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Articles

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Reactions of the Diboron Tetrahalides B_2Cl_4 and B_2Br_4 with B_5H_9: Preparation and Properties of the (Dihaloboryl)pentaborane Derivatives $1\text{-}BX_2B_5H_8$, (X = Br, Cl, F, OCH_3, *t*-Bu, H) and Synthesis of $(BCl_2)_3B_5H_6$

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The reactions of B_2Cl_4 with excess B_5H_9 yield $1\text{-}BCl_2B_5H_8$ (73%) while those of B_2Br_4 generate $1\text{-}BBr_2B_5H_8$ (80%). Ligand exchange of $1\text{-}BCl_2B_5H_8$ with excess BBr_3 forms $1\text{-}BBr_2B_5H_8$ (86%), that with $Hg(CF_3)_2$ results in $1\text{-}BF_2B_5H_8$ (96%), that with CH_3OH generates $1\text{-}B(OCH_3)_2B_5H_8$ (46%), and that with Li(*t*-Bu) prepares $B(t\text{-}Bu)(Cl)B_5H_8$ (23%) and $B(t\text{-}Bu)_2B_5H_8$ (20%). The relative thermal stabilities of these products are $BF_2B_5H_8 > BCl_2B_5H_8 > BBr_2B_5H_8 > B(OCH_3)_2B_5H_8 > B(t\text{-}Bu)_2B_5H_8$. All of these $BX_2B_5H_8$ compounds (X = F, Cl, OCH_3, *t*-Bu) decompose to form BX_3 and B_5H_9 as the volatile products. Reactions of $BCl_2B_5H_8$ with excess B_2Cl_4 yield $(BCl_2)_3B_5H_6$, a compound of limited thermal stability, but no evidence for further BCl_2 substitution on the pentaborane cage was obtained. Reductions of $BCl_2B_5H_8$ with $LiBH_4$ in C_6H_5Cl or $C_6H_4Cl_2$ form apparent equilibrium mixtures of $1{:}1',2'\text{-}[B_5H_8][B_2H_5]$ and $1{:}1'\text{-}[B_5H_8][B_2H_5]$. One or both of these compounds decompose with the evolution of B_2H_6, B_5H_9, and coupled pentaborane cages $(B_5H_7)_n$, where *n* can be at least as large as 8. The ^{11}B NMR and mass spectrometric evidence from the last reaction is consistent with the initial dimerization of the hexaborane $1\text{-}BH_2B_5H_8$, which is rapidly followed by the formation of $1{:}1'\text{-}[B_5H_8][B_2H_5]$, the cross product arising from the interaction of B_2H_6 with $(BH_2B_5H_8)_2$, and then isomerization of this heptaborane to $1{:}1',2'\text{-}[B_5H_8][B_2H_5]$.

Introduction

The chemistry of diboron tetrachloride, one of the simplest molecules that contains a boron–boron σ bond, was initially examined by Schlesinger and his students who found that B_2Cl_4 reacts with SbF_3, BBr_3, ROH, HNR_2, and, in the gas phase, H_2 to generate B_2F_4, B_2Br_4, $B_2(OR)_4$, $B_2(NR_2)_4$, and B_2H_6, respectively, but that B_2Me_4 could not be isolated from the interaction of B_2Cl_4 with $ZnMe_2$.[1,2] They also determined that B_2Cl_4 adds across the carbon–carbon multiple bonds in, e.g., C_2H_4 or butadiene to give (dichloroboryl)alkanes, i.e., $CH_2(BCl_2)CH_2(BCl_2)$ or $CH_2(BCl_2)CH(BCl_2)CH(BCl_2)CH_2(BCl_2)$, respectively.[3,4] Later, others uncovered two alternative B_2Cl_4 reaction pathways with organic substrates, BCl_2 for H substitution in benzene[5] and ferrocene[6] and the "replacement" of Cl by BCl_2 in, e.g., CH_2CHCl, which reacts with 2 mol of B_2Cl_4 to ultimately form $CH_2(BCl_2)CH(BCl_2)_2$ and BCl_3.[7] One of the characteristics of the reactions between the organic reagents and B_2Cl_4 is that boron–carbon single bonds can be formed in relatively high yields under very mild conditions.

Most curiously, however, aside from preliminary studies with B_2H_6 and B_6H_{10}, the interactions of the diboron tetrahalides with perhaps the most logical substrates of them all, representative boron hydrides, have never been addressed; thus one purpose of the present study was to determine if B_2Cl_4 and B_2Br_4 react with B_5H_9 to generate compounds containing new boron–boron single bonds under mild conditions and to then examine whether other derivatives could be formed by standard procedures.

A priori, two types of reaction pathways seemed most probable. The first was the direct incorporation of B_2Cl_4 into a boron hydride, a reaction similar to that reported for B_4Cl_4 and B_2H_6[8] and analogous to the reactions of B_2Cl_4 with alkenes. With B_5H_9, for example, this type of reaction would result in halogenated derivatives of the rarest of the small boranes, the heptaboranes. The second plausible B_2Cl_4 reaction scheme envisioned BCl_2 for H substitution similar to that found in benzene and ferrocene, which would form BCl_2H and dichloroboryl derivatives of the borane. (Dihaloboryl)boranes are also rare since only the three isomeric (dichloroboryl)pentaboranes $1\text{-}(BCl_2)B_5H_8$,[9] $2\text{-}(BCl_2)B_5H_8$,[10] and $\mu\text{-}(BCl_2)B_5H_8$[11] and the related $1\text{-}(BCl_2)\text{-}2\text{-}ClB_5H_7$[9] have been separated. Relatively little is known of the derivative chemistry of these compounds.[9-11]

In addition to their rarity, the (dihaloboryl)boranes are also of interest in a much different context, that of the thermal disproportionations of the diboron tetrahalides themselves. For B_2Cl_4, this reaction ultimately results in BCl_3 and the polyhedral boron halides B_nCl_n, $n = 8\text{-}12$.[12] The mechanism that has been proposed suggests that it proceeds through a series of as yet uncharacterized intermediates several of which, among them chlorodecaboranes, are structurally analogous to the *nido*-boranes.[12,13] Timms has also reported that a series of BF_2-substituted boranes, in particular the pentaborane(9) derivative $B_5(BF_2)_9$, may play a pivotal role in the thermal reactions of the polyboron fluorides.[14] Overall, the postulated B_2Cl_4 thermal reaction mechanism[13] indicates that it may well be possible to synthesize boron hydrides containing one or even a few BCl_2 groups, but derivatives that contain numerous BCl_2 substituents should be quite limited in their thermal stability; thus, the second purpose of the experiments below was to examine the reactivity of excess B_2Cl_4 with B_5H_9 in order to determine the nature of the products formed and their thermal stabilities.

