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Carborane Burning Rate Modifiers

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21. ABSTRACT (Continue on reverse side if necessary and identify by block number)			
The kinetics and mechanism of the reactions of $B_{10}H_{12}[(CH_3)_2S]_2$ with various acetylenes have been carried out. The mechanism is believed to be:			
$B_{10}H_{12}L_2 \rightleftharpoons B_{10}H_{12}L + L$ $B_{10}H_{12}L + A \rightleftharpoons B_{10}H_{12}LA$ $B_{10}H_{12}LA \rightarrow \text{Carborane} + H_2 + L$			

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20. Abstract (continued)

($L=(CH_3)_2S$, A=acetylene)

Acetylenes of the type $HC\equiv CCH_2X$ give higher yields and have higher $\Delta H^\ddagger$ and $\Delta S^\ddagger$ if x is electron withdrawing. Side products in low yield syntheses are probably hydroboration products.

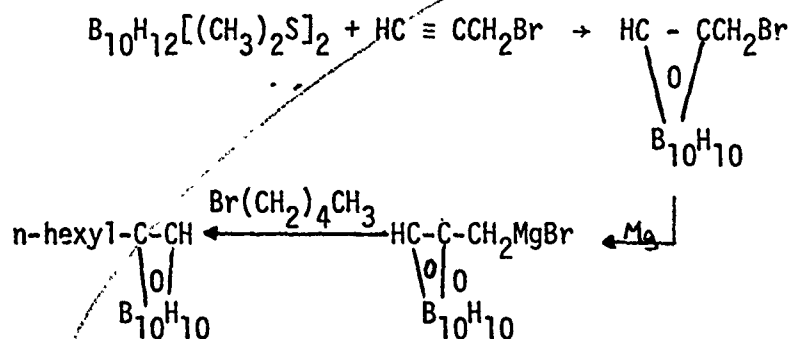
Synthesis of a number of carborane derivatives capable of adding to the polymer backbone of HTPB has been accomplished and the products have been characterized. These include a variety of derivatives containing Si-H, Hg-carboranyl, and S-H groups. No P-H containing derivatives were made.

Incorporation of the derivatives into the binder by adding across the C=C units of the polymer was accomplished in yields from 90-25%. Polymer properties were adversely affected and the resulting polymers not suitable for the propellant studies.

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SUMMARY

Because of the high cost of o-carboranes a kinetic study designed to find out the mechanism of the reaction and to elucidate the factors influencing the reactions was carried out. The goal of this study was to provide information that would allow high yield syntheses of o-carboranes. It was found that acetylenes with electronegative substituents gave highest yields of o-carborane. Therefore, functional acetylenes such as $\text{HC} \equiv \text{CCH}_2\text{Br}$ should be used to prepare precursors to other functional carboranes. For example, to make n-hexylcarborane the following route may use $\text{B}_{10}\text{H}_{12}[(\text{CH}_3)_2\text{S}]_2$ more effectively than the direct reaction with $\text{B}_{10}\text{H}_{12}[(\text{CH}_3)_2\text{S}]_2$ and octyne;



Since migration of some carboranes out of solid propellants has been observed, a study was undertaken to synthesize functional carboranes capable of adding to polybutadiene binder successfully. However, the polymer properties were greatly altered and were therefore not acceptable for propellant studies.

(A)

Table of Contents

- I. Introduction
- II. Procurement of Materials for this Study
- III. Kinetics and Mechanistic Studies of O-Carborane Formation
 - A. Reactions of $B_{10}H_{12}[(CH_3)_2S]_2$ with Various Acetylenes
 - B. Preparation of other $B_{10}H_{12}(\text{Lewis Base})_2$ Adducts
- III. Syntheses of Derivatives with a Range of Properties for Attachment to HTPB
 - A. Mercapto Derivatives
 - B. Silyl Derivatives
 - C. Mercurial Derivatives
 - D. Hydroxy Derivatives
 - E. Phosphorus Derivatives
- IV. Attachment of Derivatives to HTPB
- V. Conclusions
- VI. Recommendations

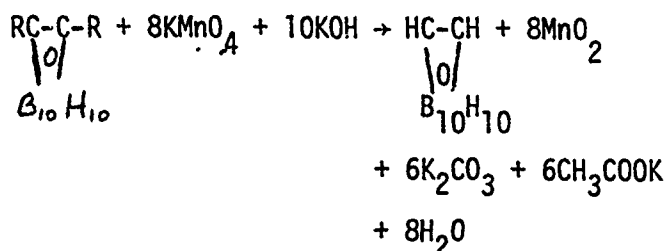
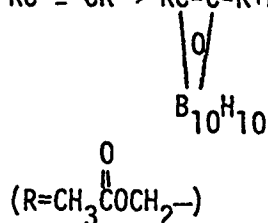
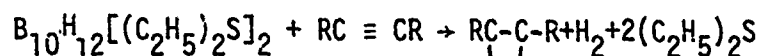
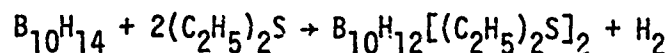
I. Introduction

Although a great deal of kinetic information has been available on substitution reactions of $B_{10}H_{12}L_2$ derivatives with other Lewis bases, little information has been reported on the mechanism of o-carborane formation from $B_{10}H_{12}L_2$. Part of the present study addresses itself to this problem.

Another problem addressed by this work is the tendency of carboranes to migrate out of composite HTPB or CTPB based propellant systems. Much of the synthesis work reported here and all of the HTPB attachment studies address this problem.

I. Procurement of Materials for this Study

Decaborane, hydroxy-terminated polybutadiene, and curing agents were obtained from the U. S. Army Missile Command in Huntsville. Approximately 300 gms of ortho-carborane, the starting point for most derivatives of interest was prepared using the route shown below:



$B_{10}H_{12}[(CH_3)_2S]_2$ was prepared from $B_{10}H_{14}$ and dimethyl sulfide by reaction in benzene. The product was recrystallized from a minimum amount of benzene by the addition of n-pentane.

During the course of this investigation, two explosions occurred resulting in some property damage but no personnel injuries. Both of the explosions took place when we attempted to prepare bis(acetoxymethyl)carborane from $B_{10}H_{14}$ and 2-butyne-1,4-dioldiacetate according to the literature preparation. The first of these explosions occurred when volatiles were being removed in vacuo on a rotary evaporator after the reaction was completed. Gentle heat ($\sim 50^\circ$) was being applied. The second explosion occurred after the

volatiles were removed and methanol was being added in very small portions to kill off reactive by-products in the preparation. The methanol was being added through a condenser column to the reaction products in 2-3 ml. portions. Vigorous refluxing occurred on each addition and as this reflux subsided somewhat, an additional 2-3 ml. of methanol would be added. After a total of approximately 25 ml of methanol had been added, the reaction suddenly began to violently heat up and the explosion occurred.

