. In separate experiments where the ratio was less than 1, the spectrum showed the presence of both μ-$(Cl_2B)B_5H_8$ and 2-$(Cl_2B{\cdot}OR_2)B_5H_8$. No evidence for the *catalytic* conversion of μ-$(Cl_2B)B_5H_8$ by the ethers into 2-$(Cl_2B)B_5H_8$ was found in these experiments.

The etherates, 2-$(Cl_2B{\cdot}OR_2)B_5H_8$, were unstable white solids that rapidly yellowed at room temperature. When prepared from μ-$(Cl_2B)B_5H_8$, they were unstable in room-temperature solutions, and $HBCl_2{\cdot}OR_2$ was the major identifiable boron-containing species in these decomposition mixtures. It was noted that when **2-$(Cl_2B)B_5H_8$** was dissolved in diethyl ether, the resultant solution of 2-$(Cl_2B{\cdot}OEt_2)B_5H_8$ in the ether appeared somewhat more stable than when this compound was prepared from μ-$(Cl_2B)B_5H_8$. No $HBCl_2{\cdot}OEt_2$ was detected in the ^{11}B NMR spectra of these solutions up to 4 h at room temperature, whereas within 0.5–1 h this compound was detected in the solutions prepared from the μ-isomer.

Preparation and Isolation of 2-$(Cl_2B)B_5H_8$. In a typical preparation, 3.04 mmol of μ-$(Cl_2B)B_5H_8$ was distilled into a 22-mm-o.d. tube (as described previously) that contained a stirring bar. An 8-mL sample of dry CH_2Cl_2 was distilled into the reactor, and the two components were mixed together to form a uniform solution. The solution was cooled to −197 °C to condense in 4.65 mmol of THF, and then the mixture was stirred for 30 min at −80 °C to complete the reaction. To this mixture at −80 °C was introduced BCl_3 (6 mmol). Approximately one-third of it was absorbed immediately. At this point solid $BCl_3{\cdot}THF$ was seen precipitating from the solution. The remaining BCl_3 was condensed in at −197 °C. After the solution was allowed to melt, it was stirred for 15 min at −80 °C, 30 min at −45 °C, and finally 20 min at 0 °C. Then the volatile component was distilled out at 0 °C into the vacuum line until only a fluffy white solid (primarily $BCl_3{\cdot}THF$) remained behind. The last of the volatile component was pumped out at room temperature. Then the volatile component was set at −63 °C and CH_2Cl_2 was pumped out. 2-$(Cl_2B)B_5H_8$ was left behind as a white solid that melted uniformly upon warming. It was purified further by distilling out at 0 °C and fractionally condensing in a −45 °C trap. This procedure allowed for final removal of the high-volatility impurities. Yield: 2.10 mmol of 2-$(Cl_2B)B_5H_8$ or 69.1% based on the original amount of μ-$(Cl_2B)B_5H_8$. The mass spectrum of the compound was obtained on the spectrometer operating at 15 eV. The observed relative intensities of the peaks in the parent cluster were as follows [m/z, observed intensity (calculated relative intensity for $B_6H_8Cl_2$)]: 148, 1.3 (1.2); 147, 1.6 (1.6); 146, 7.9 (8.4); 145, 11.0 (10.8); 144, 17.0 (17.5); 143, 17.9 (17.9); 142, 11.4 (9.7); 141, 3.4 (3.0); 140, 0.9 (0.5); 139, 1.0 (0.05). The agreement between the observed and calculated values is good and suggests that the successive losses of pairs of hydrogen atoms were minimal for this compound under the conditions of the spectrum acquisition. The losses of hydrogen atoms in mass spectrometer have been observed commonly for many borane compounds.[17]

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Infrared spectral data for 2-$(Cl_2B)B_5H_8$ (10-cm gas cell equipped with KBr windows): 2592(s), 1785 (w, br), 1395 (m, br), 1335 (w, sh), 1187 (w), 1140 (m), 975 (sh), 937 (s), 885 (s), 839 (sh), 775 (w), 722 (w), 660 (m), 590 (w, br), 448 (w) cm^{-1}.

