The Mechanism of $B_{10}H_{10}^{-2}$ Formation from $B_{10}H_{12}$(ligand)$_2$ Species

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Abstract: The formation of the polyhedral $B_{10}H_{10}^{-2}$ ion from $B_{10}H_{12}$(ligand)$_2$ compounds has been examined kinetically under a variety of circumstances. In each reaction studied, triethylamine was employed as the required base. Regardless of the identity of the ligand present in the $B_{10}H_{10}$(ligand)$_2$ compound, the over-all reaction was observed to be first order in $B_{10}H_{10}$(ligand)$_2$ and independent of triethylamine concentration at high triethylamine concentrations. Addition of ligand to the reaction suppressed the rate of $B_{10}H_{10}^{-2}$ formation. These and other experimental observations suggest that the mechanism of $B_{10}H_{10}^{-2}$ formation involves the initial reversible dissociation of $B_{10}H_{12}$(ligand)$_2$ to form a $B_{10}H_{10}$(ligand) intermediate which is converted to $B_{10}H_{10}^{-2}$ by subsequent reaction with triethylamine and expulsion of the remaining ligand molecule.

Since the first report[2] of the formation of the unusually interesting $B_{10}H_{10}^{-2}$ ion, a large effort has been devoted to the elucidation of its chemical properties[3] and the bonding[4] responsible for its high kinetic stability and aromatic character.[3,4] The $B_{10}H_{10}^{-2}$ ion has thus attained a position of importance in chemistry, and we describe here the details of a previously reported[5] study which was concerned with the mechanism of its formation from $B_{10}H_{12}$(ligand)$_2$ compounds[6,7] and the representative base, triethylamine. To date, reactions of this type provide the only useful route to $B_{10}H_{10}^{-2}$, and a variety of $B_{10}H_{12}$(ligand)$_2$ compounds and bases have been explored in a preparative sense.

$$B_{10}H_{12}(\text{ligand})_2 + 2\text{base} \longrightarrow B_{10}H_{10}^{-2} + 2H^{+}\text{base} + 2\text{ligand}$$

Among the reported variations of this reaction sequence one finds ammonia,[3] amines,[2] and triphenylphosphorane[8] employed as bases, and dialkyl sulfides,[3] amines,[2] and alkyl nitriles[2] as ligands. High yields of $B_{10}H_{10}^{-2}$ have been obtained in all cases thus far examined, but the reaction of triethylamine with $B_{10}H_{12}[N(C_2H_5)_3]_2$ has proved[2,9] to be quantitative and extremely convenient. It should be pointed out, however, that the preparation of the $B_{10}H_{10}^{-2}$ ion is sometimes complicated by a competing reaction, the ligand displacement reaction.[6b,c]

$$B_{10}H_{12}(\text{ligand})_2 + 2\text{Ligand} \longrightarrow B_{10}H_{12}(\text{Ligand})_2 + 2\text{ligand}$$

The relationship of this reaction to the mechanism of $B_{10}H_{10}^{-2}$ formation is presented in the following paper.[10] The structure of $B_{10}H_{10}^{-2}$ is a bicapped Archimedian antiprism[11] (D_{4d}), while the boron atom configuration of $B_{10}H_{12}$(ligand)$_2$ compounds is recognized[7] as an icosahedral fragment which resembles $B_{10}H_{14}$. The unusual change in structure which occurs during the formation of $B_{10}H_{10}^{-2}$ from $B_{10}H_{12}$(ligand)$_2$ compounds was the subject of an earlier study[12] which traced the course of the rearrangement through the use of deuterium atom labeling in the 1, 2, 3, and 4 positions of the $B_{10}H_{12}$(ligand)$_2$ reactant. The results of that investigation were confirmed[13] by use of a bromine atom label. The course of the rearrangement is depicted in Figure 1.

The work described in this paper was undertaken in an effort to extend further our knowledge of the mechanism of $B_{10}H_{10}^{-2}$ formation by the use of reaction kinetics. As an aside, it is worthy of note that very few reactions of the higher boron hydrides and their derivatives have been examined by this means.