Although we have performed this reaction several times in the past with no problems using the same procedure and personnel, these two attempts were unsuccessful. After a careful analysis of the probable cause of these explosions, we found that in both instances we were using decaborane obtained from Redstone Arsenal in June, 1977. We were told by the Redstone Arsenal people that this decaborane had been stored in a magazine for a long time and the purity was unknown. We attempted to purify the decaborane both by sublimation and by recrystallization from hexane. We feel, however, that the explosions resulted from some impurities that were not removed by these conventional purification routes. The identity of the main impurities in the decaborane is unknown. Redstone Arsenal was informed of the potential hazard of this very old decaborane.

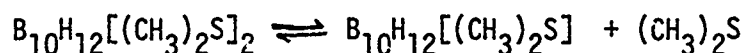
II. Kinetics and Mechanistic Studies of O-Carborane Formation

A. Reactions of $B_{10}H_{12}[(CH_3)_2S]_2$ with Various Acetylenes

A kinetic study of the reaction of $B_{10}H_{12}[(CH_3)_2S]_2$ with acetylenes has been carried out with the specific goal of elucidating the mechanism of ortho carborane formation and determining the factors necessary for a high yield conversion of $B_{10}H_{14}$ to ortho-carboranes.

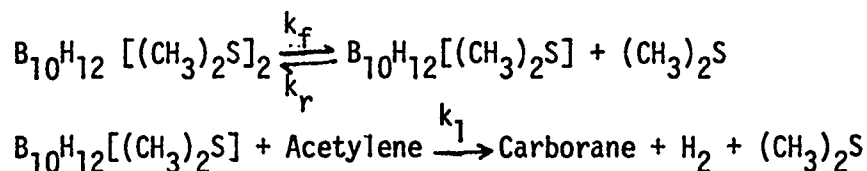
Since preliminary work had indicated that $B_{10}H_{12}[(CH_3)_2S]_2$ was soluble in chloroform (a convenient solvent for kinetic studies), $(CH_3)_2S$ was the chosen Lewis base adduct for these studies.

The $B_{10}H_{12}[(CH_3)_2S]_2$ adduct undergoes a ligand substitution reaction with $(C_2H_5)_2S$ which is first order in $B_{10}H_{12}[(CH_3)_2S]_2$ ($k = 3.21 \times 10^{-4} \text{ sec}^{-1}$ at 38°C). This suggests a rate determining step involving dissociation of the ligand according to:



K_{diss} for this reaction, determined by ^1H nmr, is $< 4 \times 10^{-3}$.

Our initial studies showed that the reaction rates of the acetylene with the adduct were slower than the ligand exchange reaction; thus the data were analyzed according to the mechanism:



Now if $BL_2 = B_{10}H_{12}[(CH_3)_2S]_2$, $BL = B_{10}H_{12}[(CH_3)_2S]$, $A = \text{Acetylene}$, and $L = (CH_3)_2S$, treating BL as a steady state intermediate:

$$[BL] \approx \frac{k_f [BL_2]}{k_r [L] + k_1 [A]}$$

so:

$$\frac{d[\text{carborane}]}{dt} \approx \frac{-d[BL_2]}{dt} \approx \frac{k_1 k_f [BL_2] [A]}{k_r [L] + k_1 [A]}$$

and if $[BL]_0 = [A]_0$, $[BL_2] = [A] = x$ and $[L] = [L]_0 + 2[(BL_2)_0 - x]$; assuming $k_1 < 2k_r$ dividing by k_r and integrating

$$([L]_0 + 2[BL_2]_0) \left(\frac{1}{[BL_2]} - \frac{1}{[BL_2]_0} \right) + 2 \ln \frac{[BL_2]}{[BL_2]_0} = k_1 K t$$

which rearranges to:

$$\frac{2[BL_2]_0 + [L]_0}{[BL_2]} + 4.606 \log [BL_2] = k_1 K t + \frac{2[BL_2]_0 + [L]_0}{[BL_2]_0} + 4.606 \log [BL_2]_0$$

Kinetic studies were carried out either directly in NMR tubes in chloroform solvent or in volumetric flasks immersed in a controlled water bath. Samples were withdrawn from the volumetric flasks through a septum by a syringe introduced to NMR tubes, and the integrals determined immediately.

The NMR spectrum of $B_{10}H_{12}[(CH_3)_2S]_2$ gives a sharp singlet at 1.5 ppm from TMS assigned to the CH_3 groups of the bound $(CH_3)_2S$. Free $(CH_3)_2S$ occurs about 20 Hz further upfield. On reaction of $B_{10}H_{12}[(CH_3)_2S]_2$ with acetylenes, the bound $(CH_3)_2S$ decreases and the free $(CH_3)_2S$ increases correspondingly. The total area under both peaks remains constant. Thus, the concentration of $B_{10}H_{12}[(CH_3)_2S]_2$ in each sample was calculated by:

$$B_{10}H_{12}[(CH_3)_2S]_2 = \frac{A_1}{A_1 + A_2} \times [B_{10}H_{12}[(CH_3)_2S]_2]_0 + \frac{[(CH_3)_2S]_0}{2}$$

Where A_1 is the area of the bound $(\text{CH}_3)_2\text{S}$ and A_2 is the area of the free $(\text{CH}_3)_2\text{S}$ peak.

Figure I shows plots from which values of k_1K were obtained. Calculations of k_1K were done by a least-squares procedure using a computer. Correlation coefficients greater than 0.99 were obtained. Calculations of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the reactions gave correlation coefficients greater than 0.994.