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Table I. ^{11}B NMR Chemical Shifts for 1-(Dihaloboryl)pentaborane Derivatives: Comparisons with Diboron Tetrahalide Derivatives[a]

compound	δ(B(boryl))	δ(B(basal))	δ(B(apical))	compound	δ(B)
$B(t\text{-}Bu)_2B_5H_8$	116.6	−10.7	−47.9	$B_2(t\text{-}Bu)_3R$	104,[b] 103[c]
$B(t\text{-}Bu)ClB_5H_8$	94.3	−10.6	−50.7	1,2-$B_2Cl_2(t\text{-}Bu)_2$	84.3[b]
$BBr_2B_5H_8$	77.9	−12.0	−45.8	B_2Br_4	69.5
$BCl_2B_5H_8$[d]	75.5	−12.4	−51.3	B_2Cl_4	63.0
$BCl(OMe)B_5H_8$	50.0	−12.6	−56.0		
$B(OMe)_2B_5H_8$	37.7	−12.7	−59.4	$B_2(OMe)_4$	30.5
$BF_2B_5H_8$	35.5[e]	−12.5	−57.7	B_2F_4	23.8
$(BH_3)BH_2B_5H_8$	30.7	−12.7	−54.5	B_2H_6	18.1
$(B_2H_5)B_5H_8$	−3.1	−11.2	−58		
B_5H_9		−13.5	−53.5		

[a] All values in ppm, positive values deshielded from $BF_3{\cdot}OEt_2$. [b] R = $CH_2C(CH_3)_3$.[20] [c] R = Me.[20] [d] Reference 9: 75.7, −13.1, and −51.8 ppm, respectively. [e] This resonance is a 1:3:4:4:3:1 sextet.

Experimental Section

General Data. All manipulations were carried out in a Teflon-valve-equipped standard vacuum line or a nitrogen-filled glovebox. The NMR spectra were obtained from an IBM 200SY instrument (64.2 MHz for ^{11}B); positive chemical shifts are deshielded from the external standards $BF_3{\cdot}OEt_2$ (^{11}B), $SiMe_4$ (^1H), or CF_3COOH (^{19}F). Low-resolution mass spectra (70 eV) were acquired from an AEI MS-30 spectrometer operating with the source at ambient temperature. Since many of the halides discussed below are air-sensitive, the samples were routinely prepared in a glovebox, transported under nitrogen, and loaded into the instrument through a nitrogen-filled glovebag that surrounded the entrance port. The exact mass determinations were obtained by standard peak matching techniques.

Diboron tetrachloride and B_2Br_4 were prepared by means of the radiofrequency discharge reactions previously described.[12,15] Pentaborane(9) was obtained commercially (Callery). All three were fractionated immediately prior to use. Boron trifluoride (Matheson) was purified by passage through a trap maintained at −130 °C; BBr_3 was fractionated after the removal of the accompanying Br_2 with mercury. Bis(trifluoromethyl)mercury was derived from the thermal decarboxylation of $(CF_3CO_2)_2Hg$.[16] The remainder of the reagents were commercially obtained and used as received. Etherial solvents were dried over sodium benzophenone ketyl; halocarbons were dried over P_2O_5.

Synthesis of 1-(Dichloroboryl)pentaborane. All of the reactions between B_2Cl_4 and B_5H_9 that are described below were carried out in 5-mm Pyrex tubes to which Teflon valves had been sealed. To insure rapid and intimate mixing, small aliquots of the reagents were alternately condensed into the reactor, resulting in thin layers of B_2Cl_4 that were sandwiched between the layers of pentaborane. The vessels were then allowed to warm from −196 °C to ambient temperature. Within 2 min of warmup the reagents always assumed a lime green coloration; within 12 min, the reaction had ceased. The components of the resulting mixtures were separated by fractionation and subsequently identified by mass spectrometry and/or boron NMR spectroscopy. Neither B_2Cl_4 nor its monovalent decomposition products, B_nCl_n, n = 8–12, were observed at the conclusion of any of these experiments.

Reaction of B_2Cl_4 with Excess B_5H_9 in a 1:3 Mole Ratio. Pentaborane 0.2984 g (4.74 mmol), and B_2Cl_4, 0.2451 g (1.490 mmol), mixed as described above, were allowed to react for 20 min at ambient temperature. Separation of the products yielded 1-$BCl_2B_5H_8$, characterized below, 0.1561 g (1.086 mmol), BCl_3, 0.65 mmol, and B_5H_9, 3.60 mmol, along with small amounts of BCl_2H, B_2H_5Cl, and B_2H_6. In addition, 0.0242 g of material was insufficiently volatile to move into the vacuum line, see below. The isolated yield of 1-$BCl_2B_5H_8$ was 73%, based upon the amount of B_2Cl_4 employed, and 95%, based upon the amount of B_5H_9 consumed.

Reaction of B_2Cl_4 with B_5H_9 in a 1.0:1.4 Mole Ratio. At ambient temperature 0.0795 g (1.26 mmol) of B_5H_9 and 0.1451 g (0.888 mmol) of B_2Cl_4 were allowed to react for 25 min. Pentaborane(9), BCl_3, and 1-$BCl_2B_5H_8$, 0.0333 g (0.232 mmol), were subsequently separated. Additionally, 0.0377 g of residue remained within the reactor. On the basis of the amount of B_2Cl_4 taken, the yield of 1-$BCl_2B_5H_8$ isolated in this reaction was 26%.

Reaction of Excess B_2Cl_4 with B_5H_9 in a 2.9:1.0 Mole Ratio. After 12 min at ambient temperature, the reaction between B_2Cl_4, 0.55964 g (3.4242 mmol), and B_5H_9, 0.7401 g (1.176 mmol), resulted in the formation of 0.03676 g (0.2557 mmol) of 1-$BCl_2B_5H_8$. Pentaborane, 0.02712 g (0.4293 mmol), and BCl_3, 0.365 g (3.12 mmol), were also recovered. After this reaction 0.2047 g of nonvolatile material remained within the vessel. Under these conditions, the yield of $BCl_2B_5H_8$ was 8%, based upon the amount of B_2Cl_4 utilized, and 34%, based upon unrecovered B_5H_9.

Table II. ^{11}B NMR Coupling Constants (Hz) for (Dihaloboryl)pentaborane Derivatives

compound	J_{B-B}[a]	J_{B-H}[b]
$B(t\text{-}Bu)_2B_5H_8$[c]	(s)	159
$B(t\text{-}Bu)ClB_5H_8$[d]	(s)	160
$BBr_2B_5H_8$	127 (q)	165
$BCl_2B_5H_8$[e]	123 (q)	163
$BCl(OCH_3)B_5H_8$	125 (q)	
$B(OCH_3)_2B_5H_8$[f]	114 (q)	165
$BF_2B_5H_8$[g]	ca. 129 (qt)[h]	167
$(BH_3)BH_2B_5H_8$	89 (q)	164
$B_2H_5B_5H_8$	23 (q)	163

[a] Boryl–apex boron coupling. [b] Basal B–H coupling. [c] $\delta(^1H(t\text{-}Bu))$ = 1.1(s) ppm. [d] $\delta(^1H(t\text{-}Bu))$ = 0.9 (s) ppm. [e] $\delta(^1H)$: H_T = 2.35 (q) (J_{B-H} = 168), H_μ = −2.60(s). [f] $\delta(^1H)$: H_T = 2.45 (q) (J_{B-H} = 168), H_μ = −2.28 (s), H_{CH_3} = 3.58 (s). [g] $\delta(^1H)$: H_T = 2.48 (q) (J_{B-H} = 167), H_μ = −2.23 (s). [h] Apparent sextet due to coupling of both apical boron and fluorine to boryl boron. In the ^{19}F NMR spectrum, δ = 36.5 (qq), coupling of both boryl and apical boron to fluorine leads to a very broad 10-line resonance.

