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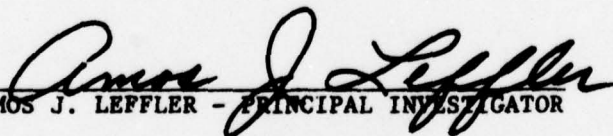
FINAL REPORT

SOLID PROPELLANT ADDITIVES FROM PENTABORANE-9

GRANT AFOSR 77-3301

PERIOD: APRIL 1, 1977 to JUNE 30, 1978

BY


AMOS J. LEFFLER - PRINCIPAL INVESTIGATOR

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Abstract

The electrochemical behavior of pentaborane-9 and its reactivity with acetylenic halides were studied. Although pentaborane-9 is itself not electroactive it does react with other electrochemically generated species. It was found that methyl iodide, iodobenzene, chromium hexacarbonyl, dimanganese decacarbonyl, and iron pentacarbonyl generated electroactive species that reacted with pentaborane-9. The reaction of pentaboryllithium and propargyl chloride and with 1,4-dichlorobutynes-2 yielded mixtures of nido-carborane polymers and some higher boranes. The propargyl chloride reaction product reacted with anhydrous cobaltous chloride and cyclopentadienyllithium to give a mixture of cobaltaboranes and cobaltacarboranes which were not separable. An attempt was made to prepare phenylpentaborane but the product could not be isolated.

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Introduction

The present report describes the work performed under Grant AFOSR 77-3301 during the period April 1, 1977 to June 30, 1978. The purpose of this work was to prepare stable propellant additives derived from pentaborane-9 containing transition metal ions. Since pentaborane-9 is both toxic and highly reactive it must be either incorporated into more complicated metalloorganic molecules with retention of structure or be altered by the introduction of other atoms into the cage to reduce the reactivity. Both approaches were attempted in the present work.

The chemistry of pentaborane-9 has been studied for more than fifty years and was reviewed¹ several years ago. For our purposes the chemistry can be divided into two types of reactions. The first type consists of reactions that result in the destruction of the boron skeleton and are exemplified by air oxidation, alcoholysis, and direct fluorination. This class of reactions is of no further interest and will not be treated further. The second type of reaction includes those that result in replacement of one or more terminal or bridge hydrogen atoms or one of the skeletal boron atoms without further degradation of the cage. Examples of this class of reactions are halogenation, Friedel-Crafts reaction, and replacement² of a boron atom by a metal carbonyl fragment. In a few cases³ it has been possible to increase the number of cage atoms by the reaction of the $B_5H_8^-$ ion with molecules such as B_2H_6 to form the $B_6H_{11}^-$ species which can be converted to B_6H_{12} . Finally Wreford⁴ has shown that B_5H_9 can be incorporated into transition metal complexes by oxidative addition with Vaska's complex, $IrCl(CO)(PPh_3)_2$. Although all of these are useful reactions, many go with poor overall yields and require a number of steps. For this reason the effort in the present work was focussed on simple reactions giving good yields of substances that can be used directly or readily converted into stable products.

As described in the proposal, the work and this report have been divided into two portions, one describing the electrochemical approach to introducing functional groups into B_5H_9 , and the second in which traditional chemical methods have been employed. In the following section the work is described and the results discussed separately for each portion and the experimental details are given in a separate section.

Results and Discussion

A. Electrochemistry - Electrochemical measurements have become widely used recently due to the development of commercial instrumentation, especially for polarography and cyclic voltammetry. Hawthorne⁵ has applied cyclic voltammetry to the measurement of oxidation and reduction potentials many carbollide complexes based on B_{10} and other large boron cage structures. Very little work has been carried out on the smaller boron hydrides; the only reference in the literature is to the work of Anderson⁶ in which a passing reference is made to testing boron hydrides in a paper devoted to describing the cell that was used in the present work. It was later found in a paper given⁷ at the 160th American Chemical Society Meeting in 1970 that the cyclic voltammetry of pentaborane-9 had been studied in tetrahydrofuran using a mercury electrode and no activity was found. In the present work this was confirmed for the glassy carbon electrode in the voltage range of +0.5 to -2.5 volts vs $Ag/0.01\ M\ Ag^+$. No cathodic or anodic peaks were observed over the full voltage range.

Since pentaborane-9 is not electroactive it seemed reasonable to determine whether pentaborane-9 is susceptible to attack by other generated electroactive species. Accordingly a number of potentially interesting species were generated, usually by a cathodic sweep first in the absence and then in the presence of pentaborane and the difference between the two sweeps observed. These are described below.

1. Methyl Iodide: Methyl iodide exhibited no electroactivity at the glassy carbon electrode. However, with a platinum electrode there was a reduction peak at -3.3 V and a much smaller oxidation peak at -1.1 V. In the presence of pentaborane the oxidation peak disappeared while the reduction peak appeared smaller and shifted to a slightly more positive potential. The data are summarized in Table I and typical voltammograms are shown in Figure 1.

2. Iodobenzene: A study of iodobenzene in the presence and absence of pentaborane-9 proved quite interesting. Cyclic voltammograms exhibited reduction peaks at -1.8 and -2.3 V respectively. Two anodic peaks were found at -1.6 and +0.2 V respectively. A typical voltammogram is shown in Figure 2A. The reduction peak at -1.8 V appears "quasi-reversible" while that at -2.3 V seems totally irreversible. The anodic peak at -1.6 V seems to correspond to reoxidation of the product from the first reduction step. Using the Nicholson and Shain treatment^{8,9,10} of electrode reaction kinetics the measured cathodic - anodic peak separation corresponds to a standard rate constant, k_s , for this electron transfer step of approximately $7 \cdot 10^{-4} \text{ cm sec}^{-1}$.

Upon addition of pentaborane-9 the behavior changed dramatically as shown in Figure 2B. Initially the first reduction peak increased slightly while its reduction peak disappeared completely. The second reduction peak also disappeared. Quite evidently the pentaborane-9 has reacted with the product from the first reduction step and removed it from further reaction. In addition, within a period of about one hour after addition of pentaborane-9, all peaks have disappeared entirely. The cause of this behavior is not understood. Data for iodobenzene are summarized in Table II.

3. Chromium Hexacarbonyl: At the glassy carbon electrode chromium hexacarbonyl showed one cathodic peak at -2.1 V and an anodic peak at 0.0 V as