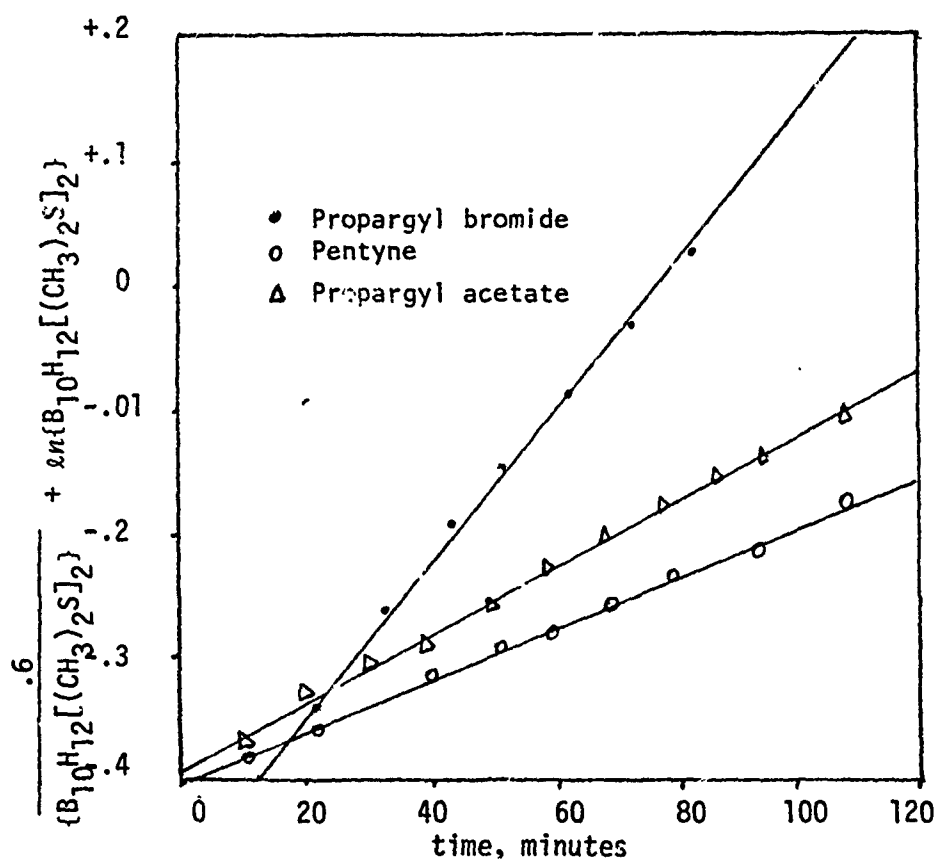


Figure I. Typical plots to determine k_1K . $[\text{Acetylene}]_0 = 0.30\text{M}$, $\{\text{B}_{10}\text{H}_{12}[(\text{CH}_3)_2\text{S}]\}_0 = 0.30\text{M}$, $[(\text{CH}_3)_2\text{S}]_0 = 0.00\text{M}$, $T = 37^\circ\text{C}$.

The reactions of $\text{B}_{10}\text{H}_{12}[(\text{CH}_3)_2\text{S}]_2$ with various acetylenes were investigated over a temperature range of $37\text{--}60^\circ\text{C}$. In general the reactions were followed to 75% completion. Acetylenes were chosen to give as large a range as possible, subject to the limitations imposed on the acetylene by the system (i.e. no strongly coordinating site, e.g. OH, CN, R-C=O , NH_2 ; no strongly

oxidizing group, e.g. NO_2). Acetylenes with functional groups directly attached to the $\text{C} \equiv \text{C}$ linkage gave extremely low yields (<10%) and therefore their kinetics were not studied. Examples of these acetylenes were $\text{HC} \equiv \text{C}\phi$ and $\text{HC} \equiv \text{CC}(\text{O})\text{CH}_3$. Products were identified by gas chromatography and the percent yield of carborane was measured. The acetylenes $\text{HC} \equiv \text{CCH}_2\text{OC}(\text{O})\text{CH}_3$, $\text{HC} \equiv \text{CCH}_2\text{Br}$, and $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{C} \equiv \text{CCH}_2\text{OC}(\text{O})\text{CH}_3$ gave yields in excess of 80%. 1-Octyne and 1-pentyne gave yields of only 30%, although the reactions accurately followed second-order kinetics. Yields of carborane were independent of temperature over the range of 38-100°C suggesting that activation parameters for the formation of side products were essentially the same as for the formation of carboranes. In all cases the reaction system remained homogeneous throughout the course of the investigation.

Table I contains the collected rate data. Yields of the carboranes were 92% for $\text{HC} \equiv \text{CCH}_2\text{Br}$, 88% for $\text{HC} \equiv \text{CCH}_2\text{OC}(\text{O})\text{CH}_3$, 85% for $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{C} \equiv \text{CCH}_2\text{OC}(\text{O})\text{CH}_3$, 55% for $\text{HC} \equiv \text{C}(\text{CH}_2)_3\text{Cl}$, 30% for $\text{HC} \equiv \text{C}(\text{CH}_2)_5\text{CH}_3$, and 32% for $\text{HC} \equiv \text{C}(\text{CH}_2)_2\text{CH}_3$.

Experimental difficulties associated with the sensitivity of the NMR technique used to follow the reaction and with the solubility of $\text{B}_{10}\text{H}_{12}[(\text{CH}_3)_2\text{S}]_2$ precluded the desired large variation in initial reactant concentration. However, it should be pointed out that initial addition of 0.3 M $(\text{CH}_3)_2\text{S}$ tripled the half-life of the reaction with no variation in the observed value of k_1K . Figure II illustrates the variation in rate with different concentrations of $(\text{CH}_3)_2\text{S}$ for the acetylene, $\text{HC} \equiv \text{CCH}_2\text{Br}$.

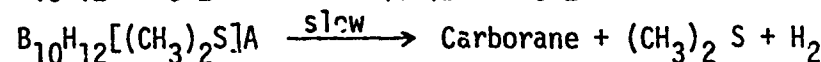
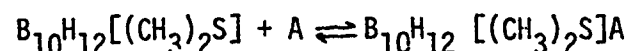
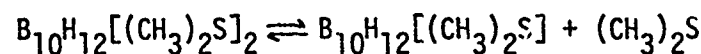
The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for each reaction are reported in Table I also. It should be pointed out that $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are really the sums of ΔH or ΔS for the equilibrium (or equilibria) steps plus $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the slow step. Hence it is not surprising that the values of $\Delta S^\ddagger$ are very different from those expected