Reaction of 2-$(Cl_2B)B_5H_8$ with Diethyl Ether. Into a 9-mm-o.d. tube (as described previously) were condensed at −197 °C 0.2 mmol of 2-$(Cl_2B)B_5H_8$ and 1 mL of diethyl ether. The tube was warmed to −80 °C, agitated, and then placed in the probe of the NMR spectrometer for ^{11}B analysis. At −80 °C complexation of the ether had already occurred and only the signals of 2-$(Cl_2B{\cdot}OEt_2)B_5H_8$ were present in the spectrum.

Reaction of 2-$(Cl_2B)B_5H_8$ with Bromine. Into a 9-mm-o.d. tube (as described previously) were condensed at −197 °C 0.11 mmol of 2-$(Cl_2B)B_5H_8$, 1 mL of CH_2Cl_2, and 0.13 mmol of Br_2 (the once fractionated bromine was dried over P_2O_5 at room temperature). The mixture was warmed to −80 °C with agitation and then placed in the NMR probe. At 0 °C the signals of 2-BrB_5H_8[18] began to slowly grow, and after 1.5 h at room temperature the reaction was essentially complete. The color of the solution, which had been previously a very dark orange-red, had faded to a light yellow.

Since immediate assignment of the ^{11}B NMR signals of the products was quite difficult due to extensive peak overlap, the product mixture was fractionated on the vacuum line. When the volatile component was passed through a −63 °C trap, the high-volatility (BCl_3, BBr_3) component could be separated and identified. The low-volatility fraction consisted of 2-BrB_5H_8 (signals at −13.2, −20.9, and −52.9 ppm; lit.[18] ~−11, ~−15, ~−20, and −53.5 ppm) and possibly a small amount of 1-BrB_5H_8 as identified by the presence of signals at −12.6 and −35.9 ppm (lit.[18] −12.5 and −36.1 ppm).

Reaction of 2-$(Cl_2B)B_5H_8$ with Ethylene: Synthesis of 2-$(Cl_2BC_2H_4)B_5H_8$. In a typical preparation 0.75 mmol of 2-$(Cl_2B)B_5H_8$ was condensed at −197 °C into a 22-mm-o.d. tube (as described previously). Above the borane compound were condensed 2 mL of CH_2Cl_2 and 1.33 mmol of C_2H_4. The mixture was then warmed to room temperature, and stirring was commenced. After 2–3 h the solution had turned slightly yellow, but this color did not appear to intensify with prolonged reaction. The stirring was continued for 2 weeks, constantly at room temperature. Then the reactor vessel was connected to the vacuum line and all of the volatiles were condensed into a −197 °C trap. The new compound, 2-$(Cl_2BC_2H_4)B_5H_8$, was isolated in a pure form by fractional condensation of the volatile component into a −35 °C trap. The compound was a colorless liquid. The ^{11}B NMR spectra of the neat compound or its CH_2Cl_2 solution showed no sign of decomposition after 2 h of standing at room temperature. Yield: 0.14 mmol or 18.6% based on the original amount of 2-$(Cl_2B)B_5H_8$. The other major identifiable boron-containing product was B_5H_9, which was identified by its ^{11}B NMR spectrum.

Reaction of 2-$(Cl_2BC_2H_4)B_5H_8$ with THF. A 0.10-mmol sample of 2-$(Cl_2BC_2H_4)B_5H_8$ was condensed at −197 °C into a 9-mm-o.d. reaction tube (as described previously). Above this compound was condensed 1.5 mL of THF; the mixture was warmed with agitation to −80 °C and then placed into the probe of the NMR spectrometer. At this point the reaction was complete, and quantitative conversion into the THF complex was indicated by the ^{11}B NMR spectrum (see Table I).