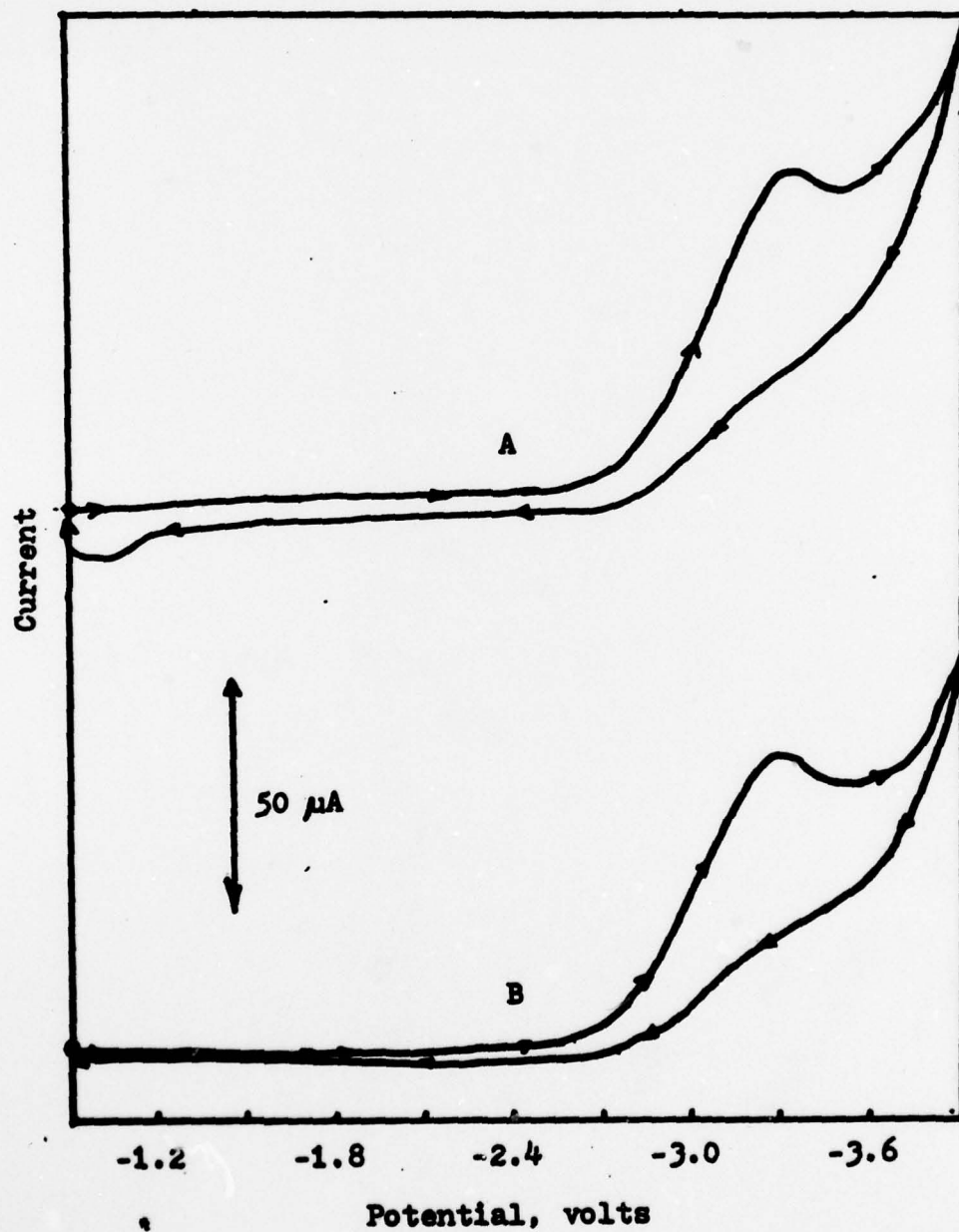


Figure 1

Cyclic Voltammogram at Pt in 0.1M $(C_4H_9)_4NBF_4$ of (a) CH_3I and (b) $CH_3I + B_5H_9$.

Sweep rate = 200 mV/sec.

Table I

Cyclic Voltammetry at Pt of CH_3I in 0.1 M $(\text{C}_4\text{H}_9)_4\text{NBF}_4$

Sweep Rate	Cathodic		Anodic	
	E_p	i_p	E_p	i_p
V/sec	V	μA	V	μA
0.050	-3.27	46.4	-1.05	1.0
0.200	-3.36	70.4	-1.03	3.2
* B_5H_9 :				
0.200	-3.24	59.0	*	*

* No peak observed.

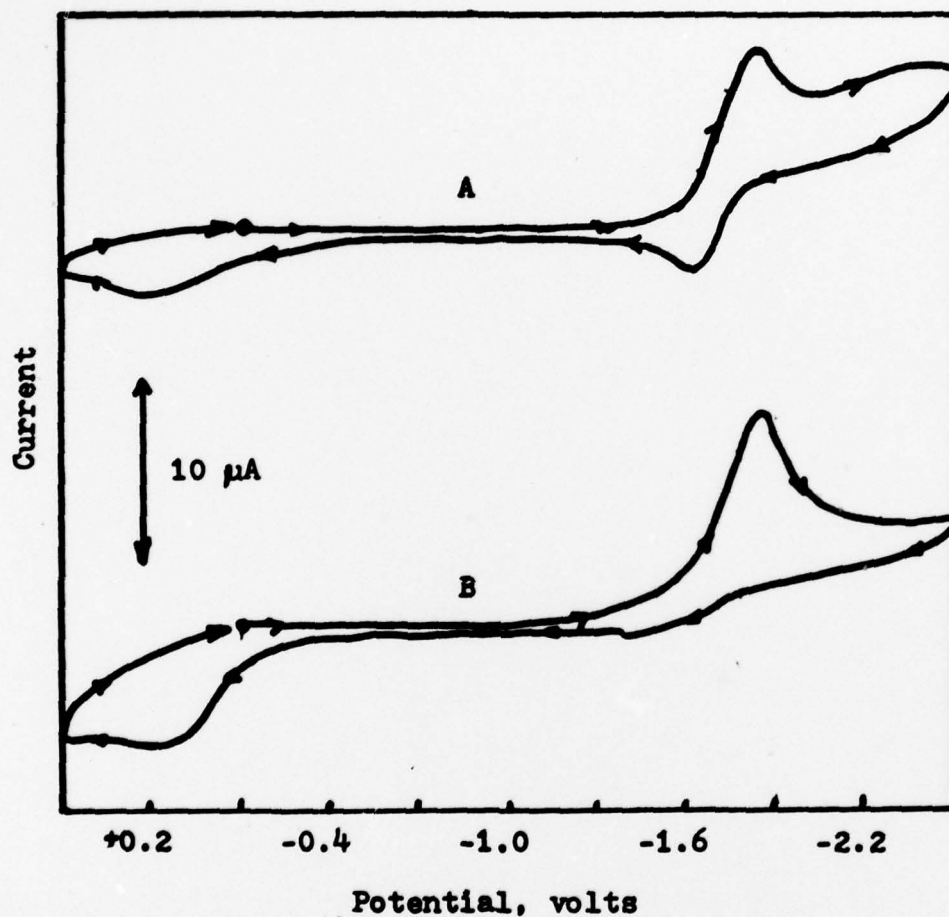


Figure 2

Cyclic Voltammograms at the GCE in $0.1\text{M } (\text{C}_4\text{H}_9)_4\text{NBF}_4$ of (a) $\text{C}_6\text{H}_5\text{I}$ and (b) $\text{C}_6\text{H}_5\text{I} + \text{B}_5\text{H}_9$.

Sweep rate = 50 mV/sec.

Table II

Cyclic Voltammetry at the GCE of C_6H_5I in 0.1 M $(C_4H_9)_4NBF_4$

Sweep Rate V/sec	<u>Cathodic</u>				<u>Anodic</u>			
	<u>peak 1</u>		<u>peak 2</u>		<u>peak 1</u>		<u>peak 2</u>	
	E_p V	i_p μA	E_p V	i_p μA	E_p V	i_p μA	E_p V	i_p μA
0.050	-1.81	9.5	-2.28	1.7	-1.62	4.0	+0.19	2.2
0.200	-1.89	15.2		...	-1.58	6.8		...
* B_5H_9 :								
0.050	-1.82	11.7	*	*	*	*	+0.16	6.3

* No peak observed.

illustrated in Figure 3A. Neither peak appeared reversible. With a platinum electrode, however, a reduction peak was found at -3.2 V and two oxidation peaks at -2.1 and -1.2 V respectively as shown in Figure 3B. The two reduction peaks at about -1.8 V are due to background impurities in the solution and neither appeared reversible. It seems likely that some chemical reaction with the solvent intervened between the reduction peak and its reoxidation. It would be most interesting to examine this system at much higher sweep rates. The observed behavior is in agreement with that observed by Pickett and Pletcher¹¹.

On addition of pentaborane-9 with the platinum electrode both oxidation peaks disappeared as seen in Figure 3C. Evidently the reaction of the reduction product with pentaborane is rapid enough to eliminate the species responsible for the oxidation peaks. Also a new reduction peak appeared at ca. -1.8V. It is possible that this new peak is caused by the impurities mentioned above. In addition there may be another reduction peak beyond that at -3.2 V but this is beyond the available range. The data for chromium hexacarbonyl is summarized in Table III.

4. Dimanganese Decacarbonyl: At the glassy carbon electrode dimanganese decacarbonyl exhibited one reduction peak at -2.3 V and an oxidation peak at -0.6 V as shown in Figure 4A, with both peaks appearing irreversible. The latter was considerably smaller than the former. In the presence of pentaborane-9 the anodic peak was also smaller while the cathodic peak remains essentially the same as seen in Figure 4B. Evidently there is some reaction product of pentaborane with the reduction product of the decacarbonyl but this occurred slowly enough not to eliminate the oxidation peak.