Table I. Rates of Carborane Formation^a

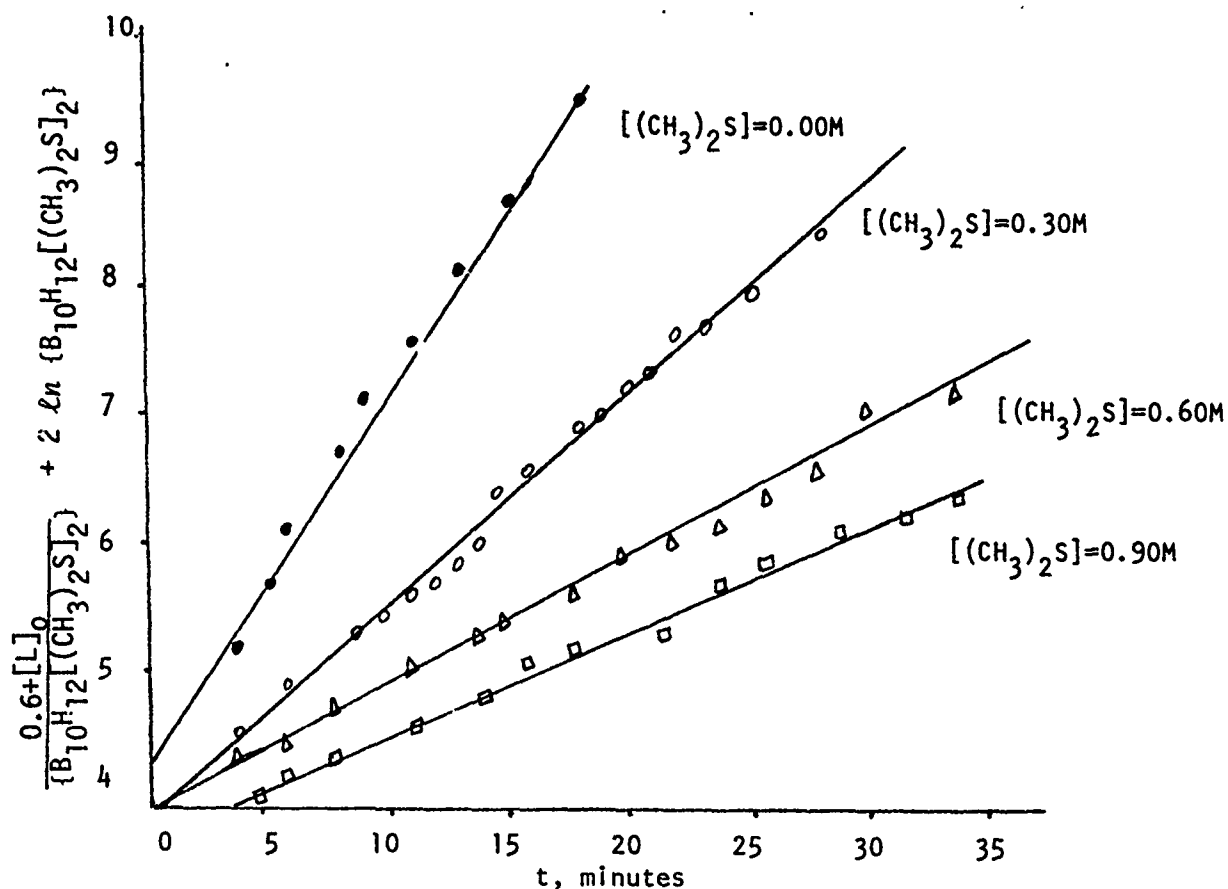
Acetylene	$[(CH_3)_2S]_0, M$	T, °C	k_1, sec^{-1}	$\Delta H^\ddagger (\pm 0.7), \text{kcal/mol}$	$\Delta S^\ddagger (\pm 2.0), \text{eu}$
Propargyl bromide	0.0	37.0	1.04×10^{-4}	36.1	40
	0.0	48.0	7.68×10^{-4}		
	0.0	56.0	1.68×10^{-3}		
	0.3		1.74×10^{-3}		
	0.6		1.52×10^{-3}		
	0.9		1.46×10^{-3}		
Propargyl acetate	0.0	58.1	5.76×10^{-3}	34.9	34
	0.0	36.8	4.35×10^{-5}		
	0.0	41.1	9.32×10^{-3}		
	0.0	56.5	1.36×10^{-3}		
5-chloro-1-pentyne	0.0	59.8	1.95×10^{-3}	26.6	6
	0.0	36.8	1.80×10^{-5}		
	0.0	37.9	2.16×10^{-5}		
	0.0	56.0	2.57×10^{-4}		
2-Butyne-1,4-diacetate	0.0	59.4	3.39×10^{-4}	33.4	29
	0.0	37.6	5.22×10^{-5}		
		38.6	5.70×10^{-5}		
		57.6	1.39×10^{-3}		
1-pentyne	0.0	37.0	3.35×10^{-5}	26.4	6
		50.6	1.90×10^{-4}		
		58.0	5.56×10^{-4}		
1-Octyne	0.0	39.0	2.62×10^{-5}	24.8	0
		39.9	2.98×10^{-5}		
		51.7	1.04×10^{-4}		
		58.7	2.90×10^{-4}		
		59.0	3.39×10^{-4}		

^a $[B_{10}H_{12}[(CH_3)_2S]_2]_0 = 0.300 M$; $[acetylene]_0 = 0.300 M$; solvent = chloroform.

for a simple bimolecular reaction. A three step mechanism, kinetically indistinguishable from the two step mechanism used in this analysis is also possible. Thus:



In this mechanism, as in the two-step case, the contribution of the equilibria to $\Delta S^\ddagger$ is small while the contribution of the dissociative step may vary from



near zero to highly positive as the transition state varies from "reactant-like" to "product-like". We prefer to stick to the simple two step mechanism in view of the uncertainties of interpreting $\Delta S^\ddagger$ for complex processes in solution. Strict interpretations of $\Delta S^\ddagger$ for complex processes in solution are notoriously uncertain. Steric factors do not seem to be important since the $\Delta S^\ddagger$ for a disubstituted acetylene, $(\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{-C}\equiv\text{C}_2$, is not markedly different from the mono-substituted case. $\Delta S^\ddagger$ values for the more nucleophilic acetylenes (1-octyne, 1-pentyne and 5-chloro-1-pentyne) are much smaller than those of the less electrophilic acetylenes.

The values of $\Delta H^\ddagger$ reflect the nucleophilicity of the acetylenes. 1-Octyne, 1-pentyne, and 5-chloro-1-pentyne all have activation energies lower than the less nucleophilic acetylenes. In fact, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ correlate quite well with the Taft polar substituent constants, σ^* , for monosubstituted acetylenes (Figure III).

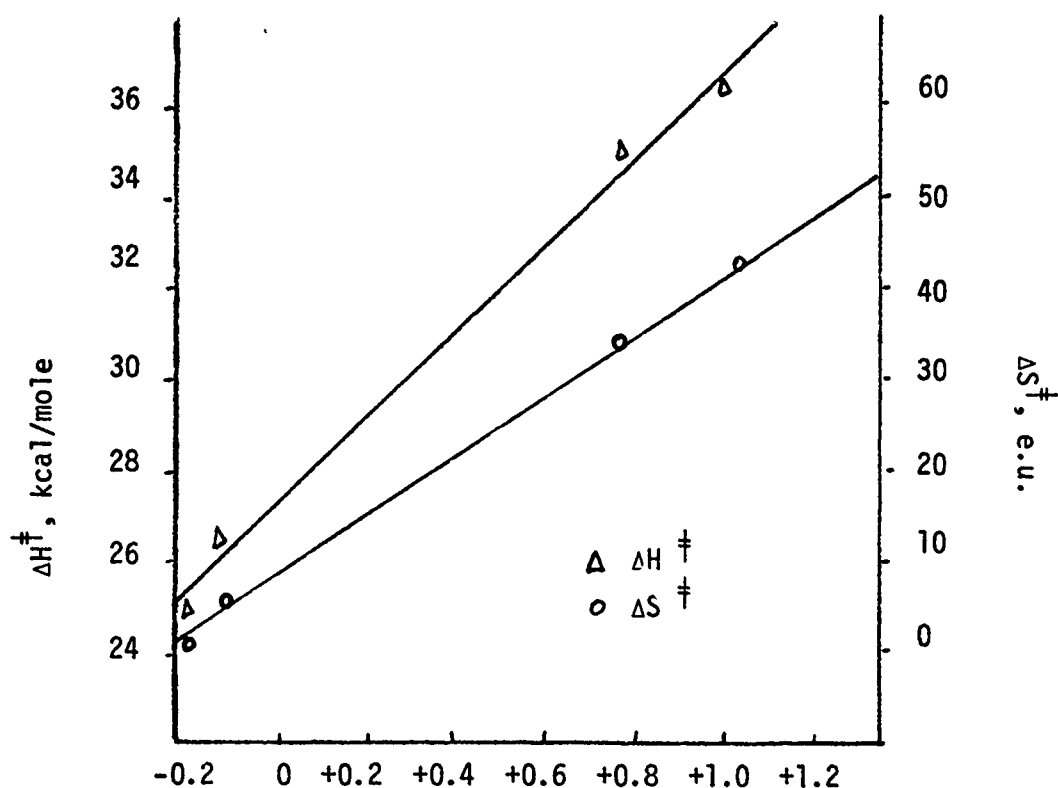


Figure III. Plot of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ vs. Taft polar substituent constant, σ^+ , for acetylenes of the type $\text{HC}\equiv\text{CCH}_2\text{R}$.