Results

The kinetic methods employed in this investigation were made possible by the discovery of an accurate spectrophotometric method for the quantitative determination of $B_{10}H_{10}^{-2}$ at extremely low concentrations. The basis of this method rests upon the reaction of the $B_{10}H_{10}^{-2}$ ion with benzenediazonium tetrafluoroborate in acetonitrile solution and in the presence of trifluoroacetic acid. Under these conditions the previously reported[14] coupling reaction occurs to produce the highly colored $B_{10}H_9NH{=}NC_6H_5$ (ϵ 19,400 at 520 mμ) anion.

$$B_{10}H_{10}^{-2} + C_6H_5N_2^{+} \longrightarrow B_{10}H_9NH{=}NC_6H_5^{-}$$

This analytical method was sufficiently sensitive to allow kinetic measurements to be made during the initial portion of each rate run. In this manner it was possible, where necessary, to collect pseudo-zero-order rate data which were not complicated by competing side reactions. Only two of the $B_{10}H_{12}$(ligand)$_2$ substrates employed in this study gave essentially quantitative conversions to $B_{10}H_{10}^{-2}$ under the conditions of the kinetic

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(3) E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).

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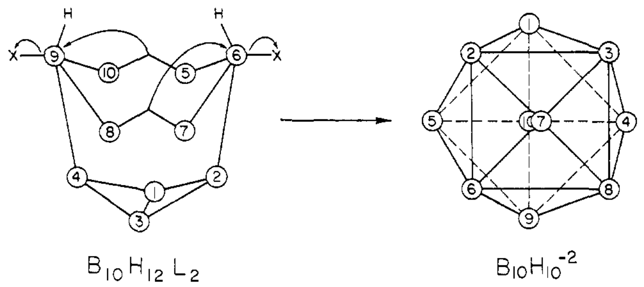

Figure 1. Geometrical change which converts $B_{10}H_{12}(ligand)_2$ derivatives to $B_{10}H_{10}^{-2}$.

experiments. The $B_{10}H_{12}(ligand)_2$ compounds which were examined with triethylamine serving as the base were selected to provide a spectrum of ligand donor strengths ranging from weakly bound dialkyl sulfides to more tightly bound triethylamine.

The Reaction of $B_{10}H_{12}[(C_2H_5)_3N]_2$ with Triethylamine. The reaction of $B_{10}H_{12}[(C_2H_5)_3N]_2$[2] with triethylamine in acetonitrile solution at 100° was selected for initial study. Preparative experiments[9] had previously illustrated that these reactants produced $B_{10}H_{10}^{-2}$ in virtually quantitative yield. The fact that the expelled ligand, triethylamine, is identical with the basic reagent provided a system in which the rather generally observed ligand displacement reaction[6b,c] would not complicate the observed reaction kinetics by forming a second unsymmetrical substrate, $B_{10}H_{12}[(C_2H_5)_3N](ligand)$, during the course of the reaction. In addition, previous work had shown that the displacement of triethylamine by acetonitrile solvent was thermodynamically

$$B_{10}H_{12}(\text{ligand})_2 + (C_2H_5)_3N \longrightarrow B_{10}H_{12}[(C_2H_5)_3N](\text{ligand}) + \text{ligand}$$

unfavorable and that $B_{10}H_{12}[(C_2H_5)_3N](CH_3CN)$ would not enter the system as $B_{10}H_{10}^{-2}$ was produced. Finally, the identity of the expelled ligand and the base reagent required the concentration of triethylamine to remain equal to the initial triethylamine concentration throughout the reaction.

$$B_{10}H_{12}[(C_2H_5)_3N]_2 + 2N(C_2H_5)_3 \longrightarrow B_{10}H_{10}^{-2} + 2HN^+(C_2H_5)_3 + 2N(C_2H_5)_3$$