With a platinum electrode, two reduction peaks occurred at -2.1 and -3.0 V respectively and an oxidation peak at -0.7 V as illustrated in Figure 4C. The

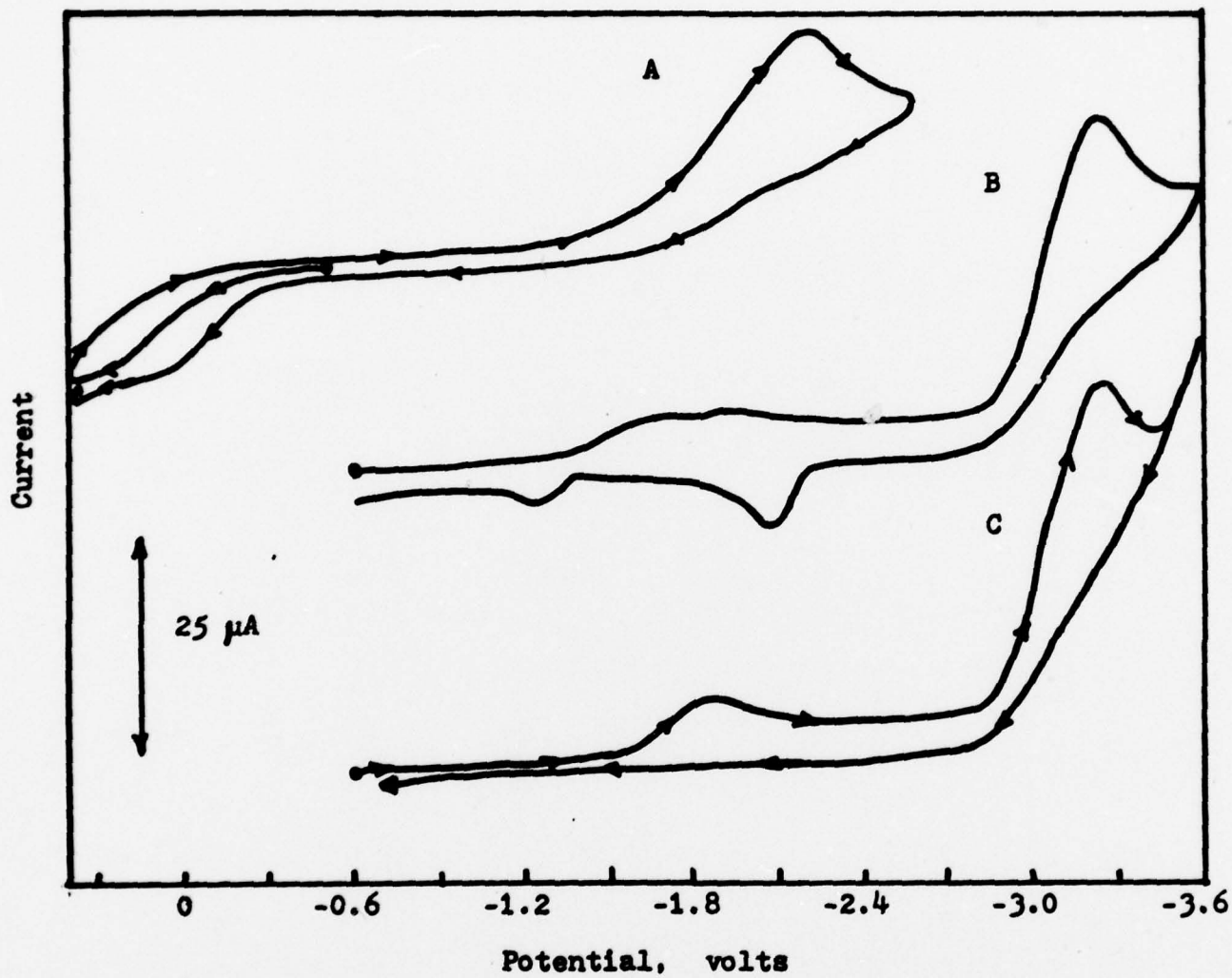


Figure 3

Cyclic Voltammograms of $\text{Cr}(\text{CO})_6$ in $0.1\text{M } (\text{C}_4\text{H}_9)_4\text{NBF}_4$ (a) at the GCE, (b) at Pt, (c) at Pt in the presence of B_5H_9 .

Sweep rate = 100 mV/sec.

Table III

Cyclic Voltammetry of Cr(CO)_6 in 0.1 M $(\text{C}_4\text{H}_9)_4\text{NBF}_4$

Electrode	Sweep Rate V/sec	Cathodic		Anodic			
		E_p	i_p	peak 1		peak 2	
				E_p	i_p	E_p	i_p
		V	μA	V	μA	V	μA
GCE	0.100	-2.13	25.0	+0.003	10.8		
GCE	0.200	-2.27	31.4	ca. +0.1	12.0		
Pt	0.050	-3.08	26.6	-2.09	3.3	-1.25	1.1
Pt	0.100	-3.24	35.0	-2.06	8.6	-1.21	3.2
Pt	0.200	-3.30	45.0	-2.03	10	-1.21	3.7
+ B_5H_9 :							
Pt	0.100	-3.19	38.7	*	*	*	*
Pt	0.500	-3.35	72.5	*	*	*	*

* No peak observed.

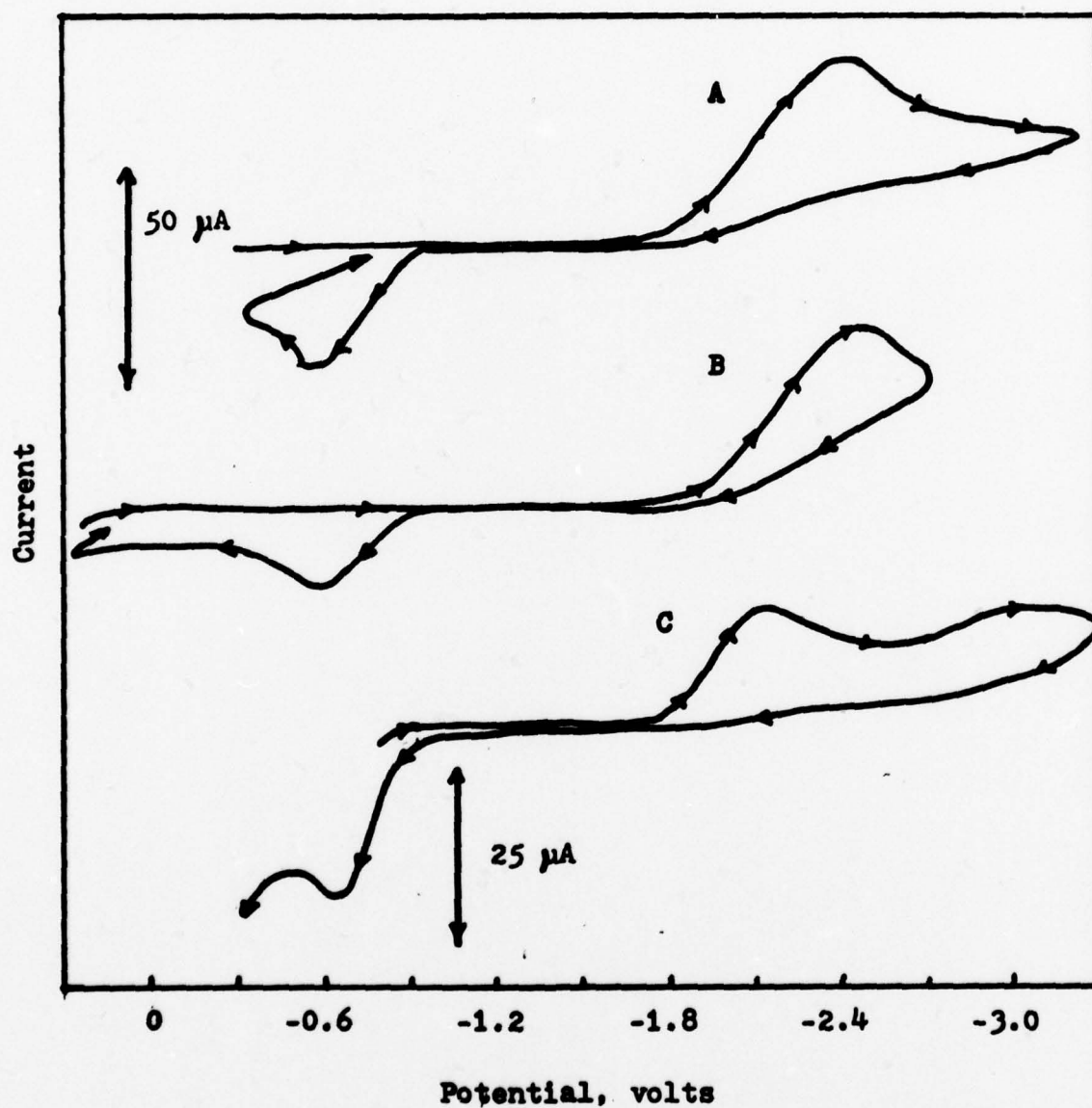


Figure 4

Cyclic Voltammograms of $\text{Mn}_2(\text{CO})_{10}$ in $0.1\text{M } (\text{C}_4\text{H}_9)_4\text{NBF}_4$ (a) at the GCE, (b) at the GCE with added B_5H_9 , (c) at Pt.

Sweep rate = 200 mV/sec.

anodic peak, in this case, was slightly larger than either reduction peak. The data for dimanganese decacarbonyl are summarized in Table IV.