This compound is a clear, colorless liquid that is retained in a trap held at −45 °C. The half-life at ambient temperature is ca. 3–4 months; the volatile decomposition products are BCl_3 and B_5H_9.

Exact mass for $^{11}B_6H_8{}^{35}Cl_2$: exptl, 144.0558; calcd, 144.0561; $\Delta m/m$, 2 ppm. The cutoff in the low-resolution mass spectrum is found at m/e 148, in agreement with the formulation $^{11}B_6{}^{37}Cl_2H_8$ and, with the exception of the ions associated with the $B_5H_n{}^+$ ion envelope, the most intense ion in the spectrum is at m/e 143 ($^{10}B^{11}B_5{}^{35}Cl_2H_8{}^+$). The boron NMR data, which are in agreement with the data reported by Gaines,[9] are collected in Tables I and II.

Synthesis of 1-(Dibromoboryl)pentaborane. Reaction of B_2Br_4 with Excess B_5H_9. Pentaborane, 0.466 g (7.38 mmol), and B_2Br_4, 0.514 g (1.51 mmol), were separately condensed into a 20 × 200 mm Pyrex reactor that had been equipped with a magnetic stirring bar. Four minutes after the initiation of the reaction, the originally clear, colorless solution had become an opalescent light green mixture. After 20 min at ambient temperature, the vessel was cooled to −10 °C, and over the course of the following 10 h, all material volatile at that temperature, including B_5H_9, 6.0 mmol, and BBr_3, 1.2 mmol, was removed into the line. The reactor was then allowed to warm to ambient temperature, and over the next 10 h all of the components volatile at room temperature were moved into a demountable trap maintained at −196 °C.

After removal of the demountable trap into a glovebox, 0.27 g (1.2 mmol), of $BBr_2B_5H_8$ was isolated by extraction with CH_2Cl_2. On the basis of the amount of B_2Br_4 employed, the yield of $BBr_2B_5H_8$ was 80%; on the basis of unrecovered B_5H_9, the yield was 86%. Additionally, 0.34 g of material that was not volatile at ambient temperature was contained within the reactor.

The compound $BBr_2B_5H_8$ is a colorless liquid that is retained in a trap held at −22 °C. The half-life of (dibromoboryl)pentaborane at ambient temperature is several weeks, the compound eventually decomposing into pentaborane, BBr_3, and yellow solids.

The boron NMR data for $BBr_2B_5H_8$, Figure 1, are contained in Tables I and II. Exact mass: measd, 232.9559; calcd for $^{10}B^{11}B_5{}^{79}Br^{81}BrH_8$, 232.9566 ($\Delta m/m$ 3.0 ppm). The low-resolution mass spectrum was complicated by the decomposition and/or hydrolysis of the compound

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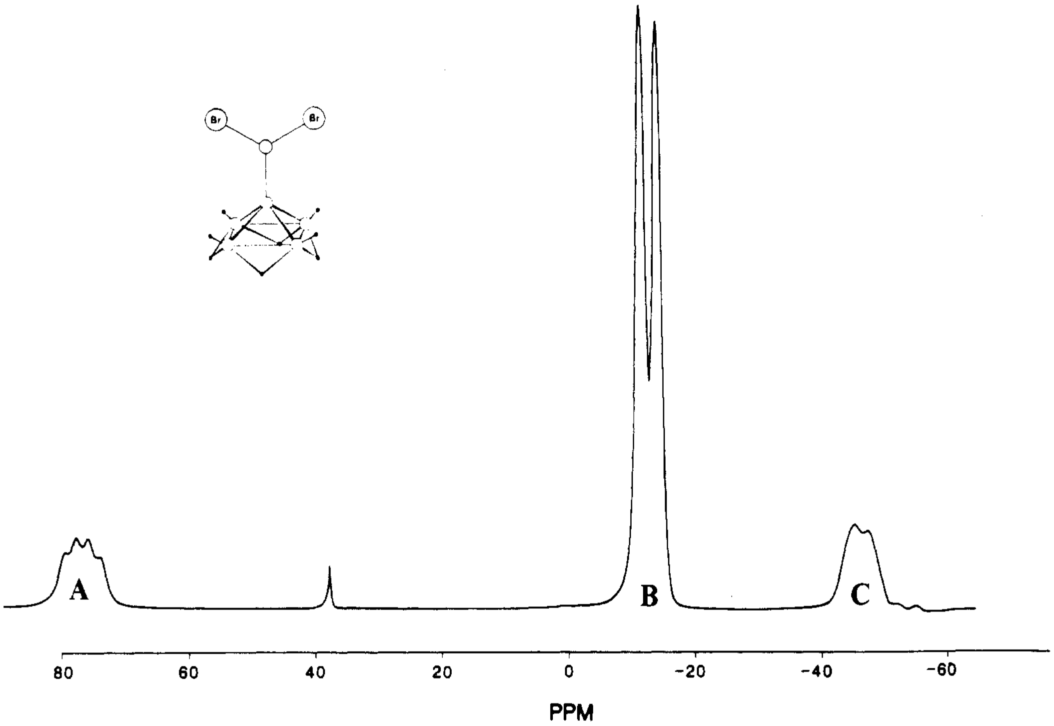

Figure 1. 64.2-MHz ^{11}B NMR spectrum of $BBr_2B_5H_8$. The chemical shift of the boryl boron (A) is 78 ppm. The chemical shift of the four basal boron atoms (B) is −12 ppm. The chemical shift of the apical boron atom (C) is −46 ppm. The small singlet at 39 ppm and the doublet evident at −54 ppm are from BBr_3 and the apical resonance of B_5H_9, respectively.

within the spectrometer, but a molecular ion envelope that cuts off sharply at *m/e* 236 and is centered at *m/e* 233, 6%, is clearly evident as are other envelopes that are centered at 171, 5% (BBr_2); 153, 51%, (B_6BrH_n); 138, 17% (B_5BrH_n); and 59, 100%, (B_5H_n).