Interestingly, yields of the corresponding carboranes are dramatically increased in cases where the acetylene has an electron withdrawing substituent (e.g. $\text{HC}\equiv\text{CCH}_2\text{Br}$).

A plot of $\Delta H^\ddagger$ vs. $\Delta S^\ddagger$ for the various acetylenes gives a straight line with an isokinetic temperature of 12° , so that it is not surprising that the variation in reaction rates with the various acetylenes is small.

Attempts were made to identify the by-products of the low-yield reactions. While complete characterization was not accomplished, the by-products were polymeric containing both acetylene and ligand units in addition to the boron moiety. The molecular weights of the residues in benzene for both 1-octyne and 1-pentyne were ~ 500 and elemental analysis showed $\sim 3 \text{ B}_{10}\text{H}_{10}$ units, 2 acetylene units and $2(\text{CH}_3)_2\text{S}$ units. Oxidative degradation gave either 1-octanoic acid or 1-pentanoic acid respectively. These data suggest that the by-products are hydroborated acetylenes. If this process is occurring it is not surprising

that alkylcarboranes are obtained in lower yield since the alkyl acetylenes are much more readily hydroborated than those containing electronegative substituents.

Partially deuterated $B_{10}H_{12}[(CH_3)_2S]_2$ was prepared and reacted with $(CH_3C(O)OCH_2-C\equiv C)_2$. The amount of B-D bond breaking was determined by the abundance of deuterium in the effluent gas. The gas composition as determined by mass spectroscopy was as follows: D_2 , 24.5%; HD 48.4%; H_2 , 27.7%. The ratio $(k_1K)_D/(k_1K)_H$ was 1.09 indicative of a secondary isotope effect.

The correlation between $\Delta H^\ddagger$ and the nucleophilicity of the acetylene plus the lack of a primary isotope effect suggests that the rate determining step in the synthesis is attack by the acetylene on $B_{10}H_{12}[(CH_3)_2S]_2$ or $B_{10}H_{12}[(CH_3)_2S]$ to give $B_{10}H_{12}[(CH_3)_2S]A$ which reacts further to give carborane. Clearly for $B_{10}H_{12}[(CH_3)_2S]_2$ acetylenes which are not hydroborated readily (i.e. those containing electronegative substituents) give much higher yields of δ -carboranes. Therefore, if alkyl carboranes are desired, better yields may be obtained by first preparing an electronegatively substituted carborane that can be converted to the alkyl derivatives

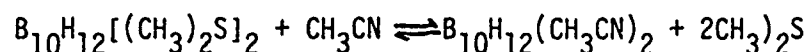


B. Preparation of other $B_{10}H_{12}$ (Lewis Base) $_2$ Adducts

Several other Lewis Base adducts have been prepared by us with a goal of examining these derivatives as substitutes for $B_{10}H_{12}[(CH_3)_2S]_2$ in the carborane synthesis. Unfortunately to date none of the derivatives display solubilities in good solvents for NMR studies of their reactions with

acetylenes. We have prepared the adducts, $B_{10}H_{12}[CH_3P(C_6H_5)_2]_2$, $B_{10}H_{12}[(CH_3)_2NPF_2]_2$, $B_{10}H_{12}(CH_3CN)_2$, and $B_{10}H_{12}[(CH_3)_3CCN]_2$. These adducts were prepared by the reaction of $B_{10}H_{14}$ with the ligand in benzene solution under N_2 . All precipitated from solution on cooling and displayed little solubility in benzene or chloroform (solvents of choice for kinetic studies). Thus, kinetics of the reactions of these adducts could not be measured under the second-order conditions observed for $B_{10}H_{12}[(CH_3)_2S]_2$. Several pseudo first order runs were carried out in benzene with CH_3CN and $(CH_3)_3CCN$ and yields of the o-carboranes were comparable to those obtained with $B_{10}H_{12}[(CH_3)_2S]_2$. No carborane was observed when $B_{10}H_{12}[CH_3P(C_6H_5)_2]_2$ or $B_{10}H_{12}[(CH_3)_2NPF_2]_2$ were used as adducts.

The equilibrium for the reaction of $B_{10}H_{12}[(CH_3)_2S]_2$ with CH_3CN was studied to ascertain whether the $B_{10}H_{12}(CH_3CN)_2$ adduct is more or less stable than $B_{10}H_{12}[(CH_3)_2S]_2$. Results of this study are summarized below:



Temp, °K	K, equilibrium constant
302.11	2.24×10^{-2}
303.03	2.29×10^{-2}
307.69	2.48×10^{-2}
314.46	2.79×10^{-2}
321.54	3.16×10^{-2}
322.58	3.31×10^{-2}

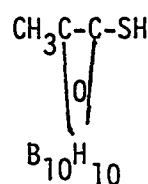
From this data ΔH for the reaction was calculated and found to be +2.6 kcal/mole. This indeed suggests that $B_{10}H_{12}[(CH_3)_2S]_2$ is less stable than $B_{10}H_{12}(CH_3CN)_2$. It is somewhat surprising that yields of the various carboranes were about the same as with $B_{10}H_{12}[(CH_3)_2S]_2$ but, of course, the reactions were

run under quite different conditions due to the low solubility of the CH_3CN adduct.

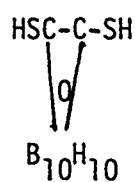
Attempts to prepare $\text{B}_{10}\text{H}_{12}(\text{PF}_3)_2$ and $\text{B}_{10}\text{H}_{12}[(\text{CH}_3)_2\text{Se}]_2$ were unsuccessful perhaps due to the low basicity of the ligands. Earlier we felt we had prepared $\text{B}_{10}\text{H}_{12}[(\text{CH}_3)_2\text{Se}]_2$ but analysis of the residues of the reaction gave only $\text{B}_{10}\text{H}_{14}$. We feel that the reaction of $\text{B}_{10}\text{H}_{12}[(\text{CH}_3)_2\text{S}]_2$ with $(\text{CH}_3)_2\text{Se}$ might yield $\text{B}_{10}\text{H}_{12}[(\text{CH}_3)_2\text{Se}]_2$ and this should be a point of further study.