5. Iron Pentacarbonyl: With a platinum electrode, iron pentacarbonyl exhibited a reduction peak at -2.8 V and oxidation peaks at -1.8, -1.5 and -0.6 V respectively as shown in Figure 5A. Each of the oxidation peaks was smaller than the reduction peak and did not appear to correspond to reoxidation of the primary reduction product. Rather there is probably an intervening chemical reaction, perhaps with the solvent. When pentaborane-9 was added the oxidation peaks at -1.8 and -1.5 V disappeared as shown in Figure 5B. This indicates a rapid reaction of the reduction product with the pentaborane-9. The data for iron pentacarbonyl are summarized in Table V.

6. 1-Bromopentaborane-9: Using 1-bromopentaborane prepared in this work, two irreversible anodic peaks were shown at potentials +0.10 and 0.56 V, respectively as shown in Figure 6. No cathodic peaks were observed. Direct addition of the solid 1-bromopentaborane to the background solution produced essentially the same behavior although the peaks were not as well defined. This system is potentially of some interest but was not further investigated.

7. Active Metal Electrodes: Cyclic voltammetry was performed using iron, copper, and nickel electrodes. It was hoped that a metal atom could be incorporated into the pentaborane-9 molecule during an oxidation-reduction cycle. Cyclic voltammetry was carried out at each of these electrodes in the background solution as well as in the presence of pentaborane-9 but the results were inconclusive.

Although the present work is only a survey of the susceptibility of pentaborane-9 to attack by electrochemically generated species, the results clearly indicate that such attack does occur. This is a significant finding

Table IV

Cyclic Voltammetry of $\text{Mn}_2(\text{CO})_{10}$ in 0.1 M $(\text{C}_4\text{H}_9)_4\text{NBF}_4$

Electrode	Sweep Rate V/sec	<u>Cathodic</u>				<u>Anodic</u>	
		<u>peak 1</u>		<u>peak 2</u>			
		E_p	i_p	E_p	i_p	E_p	i_p
		V	μA	V	μA	V	μA
GCE	0.050	-2.25	24.6			-0.719	8.7
GCE	0.100	-2.31	31.8			-0.66	17.6
GCE	0.200	-2.40	41.0			-0.57	26.2
* B_5H_9 :							
GCE	0.050	-2.27	22.4			-0.70	4.3
GCE	0.200	-2.46	40.5			-0.57	16.6
Pt	0.050	-2.09	7.0	-3.05	3.6	-0.71	8.3
Pt	0.200	-1.83	12.5	-2.14	4.8	-0.66	15.4

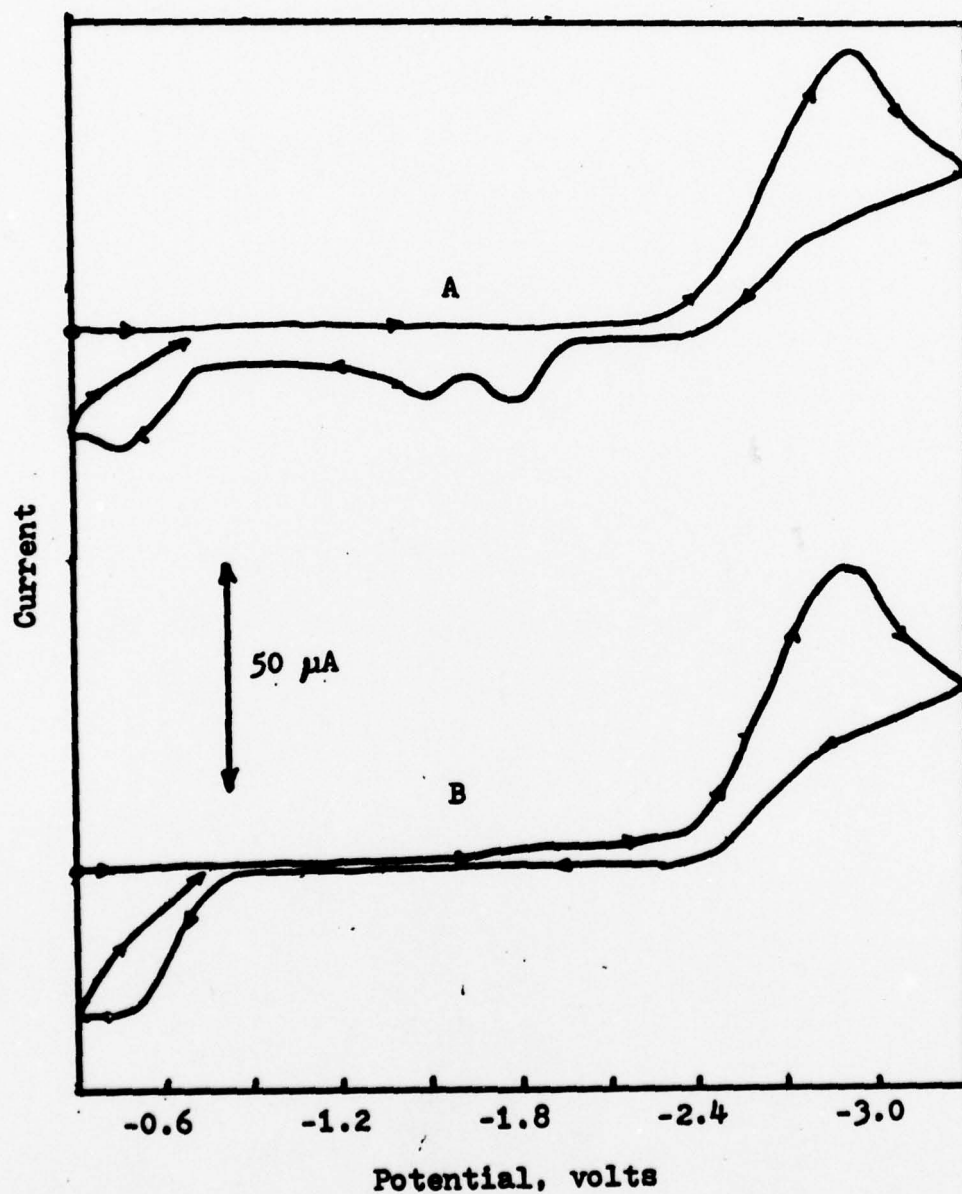


Figure 5

Cyclic Voltammograms at Pt in 0.1M $(\text{C}_4\text{H}_9)_4\text{NBF}_4$ of (a) $\text{Fe}(\text{CO})_5$ and (b) $\text{Fe}(\text{CO})_5 + \text{B}_5\text{H}_9$.

Sweep rate = 200 mV/sec.

Table V

Cyclic Voltammetry at Pt of $\text{Fe}(\text{CO})_5$ in 0.1 M $(\text{C}_4\text{H}_9)_4\text{NBF}_4$

Sweep Rate	<u>Cathodic</u>		<u>Anodic</u>					
			<u>peak 1</u>		<u>peak 2</u>		<u>peak 3</u>	
	E_p	i_p	E_p	i_p	E_p	i_p	E_p	i_p
V/sec	V	μA	V	μA	V	μA	V	μA
0.050	-2.77	25.1	-1.87	1.2	-1.58	1.5	-0.68	4.4
0.200	-2.80	50.4	-1.80	9.1	-1.53	2.8	-0.56	13.4
0.500	-2.96	71.9	-1.77	15	-1.55	3.0	-0.59	23.3
+ B_5H_9 :								
0.200	-2.90	61.5	*	*	*	*	-0.44	3.2
0.500	-3.00	79.5	*	*	*	*		...

* No peak observed.