Ligand-Exchange Reactions of the (Dihaloboryl)pentaboranes. Synthesis of $BBr_2B_5H_8$. Over the course of 2.5 h, three aliquots of BBr_3 that totaled 2.718 g (10.85 mmol) were added to $BCl_2B_5H_8$, 0.1714 g (1.192 mmol), that was contained in the reactor described above. After each addition, the vessel contents were magnetically stirred while the reactor was held at −78 °C, and then all of the material that was volatile at −78 °C was removed. At the conclusion of the experiment, the reactor was warmed to −10 °C and any residual boron trihalides were removed; $BCl_2B_5H_8$ was not observed.

After fractionation, $BBr_2B_5H_8$, 0.237 g (1.02 mmol), was separated in 86% yield and identified by boron NMR and mass spectrometry. Other products consisted of pentaborane, 0.11 mmol, and BBr_3 along with small amounts of B_2H_6, BCl_2H, BBr_2H, and mixed boron trihalides. The properties of $BBr_2B_5H_8$ prepared by this reaction were identical with those described above.

Synthesis of 1-(Difluoroboryl)pentaborane. In a preliminary reaction, 0.2 g of $BBr_2B_5H_8$ was condensed into a 500-mL reactor and then gaseous BF_3 was added until the pressure was 500 mm. After 48 h at ambient temperature, boron NMR spectroscopy yielded no evidence for either $BBr_2B_5H_8$ or $BF_2B_5H_8$.

Reaction of $BCl_2B_5H_8$ with $Hg(CF_3)_2$. The formation of $BF_2B_5H_8$ (96%) from the interaction of a briskly stirred mixture of $BCl_2B_5H_8$, 1.19 mmol, and $Hg(CF_3)_2$, 1.27 mmol, in the absence of solvent has been previously described.[17] Because of the large amounts of heat that can be generated, however, these reactions are better carried out at 0 °C. Alternatively, $BF_2B_5H_8$ can be prepared by the reaction of SbF_3 with $BCl_2B_5H_8$ at −78 °C.

(Difluoroboryl)pentaborane, is a clear, colorless liquid that passes through a −45 °C trap, but is held at −78 °C. At ambient temperature, the half-life of the compound is ca. 1 year; it decomposes to BF_3, B_5H_9, and yellow-orange solids. The NMR data are contained in Tables I and II. The mass spectra were entirely consistent with the formulation of the compound in that molecular ions (cutoff mass *m/e* 112) and M − F, M − 2F, B_5H_n, and BF_2 ions were observed. With the exception of the $B_5H_n^+$ ion envelope, the most intense ion in the mass spectrum is located at *m/e* 111, ($^{10}B^{11}B_5F_2H_8$; measd, 111.1188; calcd 111.1181; $\Delta m/m$, 6.3 ppm).

Synthesis of 1-(Dimethoxyboryl)pentaborane. Observation of $BCl(OCH_3)B_5H_8$. Methylene chloride, 0.48 mL, $BCl_2B_5H_8$, 17.4 mg (0.121 mmol), and degassed CH_3OH, 8.0 mg (0.25 mmol), were sequentially condensed into a 20 × 200 mm reactor and then, while the contents were magnetically stirred, the vessel was allowed to warm to ambient temperature over the course of 4 h. The reactor was opened, and the contents were fractionated. Boron NMR data (see Tables I and II) indicated the presence of $B(OCH_3)_2B_5H_8$ and $BCl(OCH_3)B_5H_8$ in the molar ratio 3:2. The sample was returned to the reactor, and an additional 10.1 mg (0.315 mmol) of CH_3OH was added. The contents of the vessel were stirred for a further 5 h with the temperature maintained between −60 and −20 °C and then separated. (Dimethoxyboryl)pentaborane, 7.51 mg (0.0556 mmol), was recovered in 46% yield. Among the other products formed were $B(OCH_3)_3$, $BCl(OCH_3)_2$, BCl_2OCH_3, $BH(OCH_3)_2$, and pentaborane.

The compound $B(OMe)_2B_5H_8$ (see Figure 2) is a clear, colorless liquid that is retained within a trap that is held at −22 °C. At ambient temperature, ca. 15% of this product decomposes within 60 min, and after 30 days only trimethyl borate and pentaborane are observed by boron NMR spectroscopy. The ^{11}B and ^1H NMR parameters are located in Tables I and II. The low mass end of the low-resolution mass spectrum was complex due to the near equivalence of the masses of the BH_3 (14) and CH_3 (15) groups as well as the decomposition and/or hydrolysis of the compound within the spectrometer. The high mass portion of the spectrum of $B(OCH_3)_2B_5H_8$ contained the following envelopes: 135, $B_6H_n(OCH_3)_2$, 40%; 120, $B_6H_n(OCH_3)O$, 68%; 104, $B_6H_n(OCH_3)$, 44%; 89, B_6H_nO, 100%. The cutoff mas was *m/e* 136.

Reactions with Alkylating Agents. Synthesis of 1-(Di-*tert*-butylboryl)pentaborane. Reactions of $BCl_2B_5H_8$ with Dimethylcadmium and Methyllithium. Dimethylcadmium, 50.5 mg (0.355 mmol), and $BCl_2B_5H_8$, 47.7 mg (0.331 mmol), were allowed to interact in $CDCl_3$, ca. 1.0 mL, for 60 min at ambient temperature. At the end of the experiment, boron NMR data indicated the presence of BMe_3 and B_5H_9 only. Reactions of $BCl_2B_5H_8$ with $LiCH_3$ yielded B_5H_9, $BClMe_2$, BCl_2Me, BMe_3, and $LiBMe_4$.

Reaction of $BCl_2B_5H_8$ with *tert*-BuLi. A hexane/BuLi solution (0.53 mmol) was added to a 15 × 80 mm Pyrex reactor that contained a small magnetic stirring bar. The reactor was evacuated and cooled to −196 °C, and then 0.933 g of pentane and 0.1158 g of $BCl_2B_5H_8$, 0.709 mmol, were condensed in. The reactor was warmed to −30 °C and stirred; white solids formed almost immediately. After 12 h at −30 °C, the solution was warmed to 0 °C, stirred for a further 45 min, and separated. Small amounts of $B(t\text{-}Bu)_2Cl$ (77.5 ppm) and much greater amounts of $B(t\text{-}Bu)Cl_2$ (63.2 ppm) and $BCl_2B_5H_8$ (61% of that taken) were observed in the fractions that passed −30 °C.