III. Syntheses of Derivatives with a Range of Properties for attachment to HTPB.

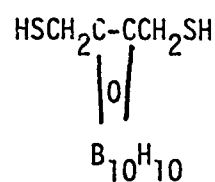
A. Mercapto Derivatives-



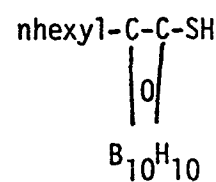
(I)



(II)



(III)



(IV)

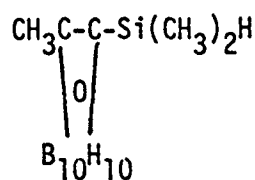
Preparation of (I), (II) and (III) were accomplished by reacting the appropriate carborane with butyl-lithium, sulfur and HCl in the following way. n-Butyl lithium [0.025 moles for (I) and (IV), 0.05 moles for (II)] was added to solution of 0.025 moles of the appropriate carborane [methyl-carborane for (I), o-carborane for (II), and n-hexylcarborane for (III)] in dry diethyl ether. One mole of butyl lithium per mole of n-hexyl or methyl carborane and two moles of butyl lithium per mole of o-carborane are required. Powdered sulfur [0.025 g atoms for (I) and (IV), 0.05 g atoms for (II)] was then added over a period of about 10 minutes to an ice-cooled

solution of the lithio-carborane. After the additions were complete, the reaction mixtures were stirred for an additional 25 minutes at room temperature, cooled again to 0°C and an excess of HCl (0.08 moles) in H₂O was added slowly. After stirring at room temperature for an additional 15-30 minutes the ether layers were separated, dried over MgSO₄, filtered, and the solvent removed in vacuo. The crude products were recrystallized from ether and/or petroleum ether to give white solids in yields of $\geq 90\%$. These products were characterized by their elemental analyses, infrared spectra (characteristic S-H absorption at $\sim 2570\text{ cm}^{-1}$), mass spectra (all show parent ions), and ¹H NMR which shows a sharp singlet for the CH₃ group in (I) at 1.30 ppm and broad absorptions in the 1-2 ppm range for the n-hexyl derivative.

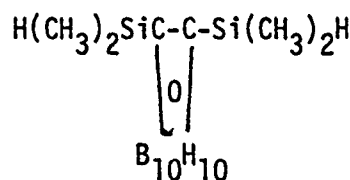
The synthesis of (III) was accomplished by reacting $\text{BrCH}_2\text{C}(\text{B}_{10}\text{H}_{10})\text{CCH}_2\text{Br}$ with thiourea by refluxing in di(n-propyl) ether. Base hydrolysis of the reaction product with aqueous NaOH gave small amounts of (III) characterized by its IR (S-H vibration at 2575 cm^{-1}) and ¹H nmr which shows a resonance at 2.4 ppm due to the CH₂ group. Due to the low yield of this product, further studies were not carried out with it.

Because of the ready synthesis of (IV) and the expected similarity of its properties with those of $\text{HC}(\text{B}_{10}\text{H}_{10})\text{C}(\text{CH}_2)_5\text{SH}$ plus the low yields of the thiourea reaction with alkyl bromides to give the corresponding SH derivative, the alkyl SH derivative was not synthesized.

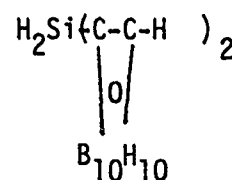
B. Silyl Derivatives



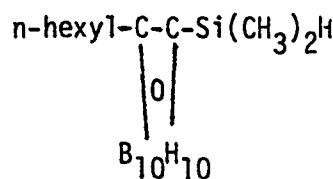
(I)



(II)



(III)



(IV)

Syntheses of (I) and (IV) were accomplished by the addition of 0.064 moles of $(\text{CH}_3)_2\text{SiHCl}$ in 50 mls of diethyl ether to a slurry of the corresponding lithio-carborane (0.064 moles) in diethyl ether at 0°C . After addition, the reactions were warmed to room temperature, allowed to stand for one hour, and then refluxed for 30 minutes. The solutions were filtered under nitrogen and the solvent removed in vacuo. Extraction of the residue with petroleum ether gave a white solid for (I) and a viscous oil for (IV). Both were identified by their ^1H nmr spectra [For (I), $\delta_{\text{Si-H}}=4.25$ ppm, $\delta_{\text{Si-CH}_3}=0.33$ ppm, $\delta_{\text{CH}_3}=1.25$ ppm, $J_{\text{H-CH}_3}=4.7\text{Hz}$; For (IV), $\delta_{\text{Si-H}}=4.24$ ppm, $\delta_{\text{SiCH}_3}=0.33$ ppm, $\delta_{\text{n-butyl}}=1-2$ ppm, $J_{\text{H-CH}_3}=4.8\text{Hz}$]. The infrared spectra showed a characteristic Si-H stretch at $\sim 2240\text{ cm}^{-1}$ for both derivatives.

Compound (II) was synthesized in a manner analogous to that of (I) and (IV) except that 2 moles of $\text{HSi}(\text{CH}_3)_2\text{Cl}$ were added per mole of dilithio-carborane. The ^1H nmr of this liquid derivative showed $\delta_{\text{Si-H}}$ at 4.22 ppm,

δ_{SiCH_3} at 0.35 ppm, and $J_{\text{CH}_3-\text{H}}=4.8\text{Hz}$. Its infrared spectrum also gave the characteristic Si-H stretch at 2240 cm^{-1} .

Compound (III) was prepared in very low yield by the reaction of lithio-carborane (0.064 moles) with SiCl_4 (0.032 moles) in diethyl ether at 0°C . After addition, the reaction was warmed to room temperature and then refluxed for 1 hour. The solvent was removed in vacuo and the residue extracted with petroleum ether to give a white solid. Recrystallization of the solid from ether by adding n-pentane gave 0.010 moles of $\text{Cl}_2\text{Si}(\text{C-CH})_2$.

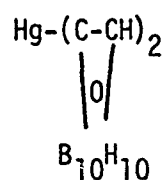
$$\begin{array}{c} \text{O} \\ | \\ \text{B}_{10}\text{H}_{10} \end{array}$$

The chloro silane was dissolved in 100 mls of THF and treated with 0.02 moles of LiAlH_4 and refluxed. The reaction was filtered and the solvent removed in vacuo to give trace amounts of the solid (III) identified by mass spectrum (parent-ion observed), ^1H NMR (which gave a characteristic $\delta_{\text{Si-H}}$ at 4.35 ppm) and infrared (which showed the Si-H stretch at 2239 cm^{-1}). Because of the extremely low yield further studies were not carried out.