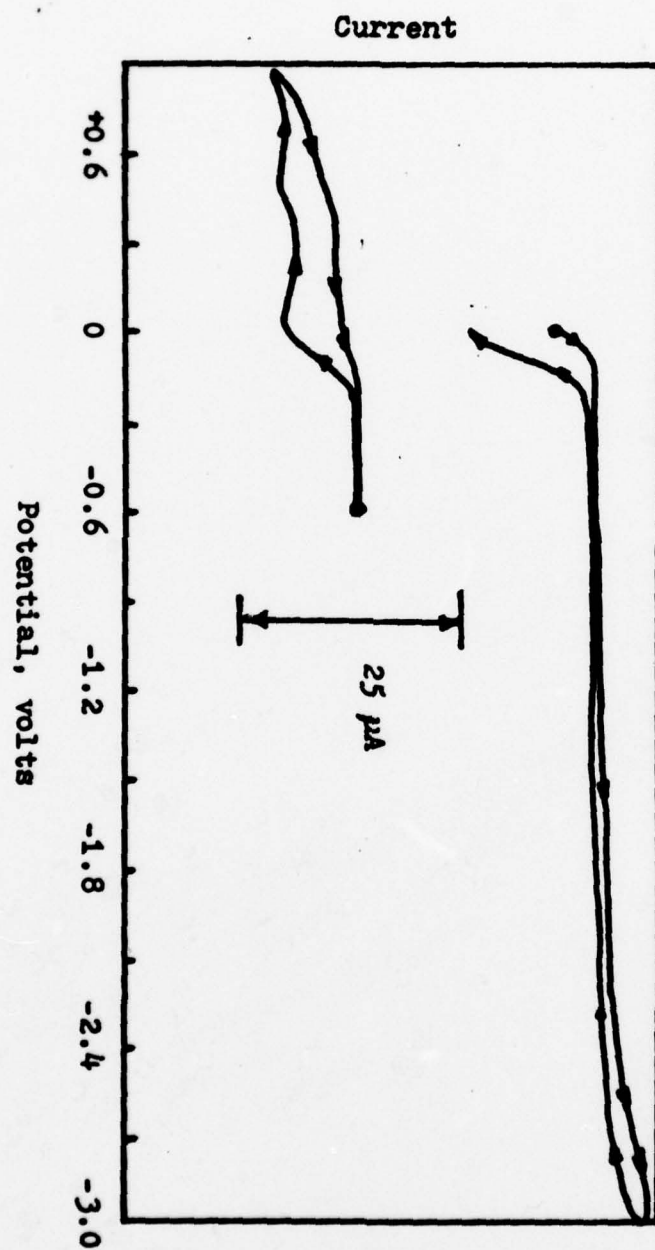
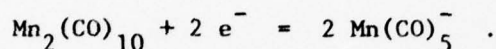


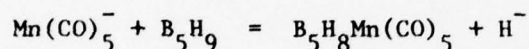
Figure 6

Cyclic Voltammograms at the GCE of $\text{B}_5\text{H}_8\text{Br}$ in $0.1\text{M } (\text{C}_4\text{H}_9)_4\text{BF}_4$.

since it shows that we have a method of attacking pentaborane-9 in a controlled manner. More work is required before the nature of the products are known but some inferences can be drawn from the known electrochemistry of the carbonyl species. Thus Pickett and Pletcher¹¹ indicate that the cathodic behavior of dimanganese decacarbonyl is:



It is reasonable to postulate that the pentacarbonyl manganese anion attacks the pentaborane-9 as follows:



and where the hydride anion attacks the solvent. The pentaboryl manganese species has been identified by Gaines¹² from the reaction of NaB_5H_8 and $\text{BrMn}(\text{CO})_5$ so that the reaction is reasonable although not demonstrated. It will clearly be necessary to produce macroscopic amounts of the reaction product for identification before any conclusive statements can be made.

It should also be pointed out that although the present work is limited to pentaborane, there is no reason for the same approach not to work with other boron hydrides or carboranes. This is not within the scope of the present work but is an obvious extension for example to the carboranes, $\text{B}_{10}\text{C}_2\text{H}_{12}$. The use of electrochemical techniques in non-aqueous systems has been widely applied in the form of cyclic voltammetry but much less has been done to produce macroscopic amounts of products. It is very attractive in the present system because of the possibility of producing single products under controlled conditions by a single step thus avoiding the multistep synthetic methods presently employed.

B Chemistry - The main effort in the present work was on the reactions of pentaboryllithium with acetylnic halides in the hope that compounds with the $\text{B}_5\text{H}_8\text{CH}_2\text{C}\equiv$ structures could be obtained and then trimerized to give transition metal complexes of the type: $(\text{B}_5\text{H}_8\text{CH}_2\text{C}\equiv\text{CH})_3)_2\text{Cr}$. Earlier reports¹⁸ showed that

when the triple bond is adjacent to the pentaboryl group, complex carboranes were formed and it was hoped that the placement of a CH_2 group between the triple bond and the pentaboryl group could prevent this. The reaction of lithium pentaborane and propargyl chloride takes place vigorously in an ether-hexane mixture at room temperature to split out lithium chloride. However, analysis has shown that the product is a complex mixture of polymeric carboranes, including nido types, that could not be separated. In addition small amounts of higher boranes were formed. When the product mixture is reacted with anhydrous cobaltous chloride and cyclopentadienyllithium, small amounts of cobaltaboranes and cobaltacarboranes are formed. It appears that the reaction cannot be run to form single compounds and thus would be difficult to use synthetically for our purposes.

A similar reaction was run with 1,4-dichlorobutyne-2 instead of propargyl chloride and again polymeric products were found. There are C_2H_5 groups in the products as shown by NMR which could be chain ends although this was not demonstrated.

An attempt was made to prepare phenylpentaborane by the reaction of 1-bromopentaborane and phenyllithium. The compounds do react but only a very small amount of a liquid of low volatility was obtained. There was a residue in the reaction vessel and this may have been an etherate of the product or a polymer but was not further investigated.

Experimental Procedures

A. Electrochemistry

1. Cell Design: The study was carried out in a three compartment vacuum line cell constructed in house and modelled after that of Anderson et al⁶. A drawing of the cell is shown in Figure 7. In place of "Torr" seals the electrodes were secured with screw type Teflon bushings and Viton-A "O" rings. The three compartments are separated by glass fritted discs. Section A contains the reference electrode. Rather than placing the reference electrode filling solution directly into this section as in the original reference, the region above the fritted disc was filled with background solution (cf. Figure) and a separate reference electrode was inserted through the top via the Teflon bushing. Section B serves as a bridge compartment between the reference and test electrode compartments. It is through this compartment that the other sections are filled with background solution. Separation from the test compartment is provided by a fine fritted disc and Luggin capillary. Section C is the test solution compartment; electroactive species are added to the background solution it contains. A combination test and counter electrode is inserted through the top via the busing.

2. Electrodes: The "glassy" carbon disc working electrode was constructed from a 1/8" diameter vitreous carbon rod as shown in Figure 8. The end of a 3 cm length of glassy carbon rod was first sealed into glass tubing with epoxy cement. The sides of the rod were insulated by shrinking irradiated polyethylene tubing (FIT-300, Alpha Wire Co.) around it. This type of "heat shrink" tubing forms a good seal since the inner wall melts as the outer wall contracts. The exposed carbon disc was polished with successively finer grades of alumina and silica wetted with isopropanol to a highly lustrous, almost metallic appearance. Electrical contact was made by a nickel wire immersed in a small amount