Pumping upon the reactor for several hours at ambient temperature allowed two (*tert*-butylboryl)pentaborane derivatives, 0.0235 g, to be slowly removed. The more volatile $B(t\text{-}Bu)ClB_5H_8$ is a colorless liquid

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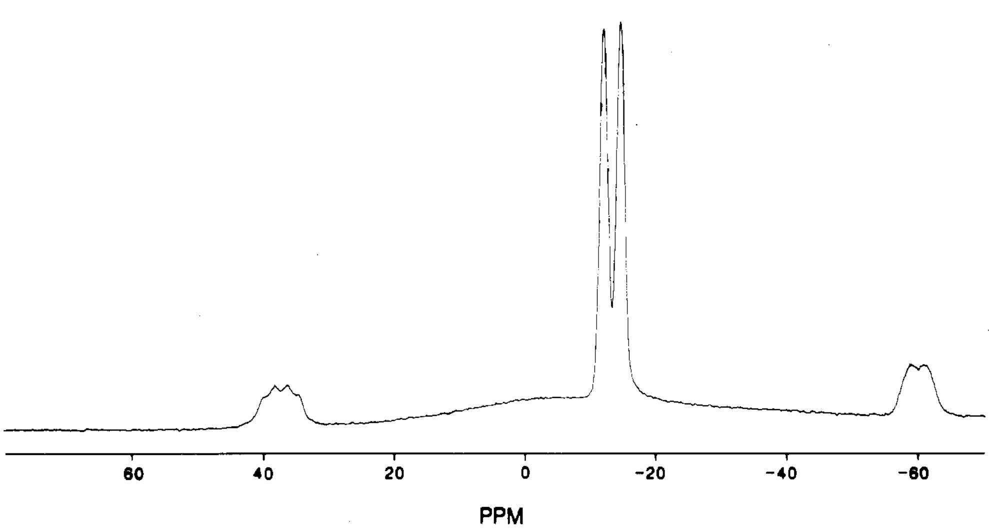

Figure 2. 64.2-MHz ^{11}B NMR spectrum of $B(OCH_3)_2B_5H_8$. From left to right the chemical shifts of the boryl, basal, and apical boron atoms are 38, -13, and -59 ppm, respectively.

that is retained at -30 °C whereas the less volatile $B(t\text{-}Bu)_2B_5H_8$ is a white solid that is held at -10 °C.

The yields of these compounds corresponded to 23 and 20%, respectively, based upon the unrecovered $BCl_2B_5H_8$. Both are of very limited stability, decomposing during the course of routine vacuum-line manipulations with the deposition of copious white or yellow solids. This decomposition precluded mass spectrometric examination of the compounds. The boron NMR data are located in Tables I and II.

Attempted Synthesis of Poly(dichloroboryl)pentaborane Derivatives. Observation of $(BCl_2)_3B_5H_6$. A variety of reactions between B_2Cl_4 and $BCl_2B_5H_8$ both with and without solvent were devoted to attempting to synthesize compounds of the type $(BCl_2)_nB_5H_{9-n}$. In one typical example, small amounts of B_2Cl_4, 0.1448 g (0.8860 mmol), and $BCl_2B_5H_8$, 0.04763 g (0.3250 mmol), in total, were alternately layered into a reactor that was then warmed from -196 °C to 0 °C over a 90-min period. Removal of the volatile components followed by CH_2Cl_2 extraction of the remaining lime green material yielded a colorless viscous liquid.

In addition to those of BCl_3 and BCl_2H, the boron NMR spectra of the products contained resonances in three discrete chemical shift regions: two very broad overlapping resonances centered at 72.9 and 67.8 ppm with the latter more intense than the former, five observable overlapping lines in the -5 to -13.5 ppm region, and a broad singlet at -46.2 ppm. Integration of the three regions yielded relative peak areas of 3.0:4.0:0.92. Proton decoupling left the resonances at 72.9, 67.8, and -46.2 ppm unaffected but resolved the multiplet located in the chemical shift region of the basal pentaborane atoms, -5 to -13.5 ppm, into four broad resonances located at -5.5, -7.7, -10.2, and -12.2 ppm.

The highest mass envelope in the mass spectrum corresponded to $(BCl_2)_3B_5H_n$, *m/e* 306, which was accompanied by envelopes centered at *m/e* 270, $(BCl_2)_2(BCl)B_5H_n$, *m/e* 234, $(BCl_2)(BCl)_2B_5H_n$, and *m/e* 225, $(BCl_2)_2B_5H_n$. The mass spectrum also contained ions from $B_{10}Cl_3H_{11}$ and $B_{10}Cl_2H_{12}$, however. Attempts to further purify the product lead to decomposition accompanied by the release of large amounts of BCl_3.

Limited mass spectral and NMR evidence for $(BCl_2)_2B_5H_7$ was obtained during a number of experiments that were carried out like that above, but under these conditions, no evidence for the existence of $(BCl_2)_4B_5H_5$ was obtained.

Reduction of $BCl_2B_5H_8$; Synthesis of 1:1′,2′-$[B_5H_8][B_2H_5]$ and 1:1′-$[B_5H_8][B_2H_5]$. Unsuccessful experiments to reduce $BX_2B_5H_8$, X = F, Cl, and Br, included reactions with B_2H_6, $LiAlH_4$, and $SnHMe_3$. (Dichloroboryl)pentaborane does react with $LiBH_4$[18] in Bu_2O, but the boranes produced are B_5H_9 and B_6H_{10}.

Successful reductions of $BCl_2B_5H_8$, 2.14 mmol, with $LiBH_4$, 15.1 mmol, were carried out in C_6H_5Cl and $C_6H_4Cl_2$, 10 mL. After the mixture was stirred for 45 min at ambient temperature, the materials sufficiently volatile to pass -63 °C were removed to a vacuum line, and then the remainder was stirred for another 20 h. Separation of the combined products yielded small amounts of B_2H_6 and B_5H_9, along with a two-component mixture that was retained at -73 °C. Boron NMR spectra of this fraction, Figure 3, contained three strong resonances for the first component at 29.9 (s), -12.7 (d) (J_{B-H} = 164 Hz), and -54.5 (s) ppm and three resonances for the second at -3.1 (t) (J_{B-H} = 125 Hz), -11.2 (d) (J_{B-H} = 163 Hz), and -58 (s) ppm. These resonances were accompanied by those of small amounts of diborane and another very small multiplet that was reminiscent of the spectrum of B_2H_6, but was centered at 17.6 ppm. The proton-decoupled ^{11}B spectrum contained multiplets centered at 29.9 ($J_{B-B} \simeq$ 79 Hz), -3.1 (q) ($J_{B-B} \simeq$ 23 Hz), and -11.2 (q) ppm (J_{B-B} = 19 Hz), along with singlets at 18.1, 17.6, -12.7, -54.5, and -58 ppm; see Figure 3. The mass spectra that were obtained immediately subsequent to separation contained ion envelopes at *m/e* 87 ($B_7H_n^+$), 100%; 71 ($B_6H_n^+$), 50%; 59 ($B_5H_n^+$), 73%, and 47 ($B_4H_n^+$), 25%. The high mass cutoff was located at *m/e* 90. The molecular ion region of the mass spectra was characterized by two maxima, one at *m/e* 87 (100%), and the second at *m/e* 83; in various samples, the intensity of the latter ranged from 50–85% of the former while, simultaneously, the ratio of the *m/e* 75 and 71 peaks varied from 1:1 to 1:2.