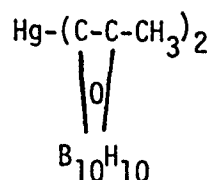
Again because of the easy synthesis of (IV) and the expected similarities between it and $\text{H-C-C}-(\text{CH}_2)_5\text{Si}(\text{CH}_3)_2\text{H}$ derivative the latter was not synthesized.

$$\begin{array}{c} \text{O} \\ | \\ \text{B}_{10}\text{H}_{10} \end{array}$$

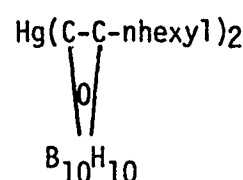
C. Mercurial Derivatives



(I)



(II)

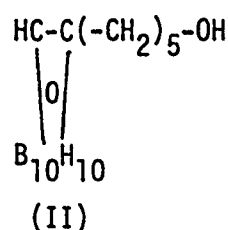
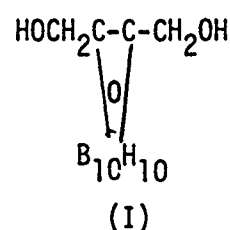


(III)

The above organo-mercurials were synthesized in the following way. The corresponding carborane (0.028 moles) was dissolved in 100 mls of diethyl ether and 0.028 moles of n-butyllithium in hexane were added

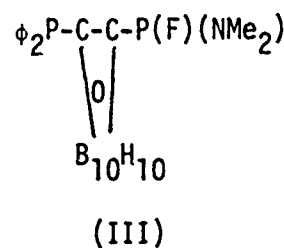
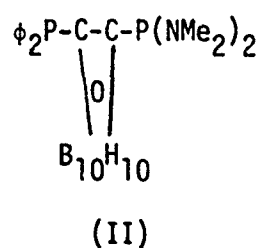
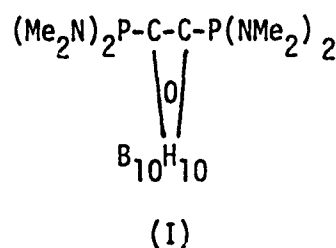
dropwise at 0°C. After the addition was complete the reaction was warmed to room temperature and stirred for 1 hour. Mercuric chloride (0.014 moles in 100 mls diethyl ether) was added dropwise at room temperature. The reaction was refluxed for 1 hour after the addition was complete. The reaction was allowed to cool to room temperature and filtered. The solvent was removed in vacuo and the solid or oil extracted with hot pentane. On cooling the pentane or removing it in vacuo white solids were obtained. These were characterized by their elemental analyses.

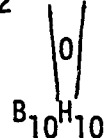
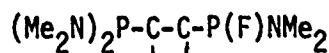
D. Hydroxy Derivatives



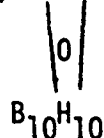
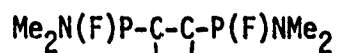
The corresponding acetoxy derivative [1,2-bis-(acetoxymethyl)-o-carborane or 1-carboranyl-5-acetoxypentane] (0.16 moles) in CH₃OH was added to a solution of 0.08 moles of KOH in 50 mls H₂O and 340 mls of CH₃OH at 20°C. The mixture was then allowed to warm to room temperature and stir for 2 hours. The reaction mixture was then poured into 1.7 liters of water and neutralized with HCl. A white precipitate formed in both cases. The precipitates were isolated by filtration, washed with water and dried in vacuo. Identification was accomplished by elemental analyses and infrared spectra showing the characteristic absorption of the OH group at 3335 cm⁻¹.

E. Phosphorus Derivatives

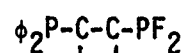




(IV)



(V)



(VI)

Syntheses of (I), (II) and (VI) were carried out by reacting $\text{ClP}(\text{NMe}_2)_2$, $\text{ClP}(\text{C}_6\text{H}_5)_2$, or PF_2Br respectively with the appropriate lithio-carborane [dilithiocarborane for (I), 1-lithio-2diphenylphosphino-carborane for (II) and (IV)] in diethyl ether at 0°C . After addition the reactions were refluxed for 20 hours, the solvents were removed in vacuo and residues extracted with hot pentane to give white solids.

The fluorine containing derivatives (III) and (V) were prepared by reacting (I) and (II) with excess PF_5 in hexane. Thus, 0.0032 moles of the carborane were reacted at room temperature. White solids were formed from which excess PF_5 was removed. The solid in hexane was heated to $\sim 130^\circ\text{C}$, immediately cooled, and the volatiles removed in vacuo. Extraction of the residue with n-pentane gave the derivatives as white solids.

Compound (IV) was prepared by reacting (I) (0.0066 moles) with 0.070 moles of PF_3 in benzene at $90-100^\circ\text{C}$ for 5 days in a high pressure reactor. After removal of the volatiles, extraction with pentane gave (IV) as a white solid.

All of these compounds were identified by elemental analysis, mass spectra, infrared spectra and ^1H , ^{31}P , and ^{19}F NMR. These NMR results are summarized in Table II and III.

Table (II)

¹ H NMR of Phosphorus Compounds ^a				
Compound	$\delta_{\text{C}_6\text{H}_5}$	δ_{Me}	$^3J_{\text{P-H}}$	$^4J_{\text{F-H}}$
I		2.08 t		
II	7.75m 7.40m	2.79 d	9.0	
III	7.80m 7.37m	2.77 dd	9.6	4.5
IV		2.72 d (~2.72 dd)	9.7 (~9.0)	~2.8
V		2.76 M	~9.2	~5.1
VI	7.25m			

^aChemical Shifts in ppm from TMS, coupling constants in Hertz, solvent CDCl_3 , m=multiplet, d=doublet, t=triplet

Table III

³¹ P NMR of Phosphorous Compounds ^a					
Compound	$\delta_{\text{P}(\text{C}_6\text{H}_5)_2}$	$\delta_{\text{P}(\text{NMe}_2)_2}$	$\delta_{\text{P}(\text{F})\text{NMe}_2}$	δ_{PF_2}	$J_{\text{P-P}}$
I		-97.1 d			73.5
II	-17.3 d	-104.0 d			120.0
III	-10.4 dd		-152.2 dd		151.2
IV		-96.6 dd	-145.5 dd		157.5
V			-147.7 m		110.0
VI	-11.1 dt			-139.4 td	177.8

^aChemical Shifts in ppm from 85% H_3PO_4 , coupling constants in Hertz, solvent CDCl_3 , m=multiplet, d= doublet, t=triplet.

Attempts were made to convert the PNMe_2 moieties to P-H so that addition could be made to the C=C in polybutadiene. However, treatment of any of the above with LiAlH_4 in THF or with HI did not yield P-H compounds but rather gave unidentified decomposition products. Therefore, binding studies could not be performed.

IV. Attachment for Derivatives to HTPB

After the syntheses of a large number of compounds and initial testing with HTPB, it became apparent that the best derivatives for HTPB attachment were those derivatives containing Si-H bonds, S-H bonds or organo-mercurials since these were found to add to the C=C bond. Those containing OH groups could be attached to the binder by reaction of the binder OH groups and the carboranyl OH groups with polyfunctional isocyanate curing agents but the incorporation could only give small amounts of boron in the polymer. Attempts to convert the PNMe_2 groups (of the phosphino-carboranes) to P-H groups by reaction with LiAlH_4 or HI were unsuccessful; thus, the phosphorus derivatives could not be attached to the binder.