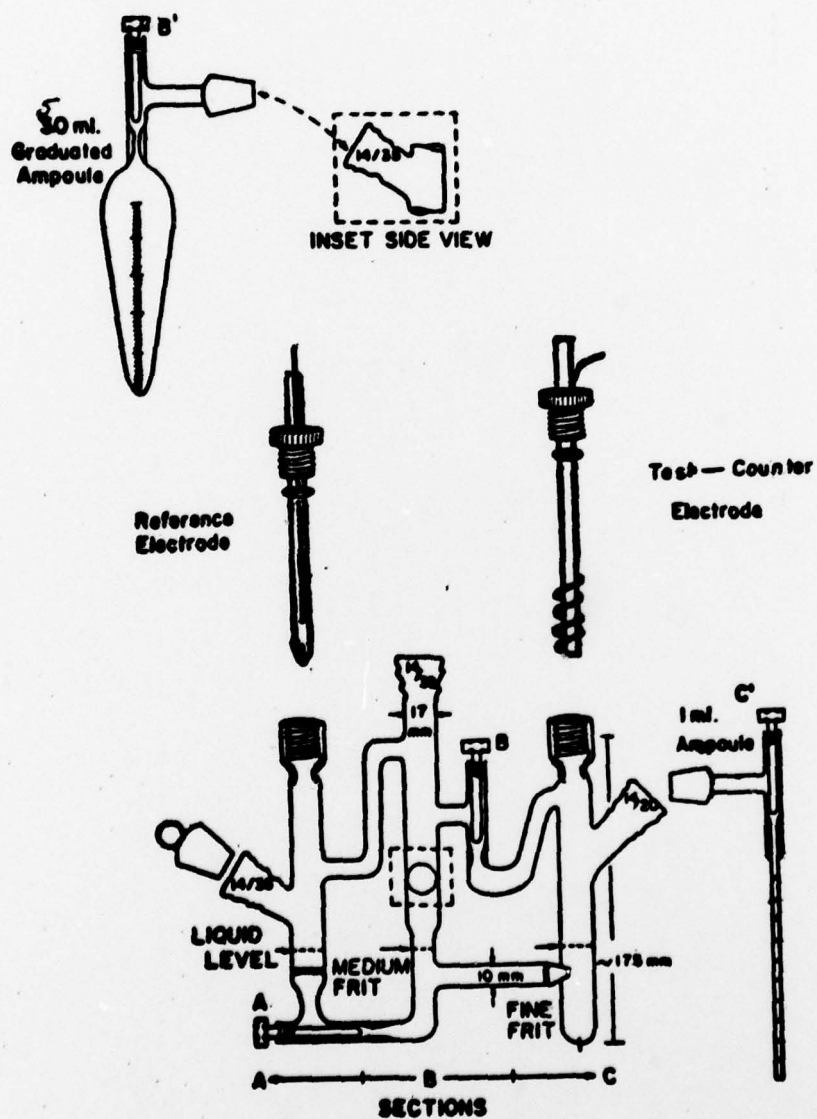


Figure 7

Vacuum-Line Electrochemical Cell

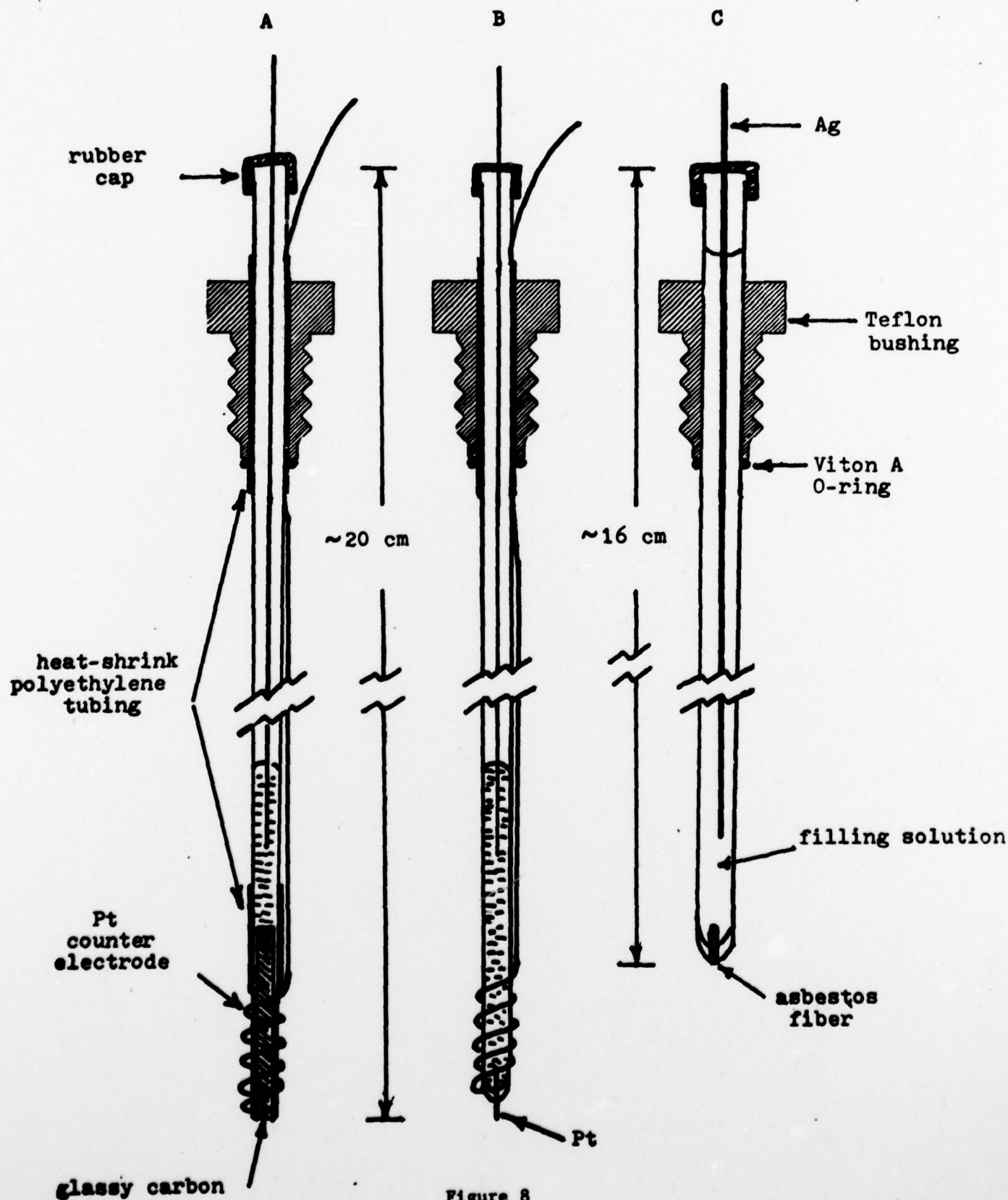


Figure 8

Electrode Construction: (a) Glassy Carbon, (b) Platinum, (c) Reference Electrode

of mercury inside of the glass tube. The counter electrode consisted of a spiral of platinum wire wrapped around the glassy carbon electrode and coaxial to it. To maintain the vacuum tight seal, a length of heat shrink tubing was applied around the top of the electrode assembly with the platinum wire fused inside.

The platinum working electrode as shown in Figure 8B consisted of a short piece of platinum wire sealed in the end of a glass tube. The platinum spiral counter electrode seal through was similar to the glass carbon electrode. The reference electrode shown in Figure 8C consisted of a Ag/0.01 AgClO₄, 0.1 M (C₄H₉)₄-NClO₄ system in the solvent and was contained in a glass tube and was contained in a glass tube fitted with an asbestos junction.

3. Equipment: Cyclic voltammograms were obtained with a PAR Model 174 polarograph and recorded on a Moseley model 1035 X-Y recorder (Hewlett-Packard). Potential sweep reversal was performed manually.

4. Chemicals: Tetra-n-butylammonium fluoborate was used as background electrolyte. It was prepared from aqueous solution of tetra-n-butylammonium bromide (Eastman) and ammonium fluoborate (Alfa). The product was rinsed with water, dried overnight in a vacuum dessicator, and recrystallized three times from ethyl acetate-30-75° petroleum ether mixtures. The final product was stored in a dessicator. Tetrahydrofuran (THF) was from J. T. Baker and was first fractionally distilled from calcium hydride and then stored over calcium hydride. Prior to each run the THF was distilled in vacuo directly into the sample containers. Silver perchlorate was reagent grade from J. T. Baker. Chromium hexacarbonyl, manganese decacarbonyl, and iron pentacarbonyl were from Alfa and were used as received. The iodobenzene and methyl iodide came from J. T. Baker and were used as received.

Procedure: Prior to a run, background electrolyte was weighed into a sample Container B' shown in Figure 7 and evacuated for at least one hour at room temperature. THF was then distilled into the container, which was then sealed with the Teflon needle valve, removed from the vacuum line, and allowed to warm to ambient temperature. In all cases the solutions were colorless. Electroactive samples to be tested were prepared in a similar manner. Solid samples were weighed into a 15 ml container with all transfers being carried out in a nitrogen filled glove bag. Liquid samples were distilled directly into the sample container. Pentaborane-9 was distilled into a 1 ml container marked C' in Figure 6.

The sealed sample containers were then attached to their appropriate cell compartments as shown in Figure 6 and the electrode connections closed with solid Teflon bushings. The cell was connected to the vacuum line and evacuated for about one hour. Nitrogen was then introduced and the cell flushed while the counter electrode assembly was inserted and secured. The background solution was then added by opening the container and inverting it. Enough of the solution was added to fill the three compartments. In a departure from the procedure of Anderson et al, background solution was allowed to fill the reference compartment A above the frit. Nitrogen was allowed to stream out of the cell while the reference electrode assembly was inserted and secured. The cell was maintained under a slight positive pressure of nitrogen.

Initially background curves were recorded to be sure that the system was working properly and there had been no air leaks. If evidence for O_2 was found, the solution was sparged with N_2 until the background returned to an acceptable level. Electroactive samples could then be added to compartment C and appropriate curves recorded. When a second test substance, usually pentaborane-9, was added the system was protected by flushing with nitrogen while sample con-

tainers were switched.

B. Chemical Reactions

1. **Materials:** The pentaborane-9 used in this work came from Edwards AFB and was used as received. The vapor pressure at 0°C was found to be 66 Torr in agreement with the literature value and showed no change with time. Propargyl chloride was obtained from Aldrich and was used as received. The 1,4-dichlorobut-2-ene was synthesized from 1,4-butanediol as described in the literature¹⁴. The boiling point was 84°C at 25 Torr. Phenyllithium came from Aldrich while the n-butyllithium was obtained from Alfa. Anhydrous cobaltous chloride was prepared by dehydration of the hexahydrate using thionyl chloride. All solvents were CP grade.

2. **Apparatus:** All reactions using pentaborane-9 were carried out using a standard vacuum system. Special equipment was fabricated as described in the individual reaction procedures.