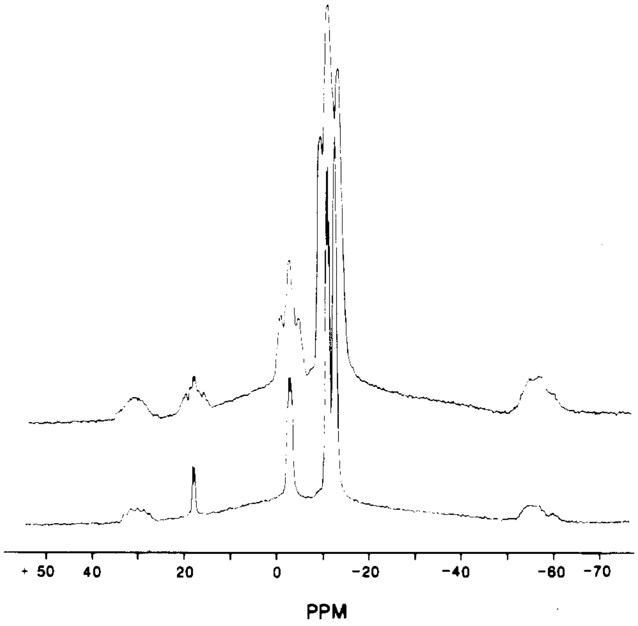

Figure 3. Proton coupled (upper trace) and decoupled (lower trace) ^{11}B NMR spectra of the products derived from the $LiBH_4$ reduction of $BCl_2B_5H_8$ shortly after separation. The resonances of 1:1′,2′-$[B_5H_8][B_2H_5]$ are found at -3.0, -11.2, and -58 ppm. The tallest peak in the decoupled spectrum (-12.7 ppm) is from the basal boron atoms of the $BH_2B_5H_8$ adducts. At this point in time there are clearly two resonances in the B_2H_6 region of the spectrum. The first (18.1 ppm) is from diborane; the second, much broader resonance (17.6 ppm) is assigned to the $(BH_3)BH_2B_5H_8$ cross product. The $\{^1H\}$ boryl resonance of the $BH_2B_5H_8$ adducts (-30 ppm) is not completely resolved into a quartet, but the apparent coupling constant is ca. 79 Hz. Later, as the concentration of B_2H_6 increases, the boryl resonance becomes more deshielded (31 ppm) and it can be cleanly decoupled into a quartet, J_{B-B} = 89 Hz.

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(18) Brown, H. C.; Choi, Y. M.; Narasimhan, S. *Inorg. Chem.* **1982**, *21*, 3657.

As time progressed the resonance of B_2H_6 grew much larger and those of B_5H_9 become evident. Along with these changes, the position of the resonance originally located at 29.9 ppm shifted toward 30.7 and the resonance could then be cleanly decoupled into a 1:1:1:1 quartet, J_{B-B} = 89 Hz.

On the basis of the boron NMR data, the formation of the major products of the reaction appeared to be nearly quantitative, but due to decomposition (see Discussion), the components of the mixture could not be separated. The half-life of the first component, which is thought to be a $BH_2B_5H_8$ adduct (see Discussion) is ca. 2 h at ambient temperature, while that of the second component is slightly longer. The volatile products that are formed in the decompositions include B_2H_6, and B_5H_9, along with traces of B_4H_{10} and B_8H_{12}. The mass spectra obtained upon the non-volatile portions of the reaction mixture contained envelopes centered at *m/e* 488, 427, 365, 304, 243, and 179.

Results and Discussion

Formation of (Dihaloboryl)pentaboranes and Their Derivatives. The reactions of B_2Cl_4 or B_2Br_4 with the *nido*-borane B_5H_9 are exceptionally convenient 20-min procedures for generating compounds that contain boron–boron single bonds. The course of the initial substitution can be represented as shown in eq 1 or 2.

$$B_2Cl_4 + B_5H_9 \rightarrow 1\text{-}(BCl_2)B_5H_8 + BCl_2H \qquad (1)$$

$$B_2Br_4 + B_5H_9 \rightarrow 1\text{-}(BBr_2)B_5H_8 + BBr_2H \qquad (2)$$

The ^{11}B and ^1H NMR data (see Tables I and II) along with the conventional 2D ^{11}B–^{11}B NMR spectra, unequivocally indicate that in the monosubstituted pentaboranes the hydrogen atom attached to the most electron-rich boron atom in the molecule, the apical boron, is substituted by the BCl_2 or BBr_2 group; thus, these reactions can be characterized as electrophilic in nature. Comparison of the products of eqs 1 and 2 with the products that have been reported from the interactions of B_2Cl_4 with various organic substrates indicates that the pentaborane reactions discussed here are directly analogous to those of benzene or ferrocene in which BCl_2 for H substitution was also demonstrated. Once formed, the second product of these reactions, BCl_2H (or BBr_2H), undergoes ligand interchanges to generate the B_2H_6, the chlorinated diboranes, and the BCl_3 that are ultimately observed.

When carried out in the presence of excess pentaborane, the yields of 1-$(BCl_2)B_5H_8$ and 1-$(BBr_2)B_5H_8$ are virtually quantitative, based upon the amount of B_5H_9 consumed, and ca. 75–80%, based upon the amount of B_2Cl_4 or B_2Br_4 originally taken. By way of comparison, in the only previous synthesis of 1-$(BCl_2)B_5H_8$ (9% yield) the presence of two catalysts was required and the reagents were maintained at 115 °C for 6 days.[9,19]

The halogen atoms in $BCl_2B_5H_8$ undergo typical displacement reactions (see Figure 4), and thus the exposure of $BCl_2B_5H_8$ to BBr_3, $(CF_3)_2Hg$, CH_3OH, and Li(*t*-Bu) results in the formation of the new compounds $BBr_2B_5H_8$ (86%), $BF_2B_5H_8$ (96%), BCl(OMe)B_5H_8, B(OMe)$_2B_5H_8$ (46%), BCl(*t*-Bu)B_5H_8 (23%), and B(*t*-Bu)$_2B_5H_8$ (20%). All of these reactions appear to initially produce the expected products in high yields, and the relatively modest amounts of some of the derivatives that were isolated are attributed to a decrease in the thermal stability of the products rather than secondary reactions between the reagents.

While the decomposition of the methoxide- and *t*-Bu-containing derivatives occurred continuously, which rendered the separation of these species difficult, the results from the $CdMe_2$ and LiMe reactions can be interpreted as suggesting an even more limited stability for the methylated species since the products expected from its decomposition were observed, but $BMe_2B_5H_8$ itself was not. This result is very similar to that which has been reported for the diboron tetraalkyls in that peralkylated diboron derivatives containing several bulky *t*-Bu groups are sufficiently stable for separation[20] whereas the permethylated B_2Me_4 has not been isolated.[1,20] Overall, 1-$(BMe_2)B_5H_8$ (in which the methylated boron atom would be tricoordinate) appears to be much less chemically accessible than the isomeric (μ-BMe_2)B_5H_8[21] (in which the methylated boron atom is tetracoordinate).