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Registry No. μ-$(Cl_2B)B_5H_8$, 81643-54-1; 2-$[Cl_2B{\cdot}O(CH_3)_2]B_5H_8$, 97826-06-7; 2-$[Cl_2B{\cdot}O(C_2H_5)_2]B_5H_8$, 97826-07-8; 2-$(Cl_2B{\cdot}OC_4H_8)B_5H_8$, 97826-08-9; 2-$(Cl_2B)C_5H_8$, 97826-09-0; 2-$(Cl_2BC_2H_4)B_5H_8$, 97826-10-3; 2-$[Cl_2B(OC_4H_8)C_2H_4]B_5H_8$, 97826-11-4; BCl_3, 10294-34-5; Br_2, 7726-95-6; C_2H_4, 74-85-1.

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New Chemistry of (Difluoromethyl)phosphines

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The new phosphines $(CHF_2)_3P$, $(CHF_2)_2PI$, and CHF_2PI_2 were made in high yields from P_4 and CHF_2I at 190 °C. A low-yield source of CHF_2I was the action of I_2 on MCO_2CHF_2 salts; the new ester $CHF_2OC(O)CHF_2$ was the major product. Phosphines made from $(CHF_2)_2PI$ were $P_2(CHF_2)_4$, $(CHF_2)_2PCl$, and $(CHF_2)_2PH$; CHF_2PI_2 was converted to CHF_2PH_2 and CHF_2PCl_2. All of these are far less volatile than the analogous CF_3 phosphines; CH···F bonding interaction is suggested. The hybrid diphosphine $(CHF_2)_2P{-}P(CF_3)_2$ was formed in equilibrium with $P_2(CHF_2)_4$ and $P_2(CF_3)_4$ at 25 °C and recognized by NMR spectroscopy. HCl cleaves it to form primarily $(CF_3)_2PH$ and $(CHF_2)_2PCl$—necessarily because $(CHF_2)_2PH$ and $(CF_3)_2PCl$ quantitatively exchange H for Cl. Also, HCl easily cleaves $P_2(CHF_2)_4$ but requires catalysis to cleave $P_2(CF_3)_4$. Base action by CHF_2 phosphines is shown further by the formation of the nonpolar complexes $(CHF_2)_2PH{\cdot}BH_3$, $(CHF_2)_3P{\cdot}BH_3$, and $P_2(CHF_2)_4{\cdot}BH_3$, but not $CHF_2PH_2{\cdot}BH_3$. Analogous is the phosphine oxide $(CHF_2)_3PO$, made from $(CHF_2)_3P$ by action of NO_2. An attempt to convert $(CHF_2)_2PH{\cdot}BH_3$ to $[(CHF_2)_2PBH_2]_n$ was encouraging but inconclusive. The action of Hg on CHF_2PI_2 gave apparent $(CHF_2P)_n$ oligomers.

Phosphines containing the P–CHF_2 linkage are of interest because their chemical and physical properties might not always be predictable from the lore of the CH_3 and CF_3 phosphines. An obvious discrepancy is low volatility; for example, CHF_2PH_2 is less than $^1/_8$ as volatile as CH_3PH_2 or CF_3PH_2, and $P_2(CHF_2)_4$ is less than $^1/_{50}$ as volatile as $P_2(CF_3)_4$. The reason must be a C–H–F hydrogen-bonding effect with ΔH about 1–2 kcal—weaker than most recognized hydrogen bonding but stronger than the usual van der Waals effects.

This low volatility is a limiting effect because such air-reactive compounds are best studied by high-vacuum methods, whereby it is possible to work safely and often quantitatively with millimole samples of volatile compounds. But the CHF_2 analogues of $P_3(CF_3)_5$, $[(CF_3)_2PBH_2]_3$, and $(CF_3P)_4$ would not be volatile enough for study by such methods. Nonvolatile mixtures formulated as $[(CHF_2)_2PBH_2]_n$ and $(CHF_2P)_n$, made by predictable methods but not resolved into individual compounds, could be confirmed only by their chemistry.

Of the previously described CHF_2 phosphines, some have come from attacks upon $(CF_3)_2PH$ by bases, often retaining CF_3 groups.[1–5] Others were formed by the basic methanolysis of $(CF_3PCF_2)_2$, but the resulting mixtures were not always completely resolved.[6] The present paper describes a more systematic ap-

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