3. **Analytical Methods:** Infrared spectra were run using a Perkin-Elmer Model 337 instrument. Proton NMR spectra were obtained with a Perkin-Elmer R-32 spectrometer while the boron-11 spectra were obtained using a JEOL 100 MHz Fourier Transform instrument.

Reaction of LiB_5H_8 and $\text{ClCH}_2\text{C}\equiv\text{H}$

The reactor used is shown below in Figure 9. Initially 4.6 ml. of 1.6 M n-BuLi (7.36 mmoles) in hexane was syringed into the nitrogen filled flask through the constriction. An additional 5.0 ml. of anhydrous Et_2O was added and the reactor attached to the vacuum system. Next, 0.7419g. of B_5H_9 (11.6 mmoles) was distilled into the reactor and the mixture stirred for four hours at ambient temperature. The volatiles were fractionated through a -78°C trap and 6.64 mmoles of n- C_4H_{10} identified by vapor pressure was collected. An amount of 0.503 g. (6.73 mmoles) of $\text{ClCH}_2\text{C}\equiv\text{CH}$ was distilled into the reaction mixture and the reactor sealed off from the vacuum system at the constriction. Reaction between the LiB_5H_8 and $\text{ClCH}_2\text{C}\equiv\text{CH}$ occurred on warming and a precipitate was formed while the solution turned yellow. The reaction mixture was filtered through the frit by tilting the reactor. The reactor was opened to the vacuum system through the breaker and all of the volatiles removed. About 5 ml. of CHCl_3 was distilled onto the gelatinous residue and the solution refiltered through a medium frit to remove a small amount of solid that had come through in the original filtration. A portion of the filtrate was used to obtain an infrared spectrum and bands were found at 2850, 2500, 1870, 1560, 1500, 1460, 1300, 1100, 970, and 900 cm^{-1} . The band at 2500 cm^{-1} is attributed to B-H stretch while that at 1870 cm^{-1} to the B-H-B bridge. The CHCl_3 was removed from a portion of the product and a ^1H NMR run in THF d^8 . Bands were found 5.1-5.7 and 7.2-8.1 values of τ . The former are associated with CH structures while the latter with B-H. An ^{11}B NMR in THF d^8 showed a very large number of peaks with some doublets indicating B-H again. However, from the lack of sharp peaks it was evident that the material is a mixture, presumably of polymers that cannot be easily separated. A mass spectral analysis indicated the presence of small amount of B_6H_{10} and $\text{B}_{10}\text{H}_{14}$. No attempt was made to separate the components because Schaeffer and coworkers

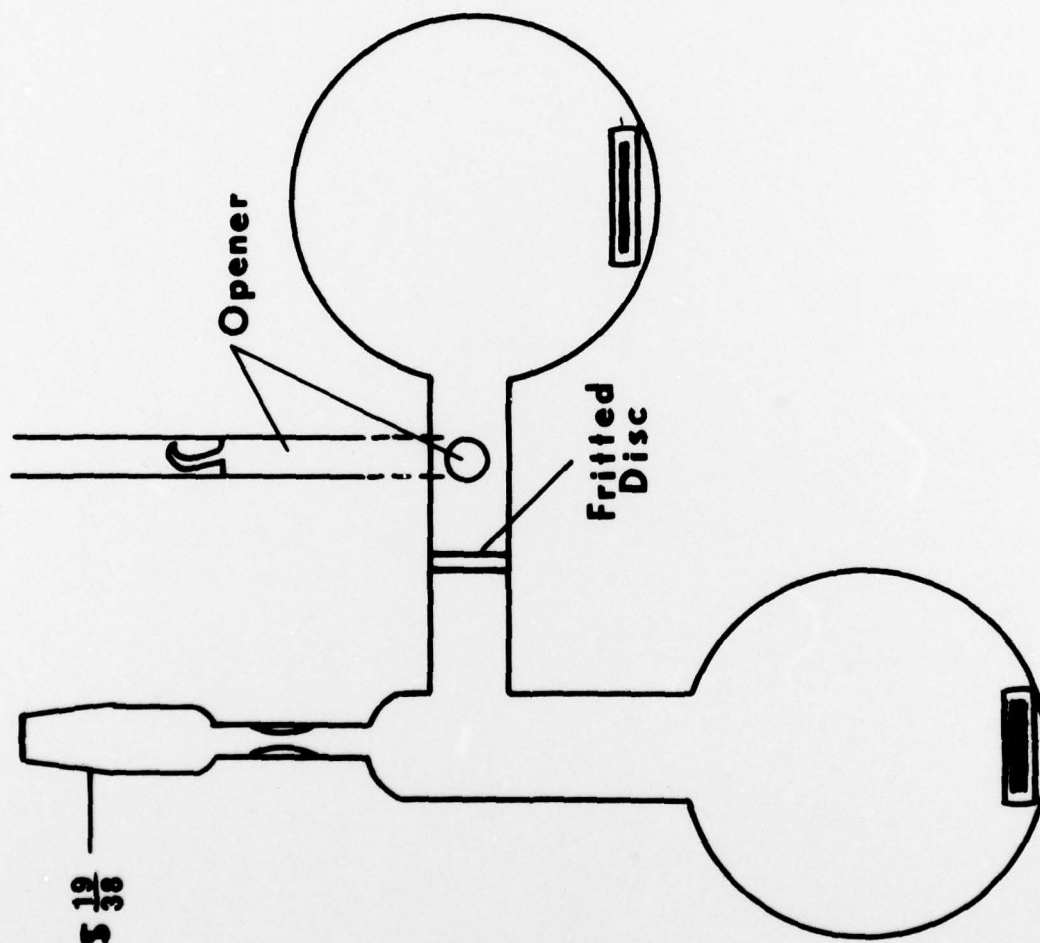


Figure 9
 Reactor for LiB_5H_8 and $\text{ClCH}_2\text{C}\equiv\text{CH}$

showed that extensive decomposition results during the chromatography on the usual substrates. The absence of an infrared peak at 2200 cm^{-1} indicates that the $\text{C}\equiv\text{C}$ structure is no longer present. The ^{11}B NMR peaks are shifted far enough downfield from $\text{BF}_3\cdot\text{Et}_2\text{O}$ to suggest that the carboranes have nido structures.

Due to the separation problem it was decided to react the polymeric product with a mixture of anhydrous CoCl_2 and LiC_5H_5 to form cobaltacarboranes which could then be more readily separated. Accordingly 1.0 ml. of C_5H_6 and 10.0 ml. of 1.6 M n-BuLi were reacted in 10.0 ml. of Et_2O . Butane was evolved and a white precipitate of LiC_5H_5 was formed. To this was added 0.3 g. of CoCl_2 and the reaction product described above. The mixture was stirred and slowly turned dark brown, indicating the presence of cobaltacarboranes. It was treated with a mixture of 125 ml. of H_2O and 25 ml. of acetone, air bubbled through for three hours to remove the acetone and oxidize the cobalt to Co(III) , and the solid filtered off. The solid was extracted with acetone, some of the acetone evaporated, the solution diluted with n-hexane, and the solution decanted. TLC strips were used to find the best chromatographic procedure. It was found that two fractions could be separated using CH_2Cl_2 -30-60° pet ether and CH_2Cl_2 -EtOH mixtures. Column chromatography was carried out with Baker-Adamson 1-3405 60-200 mesh silica gel as the adsorbant in a column 22 cm long and 2 cm in diameter. The initial yellow fraction was eluted with a 33-67 CH_2Cl_2 -pet ether mixture and a second dark brown fraction with 33-67 CH_2Cl_2 -ethanol mixture. The yellow fraction was dried on a hot plate to give a small amount of liquid while the dark brown fraction was dried by heating under vacuum to give a dark brown solid. The yellow fraction was soluble in CCl_4 and a ^1H NMR showed peaks at τ of 10.0, 9.16 and 8.84, all relatively broad. The appearance and properties of this fraction makes it seem to be similar to the cobaltboranes very recently described by Grimes¹⁵. The dark brown fraction was insoluble in CCl_4 and a ^1H

NMR was obtained in THF d⁸. It showed a very large number of peaks including one indicative of a cyclopentadienyl proton plus broad ones suggesting B-H structures. It was attempted to obtain ¹¹B spectra on these samples but they slowly decomposed during the waiting period.

In one earlier reaction of LiB₅H₈ and ClCH₂C≡CH a small amount of a volatile white material was recovered by sublimation. An infrared spectrum showed bands at 2900, 2565, 1515, 1460, 1010, and 920 cm⁻¹ indicating C-H and B-H bands but no B-H-B bridges. The ¹H NMR showed peaks at τ of 9.3, 9.05, 8.6, 10.87, 10.97, and 11.70 again showing B-H peaks. It is suspected that the material has a B₅CH₆ or similar type structure but the very small amount of material precluded further investigation.