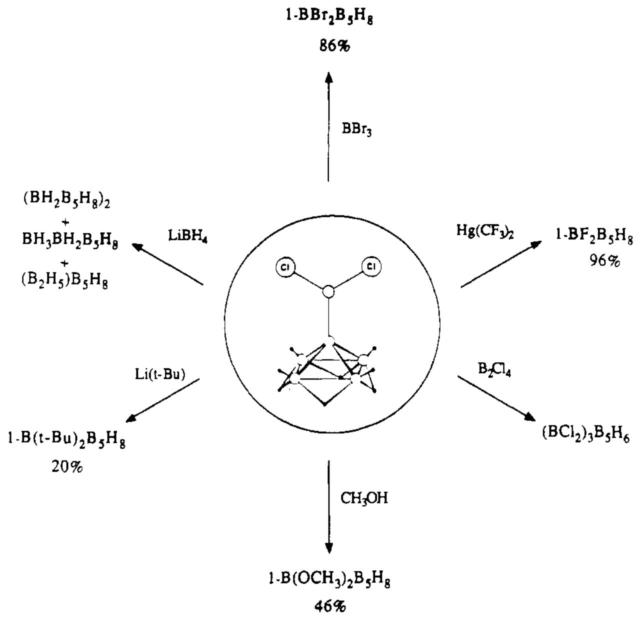

Figure 4. Reactions of 1-$BCl_2B_5H_8$.

In a formal sense the (dihaloboryl)pentaborane derivatives can be generated from the corresponding diboron tetrahalide derivatives by the replacement of one of the BX_2 groups in the latter with a pentaboranyl (B_5H_8) cage. The boron NMR data contained in Table I are easily interpreted in this light since the chemical shifts of the trigonal boryl boron atoms are all 7–14 ppm deshielded from the boron atoms in the analogous diboron tetrahalide derivatives. Alternatively, the boryl resonances can be thought of as 20–40 ppm deshielded from the resonances of the corresponding boron trihalide derivatives.

The chemical shifts of the apical boron atoms are all within 8 ppm of the apical resonance of B_5H_9, and like the proton-decoupled apical resonance of B_5H_9, they are broad due to relaxation effects. The resonances of the final type of boron atoms in the (dihaloboryl)pentaboranes, the basal atoms, are fairly insensitive to the identity of the ligands affixed to the boryl boron atoms since the chemical shifts vary over only a small range, ca. 3 ppm. In general, the integrated peak areas of the resonances of the ^{11}B spectra were in the expected 1:4:1 ratios, although in routine spectra the areas of the broadest of the boryl and apical resonances were commonly 10–15% less than indicated by the molecular formation. The apparent B–B couplings between the boron atoms joined by σ bonding, 110–130 Hz, Table II, are all within the normal range for this type of linkage[22] as are the apical to basal B–B couplings, e.g., 19.2 Hz for $BF_2B_5H_8$. The extreme precautions that must accompany further discussion of B–B couplings of even the parent boron hydride B_5H_9 (apparent J_{B-B} = 19.5 Hz) have been amply demonstrated.[23] The chemical shifts of all of the boron trihalide derivatives that were produced in the reactions described above were substantially in agreement with those found in ref 24.

The confirmatory ^1H NMR data from the (dihaloboryl)pentaborane derivatives contained two resonances of equal intensity, a quartet at ca. 2.4 ppm for the terminal protons and a broad singlet at ca. −2.5 ppm for the bridging protons. The data for three of these derivatives are appended to Table II.

One of the interesting characteristics of the mass spectra is that in contrast to most boron hydride derivatives, very little loss of hydrogen from the molecular ion occurs. For all three of the

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(19) A related species 2-BBr_2-1,6-$C_2B_4H_5$ has been formed (7%) from the interaction of BBr_3 with 1,6-$C_2B_4H_6$ at 260 °C. Nam, W.; Onak, T. *Inorg. Chem.* **1987**, *26*, 48.

(20) Biffar, W.; Noth, H.; Pommerening, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 56. Schluter, K.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 57. Presumably because of steric strain, $B_2(t\text{-}Bu)_4$ itself cannot be formed.

(21) Gaines, D. F.; Iorns, T. V. *J. Am. Chem. Soc.* **1970**, *92*, 4571.

(22) Anderson, J. A.; Astheimer, R. J.; Odom, J. D.; Sneddon, L. G. *J. Am. Chem. Soc.* **1984**, *106*, 2275.

(23) Weiss, R.; Grimes, R. N. *J. Am. Chem. Soc.* **1978**, *100*, 1401.

(24) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1988**, *20*, 61.

halides the most intense ion in the molecular ion region corresponds to the anticipated $BX_2B_5H_8$ ion of greatest natural abundance. For $BF_2B_5H_8^+$, for example, the expected ratio of the peak intensities at *m/e* 112, 111, and 110 is ca. 1.00:1.50:0.94; the measured ratio is 1.00:1.46:1.02. Relative to the peak at *m/e* 111, the intensity of the peak at *m/e* 107 is 8%. In contrast, in the 70-eV spectrum of B_5H_9 (cutoff mass *m/e* 64) obtained from the MS-30 instrument, the most intense ion in the molecular region is located at *m/e* 59, which nominally corresponds to the loss of four hydrogens from the molecule.[25] Presumably, the sites of initial ionization differ in the two types of molecule.

Finally, in the absence of basic solvents, the decomposition of all of the (dihaloboryl)pentaborane derivatives, $BX_2B_5H_8$, discussed here yields only BX_3 and pentaborane as volatile species. Neither the isomeric B_6H_{10}, its derivatives, nor $B_{10}H_{14}$ was observed.[26] Similarly, no evidence for the isomerization of the 1-substituted isomers to the 2-substituted isomers or ligand exchange of the type $2BCl_2B_5H_8 \rightleftarrows BCl_3 + BCl(B_5H_8)_2$ has been obtained. The overall stability order of the products formed is $BF_2B_5H_8 > BCl_2B_5H_8 > BBr_2B_5H_8 > B(OCH_3)_2B_5H_8 > B(t\text{-Bu})ClB_5H_8 > B(t\text{-Bu})_2B_5H_8$.

Synthesis of $(BCl_2)_3B_5H_6$. In 1-$(BCl_2)B_5H_8$ the chemical shift of the BCl_2 group is 75.5 ppm, Table I, and Kodama[10] has reported that in 2-$BCl_2B_5H_8$ the chemical shift of the BCl_2 group is 67.5 ppm. The most deshielded region of the ^{11}B NMR spectrum of the products obtained from the reaction of 1-$BCl_2B_5H_8$ with excess B_2Cl_4 is thus easily interpreted in terms of one apical BCl_2 group (72.9 ppm) and two basal BCl_2 groups (67.6 ppm) attached to the pentaborane cage. The chemical shift of a BCl_2 group in the third possible position, a bridging site, has been reported to be 74.8 ppm,[11] but in the present case, a bridging BCl_2 group is precluded since B–H coupling to the apical boron resonance would be required.