Reactions between the binder and the derivatives were carried out in the following ways. The derivatives were mixed neat with the binder in a one to one mole ratio and heated for from 3 to 12 hours at 90°C , or the mixtures were made on a one to one mole ratio in CH_2Cl_2 , the solvent removed in vacuo after mixing and the mixture heated. After the addition had been carried out, the resulting polymer was extracted with methylene chloride and the unreacted carborane isolated and weighed. Table IV reports the results of our studies.

Table IV

Incorporation of Carborane Derivatives Into Hydroxyterminated Polybutadiene Binder (A)

Carborane	Polymer State	%Incorporation (B)
$\begin{array}{c} \text{HSC-CSH} \\ \\ \text{O} \\ \\ \text{B}_{10}\text{H}_{10} \end{array}$	Orange-yellow, hard Solid	97
$\begin{array}{c} \text{CH}_3\text{C-CSH} \\ \\ \text{O} \\ \\ \text{B}_{10}\text{H}_{10} \end{array}$	Yellow, hard solid	95
$\begin{array}{c} \text{n-hexyl-C-CSH} \\ \\ \text{O} \\ \\ \text{B}_{10}\text{H}_{10} \end{array}$	Yellow, hard solid	93
$\begin{array}{c} \text{H(CH}_3)_2\text{SiC-C-CH}_3 \\ \\ \text{O} \\ \\ \text{B}_{10}\text{H}_{10} \end{array}$	Light yellow, gum	54
$\begin{array}{c} \text{H(CH}_3)_2\text{SiC-CSi(CH}_3)_2\text{H} \\ \\ \text{O} \\ \\ \text{B}_{10}\text{H}_{10} \end{array}$	Light yellow solid	52
$\begin{array}{c} \text{n-hexyl-C-CSi(CH}_3)_2\text{H} \\ \\ \text{O} \\ \\ \text{B}_{10}\text{H}_{10} \end{array}$	Light yellow gum	55
$\left(\begin{array}{c} \text{HC-C-Hg} \\ \\ \text{O} \\ \\ \text{B}_{10}\text{H}_{10} \end{array} \right)_2$	Tan solid	31
$\left(\begin{array}{c} \text{CH}_3\text{C-C-Hg} \\ \\ \text{O} \\ \\ \text{B}_{10}\text{H}_{10} \end{array} \right)_2$	Tan solid	35
$\left(\begin{array}{c} \text{n-hexyl-C-C-Hg} \\ \\ \text{O} \\ \\ \text{B}_{10}\text{H}_{10} \end{array} \right)_2$	Yellow brown gum	25

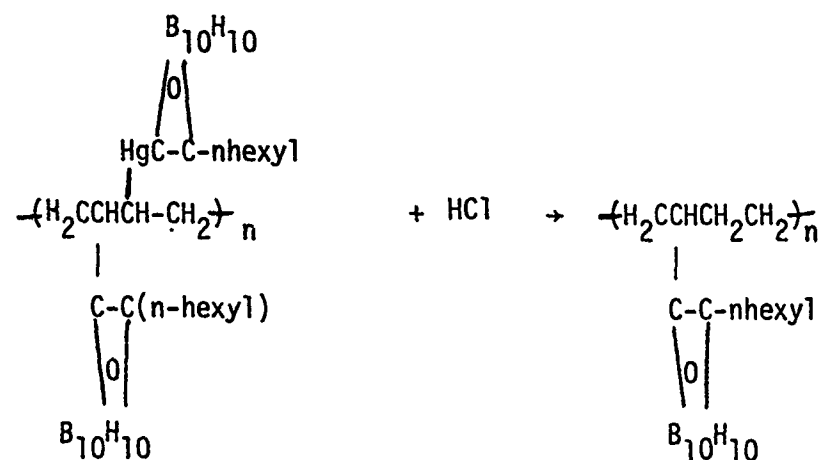
(A) Mixed in CH_2Cl_2 and then solvent removed or mixed neat and heated at 90°C for 3-12 hours.

(B) Based on polymer product of 1:1 adduct, functional group to $\text{CH}_2\text{CH=CHCH}_2$ unit.

It is of interest to note several features of the Table. First, no catalyst was used for any of the additions. Optimum Si-H addition might require a catalyst but this was not further investigated in light of the deteriorating properties of the polymer once addition had taken place. In fact, those polymers resulting from the addition of the S-H derivatives (which are incorporated nearly quantitatively) are very hard and brittle. Studies at levels of carborane incorporation lower than 1:1 carboranyl functional group to C=C showed a rapid deterioration of the fluidity of the polymer as addition occurred.

Monofunctional derivatives gave polymers with properties improved over the difunctional ones but still unacceptable for propellant mixing.

Treatment of the mercurial derivatives with HCl in ether did give the corresponding polymers free of Hg but again properties of the polymers were unacceptable. In fact the treatment of the n-hexyl derivative of Hg with the polymer followed by HCl gave the n-hexylcarboranyl polymer [the polymer we felt would be most likely to succeed in properties] as a gum according to the following equation:

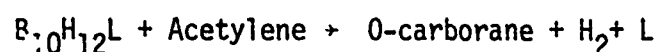
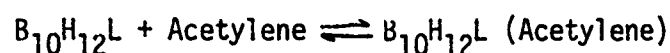
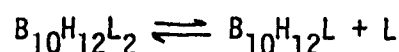


Dummy propellants and detailed quantitative polymer properties were not studied since a qualitative examination of the binders after addition showed them unacceptable for propellant systems.

V. Conclusions

The kinetic study and preparative study of $B_{10}H_{12}L_2$ (L=Lewis Base) with various acetylenes have led to several important results. These are:

- (1) The mechanism of o-carborane formation from $B_{10}H_{12}L_2$ and acetylenes is:

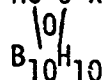


- (2) Acetylenes of the type $HC \equiv CCH_2X$ give higher yields of o-carborane, higher $\Delta H^\ddagger$, and higher $\Delta S^\ddagger$ when X is electron withdrawing.
- (3) Side products causing reduced o-carborane yield are hydroboration products with high molecular weights.
- (4) Steric factors are not especially important since $\Delta S^\ddagger$ and yields of carborane are comparable for mono and difunctional acetylenes.
- (5) Functional groups directly attached to $C \equiv C$ group drastically lower the yields of o-carborane.

The polymer attachment studies have led to the following results:

- (1) Carboranyl derivatives with Si-H, S-H, or Hg-carboranyl groups will add across the C=C of the polymer.

- (2) Monofunctional carboranes of the type $HC-C-X$ give polymers with



better properties than difunctional carboranes.

- (3) Incorporation of the carborane into the binder can be accomplished at a high level (>90% of theoretical one carborane per polymer C=C bond).
- (4) Polymer properties are severely and adversely affected by addition across the C=C.

VI. Recommendations

- (1) Although this work has suggested ways to best utilize $B_{10}H_{14}$, alternate routes to o-carboranes by passing $B_{10}H_{14}$ are needed. It is felt that the only way the cost can be greatly reduced is to develop a path to o-carboranes from BH_4^- .
- (2) No further studies involving attacking of carboranes to the binders seem necessary, since essential polymer properties are destroyed.