Reaction of LiB_5H_8 and $\text{ClCH}_2\text{C}\equiv\text{CCH}_2\text{Cl}$

The same reaction vessel was used as for the reaction of LiB_5H_8 and $\text{ClCH}_2\text{C}\equiv\text{CH}$ except that an additional magnetic opener and constriction was sealed onto the side next to the attachment to the vacuum system for the purpose of introduction of the $\text{ClCH}_2\text{C}\equiv\text{CCH}_2\text{Cl}$. LiB_5H_8 was prepared in the same manner as previously described by reacting 9.0 mmoles of $n\text{-BuLi}$ with 13.7 mmoles of B_5H_9 in 5.0 ml. of anhydrous Et_2O to give 8.73 mmoles of C_4H_{10} . The reactor was sealed off at the constriction, a weight of 0.4871 g. (3.96 mmoles of $\text{ClCH}_2\text{C}\equiv\text{CCH}_2\text{Cl}$ was sealed into the bulb which was attached to the reactor with a magnetic hammer at the opener described above, and sealed off at the constriction. The seal was broken and the reactants mixed. Considerable heat was noted. The reaction mixture separated into colorless upper and yellow lower layers. The reactor was opened to the vacuum system through the second opener and all of the solvent plus excess B_5H_9 distilled away and 8 ml of CHCl_3 distilled into the reactor. Since the LiCl produced in the reaction was so fine separation was obtained by carefully decanting the liquid through the frit. An infrared spectrum was run on the reaction product and showed bands at 2900, 2500, 1870 cm^{-1} showing C-H, B-H, B-H-B but no C $\equiv$ C bands. A ^1H spectrum in $\text{THF}-d^8$ showed the presence of CH_3 (quartet), CH_2 (triplet) plus B-H bands. An attempt was made to hydrolyze the product for active hydrogen by reaction with methanol and for boron by base titration. A sample weighing 0.4219 g. gave 1.02 mmoles of H_2 and 13.9 mmoles of boron indicating the high stability of the hydride hydrogen. The strong B-H infrared band suggest the presence of carboranes that are stable to hydrolysis.

Preparation of 1-B₅H₈Br

Since there does not seem to be a description of the synthesis of 1-B₅H₈Br in the literature, the procedure used will be described. The reactor used is shown below in Figure 10. About 1g. of anhydrous AlCl₃ was loaded into a short length of 10 mm glass tubing stoppered at both ends using a glove bag. The reactor was attached to the vacuum system and filled with nitrogen. The cork was removed from the stoppered tube and the AlCl₃ poured into the tube attached to the reactor with nitrogen flowing out. Using nitrogen for blowage the top of the tube was sealed off, the tube wrapped with nichrome wire, the system evacuated, and the AlCl₃ sublimed into the large bulb. After removing the wire the tube was sealed off from the remainder of the reactor. A tube containing a breaker and magnetic hammer was then sealed to one of the breakers and 3.7 ml. of liquid Br₂ added. This was frozen, the tube evacuated, and the top of the tube sealed at the constriction. The breaker was opened and the bromine distilled into the reactor. The tube was then sealed off at the construction. Next 12 ml. of CS₂ and 1.47 g. of B₅H₉ distilled into the vessel and the reactor sealed at the construction to the vacuum system. The reactor was allowed to stand at room temperature for 48 hours. It was opened to the vacuum system through the third breaker and the excess bromine and CS₂ distilled out. The 1-B₅H₈Br sublimed slowly into a trap and was transferred to a bottle in a dry box. Yield 3.25 g. 98% thereof. It was noted that there is a non volatile solid left in the reactor but this was not further studied.

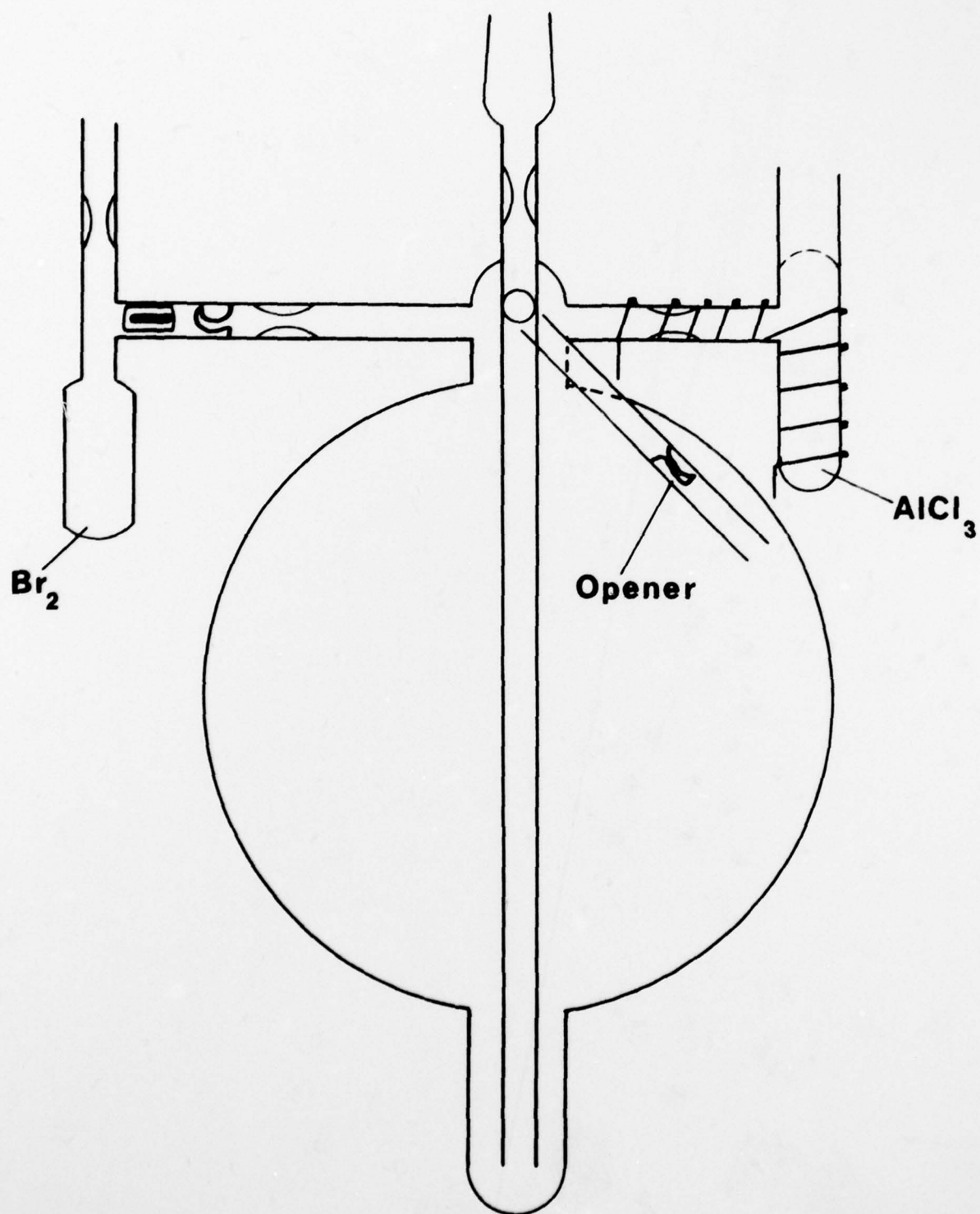


Figure 10

Reactor for Preparation of $1\text{-BrB}_5\text{H}_8$

Reaction of $1-B_5H_8Br$ and C_6H_5Li

The reaction vessel was a 100 ml. 2 necked flask equipped with a magnetic stirrer and attached to the vacuum system. In a bent tube equipped with a standard taper was placed 1.585 g. of $1-B_5H_8Br$ and this was attached to the flask using the second neck. The reactor was filled with nitrogen and 6.3 ml. of 2.28 M C_6H_5Li in 70:30 benzene: Et_2O plus 6 ml. of Et_2O were syringed into through the second neck. The $1-B_5H_8Br$ was added to the solution in small portions by turning the tube in the neck of the flask. The reaction was allowed to stir for three hours and a precipitate was formed. The volatiles were fractionated through a $-30^\circ C$ trap to separate the benzene, leaving a small amount of low volatility liquid. This was carefully refractionated to give a material with a vapor pressure of about 5 torr at room temperature. However, not enough was recovered for any further studies. Apparently the product must remain in the solid from the reaction.

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