The chemical shift of the apical resonance of B_5H_9 (−53.5 ppm) is deshielded by 2.2 ppm upon formation of 1-$BCl_2B_5H_8$, Table I, and by 3.2 ppm in 2-$BCl_2B_5H_8$.[10] Presuming that these changes in chemical shift are additive leads to an anticipated chemical shift of ca. −44.9 ppm for the apical boron atom in $(BCl_2)_3B_5H_6$, which is in reasonable agreement with the −46.2 ppm that was measured experimentally.

The two possibilities for substituting two BCl_2 groups onto the base of the pentaborane cage lead to the 1,2,3-$(BCl_2)_3B_5H_6$ and the 1,2,4-$(BCl_2)_3B_5H_6$ isomers, each of which would be expected to produce two resonances in the $^{11}B\{^1H\}$ NMR spectrum and three in the undecoupled spectrum. In the experimental $^{11}B\{^1H\}$ NMR spectrum, four lines were observed, and although extensive overlap was present in the proton coupled spectrum, five lines were readily discerned; thus, the NMR evidence strongly suggests that both isomers of $(BCl_2)_3B_5H_6$ are formed during the reaction of 1-$BCl_2B_5H_8$ with excess B_2Cl_4. Due to the overlap, however, it was not possible to reliably assign the resonances in the −5 to −13.5 ppm region of the spectrum.

Like the boron NMR spectra, the mass spectral evidence from these studies was in accord with the formulation of the products as $(BCl_2)_3B_5H_6$ species, i.e., B_5H_9 derivatives, and not the B_5H_{11} derivatives that might be expected from the addition of B_2Cl_4 to $BCl_2B_5H_8$. Additionally, the mass spectra indicated the ready conversion of the polysubstituted (dihaloboryl)pentaboranes into BCl_3 and chlorodecaboranes, e.g., $B_{10}Cl_2H_{12}$ and $B_{10}Cl_3H_{11}$. In mass spectra of samples taken from the nonvolatile residues that remained from the various syntheses of $BCl_2B_5H_8$, in addition to ions arising from $(BCl_2)_2B_5H_7$ and $(BCl_2)_3B_5H_6$, those of chlorodecaboranes containing up to six Cl atoms, i.e., $B_{10}Cl_6H_8$, were clearly evident.

Reduction of $BCl_2B_5H_8$. At −30 °C the reduction of $BCl_2B_5H_8$ with $LiBH_4$ in C_6H_5Cl proceeds smoothly to generate boron hydrides, but both the mass and the ^{11}B NMR spectra indicate that the products are a mixture of two isomers. Neither could be separated from the other, perhaps an indication of an equilibrium, and one or both continuously decompose to generate B_2H_6 and B_5H_9 along with coupled pentaborane cages, $(B_5H_7)_n$. The mass spectra (*m/e* 488) indicate that *n* can be at least as large as eight in the polymeric products.

The boron hydride that is initially present in larger amounts is that with the chemical shifts of 29.9, −12.7, and −55 ppm. In appearance, these resonances are very similar to those of the (dihaloboryl)pentaboranes discussed above with the exception that B–B coupling is not evident upon the very broad, most deshielded resonance.

When one of the chlorine atoms in BCl_3 (46 ppm) is replaced by a hydrogen atom, the ^{11}B resonance of the product (58 ppm) is deshielded relative to the reagent and the same effect is observed for both BBr_3 and BF_3. Thus one might expect that the ^{11}B chemical shift of a tricoordinate boron atom in $BH_2B_5H_8$ would be considerable larger than the 76 ppm found for $BCl_2B_5H_8$, rather than the 29.9 ppm observed here. In diborane, however, the chemical shift of the tetracoordinate boron is 18 ppm, some 12 ppm less than that of the resonance observed in the first product of the $BCl_2B_5H_8$ reduction.

The resonances of this product are currently attributed to the boryl, basal, and apical boron atoms of a $BH_2B_5H_8$ species that is probably initially dimerized and then coordinated to a BH_3 group (derived from the B_2H_6 formed during the decomposition) by means of the type of bridge bonding found in B_2H_6 itself. In the $^{11}B\{^1H\}$ NMR spectra taken immediately after separation (see Figure 3), there are two resonances in the diborane chemical shift region, a narrow line (18.1 ppm) and a much broader resonance found at 17.6 ppm. We associate the latter and the boryl resonance at 30.7 ppm, $J_{B-B} = 89$ Hz, with the $(BH_3)BH_2B_5H_8$ cross product. This product is largely the source of the relatively strong molecular ions found at higher mass (*m/e* 87) and the ions at *m/e* 75 in the mass spectrum.

When the reduced product from $BCl_2B_5H_8$ is exposed to ambient temperature, in addition to those of B_2H_6 and B_5H_9, the resonances at −3.1, −11.2, and −58 ppm all increase relative to those described above. All of the current NMR and mass spectral data are consistent with the conversion of the 1-$BH_2B_5H_8$ adduct, $(BH_3)BH_2B_5H_8$, into the isomeric 1:1′,2′-$[B_5H_8][B_2H_5]$, a diborane derivative in which one of the bridging hydrogen atoms has been replaced by the (bare) apical atom of a pentaborane cage. This second compound is largely responsible for the *m/e* 83 and 71 peaks that are observed in the mass spectra.

Both of the heptaboranes that are generated in the $LiBH_4$ reductions of $BCl_2B_5H_8$ are thus the positional isomers of the basally substituted pentaborane derivatives that were observed by Sneddon in his examination of the $PtBr_2$-catalyzed dehydrocoupling reactions of B_2H_6 and B_5H_9 mixtures.[27] As yet we have no evidence for isomerization of the apically substituted species produced here into the 2-pentaborane isomer.

Collectively, the results described above indicate that reactions of B_2Cl_4 and B_2Br_4 with boron hydrides provide a significant new entry into the chemistry of boranes since previously unknown halides, hydrides, alkoxides, and alkyls can be easily prepared and readily examined, provided that the ultimate products are of reasonable thermal stability.

Acknowledgment. The financial assistance of the National Science Foundation is gratefully acknowledged.

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[25] See, for example: Solomon, J. J.; Porter, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 1443.

[26] Schaeffer has reported that B_2Cl_4 reacts with B_6H_{10} to yield an oily yellow liquid (which could not be characterized) that decomposes to $B_{10}H_{14}$ among others: Dolan, P. J.; Moody, D. C.; Schaeffer, R. *Inorg. Chem.* **1981**, *20*, 745.

[27] Corcoran, E. W.; Sneddon, L. G. *J. Am. Chem. Soc.* **1985**, *107*, 7446.