Table I presents the results obtained with this system using a wide range of initial triethylamine concentrations and 1×10^{-2} *M* $B_{10}H_{12}[(C_2H_5)_3N]_2$. Rate data were collected to at least 80% conversion to $B_{10}H_{10}^{-2}$, and the data were correlated using the integrated first-order rate expression (method 1). These results indicated that the rate-determining step of the over-all reaction was zero order in triethylamine. The fact that the same first-order rate constant based upon the instantaneous concentration of $B_{10}H_{12}[(C_2H_5)_3N]_2$ was observed with 5×10^{-3} *M* triethylamine eliminated the possibility of prior complexation of the amine with substrate followed by the rate-determining decomposition of the complex to produce $B_{10}H_{10}^{-2}$. An alternative, and seemingly

$$B_{10}H_{12}[(C_2H_5)_3N]_2 + (C_2H_5)_3N \xrightarrow{\text{fast}} B_{10}H_{12}[(C_2H_5)_3N]_3 \xrightarrow[k_3]{\text{slow}} \text{products}$$

correct, explanation of the experimental data suggests that $B_{10}H_{10}^{-2}$ is formed by the partitioning of $B_{10}H_{12}[(C_2H_5)_3N]$ formed in a reversible dissociation of $B_{10}H_{12}[(C_2H_5)_3N]_2$ as shown in the following equation.

Table I. The Rates of Reaction of 0.01 *M* $B_{10}H_{12}[(C_2H_5)_3N]_2$ with Triethylamine at 100° in Acetonitrile Solution

$[(C_2H_5)_3N]$, *M*	First-order rate constant, k_i, sec^{-1} $\times 10^5$
0.005	5.26
0.010	5.63
0.020	5.89
0.050	5.89
0.100	5.73
0.100	5.36

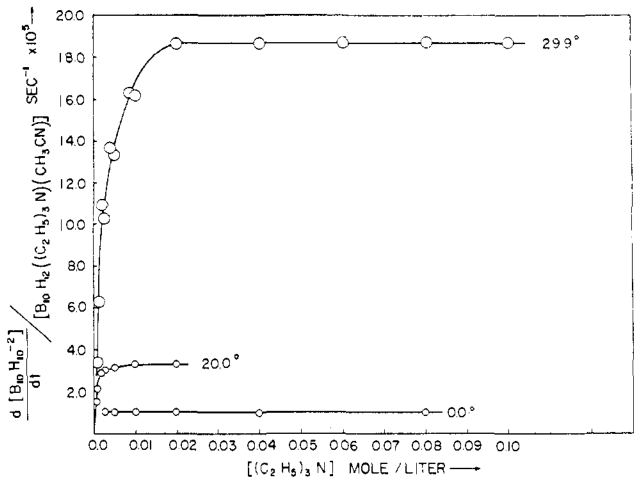

Figure 2. Dependence of k, upon triethylamine concentration with the $B_{10}H_{12}[(C_2H_5)_3N](CH_3CN)$ system in acetonitrile solution.

$$B_{10}H_{12}[(C_2H_5)_3N]_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B_{10}H_{12}[(C_2H_5)_3N] + N(C_2H_5)_3 \xrightarrow{k_2} B_{10}H_{10}^{-2} + 2HN^+(C_2H_5)_3$$

The instantaneous rate of $B_{10}H_{10}^{-2}$ formation would then be given by the following expression, based upon the usual steady-state assumption, where the observed

$$\frac{d[B_{10}H_{10}^{-2}]}{dt} = \frac{k_1k_2}{k_{-1} + k_2}[B_{10}H_{12}[(C_2H_5)_3N]_2]$$

first-order rate constant, k_i, is equal to $k_1k_2/(k_1 + k_2)$.

The Reaction of $B_{10}H_{12}[(C_2H_5)_3N](CH_3CN)$ with Triethylamine. The unsymmetrical substrate, $B_{10}H_{12}[(C_2H_5)_3N](CH_3CN)$, was prepared by a previously established route[15] and its reaction with triethylamine examined in acetonitrile solution at 0.0, 20.0, and 29.9°. This particular substrate was selected for study since it contains a weakly bound acetonitrile ligand and a strongly bound triethylamine ligand.[6b,c] In view of the results obtained with $B_{10}H_{12}[(C_2H_5)_3N]_2$, which indicated that one ligand molecule dissociates in an equilibrium prior to the formation of $B_{10}H_{10}^{-2}$ at 100°, the unsymmetrical substrate would be expected to dissociate to yield acetonitrile and $B_{10}H_{12}[(C_2H_5)_3N]$ at a much greater rate. Finally, the $B_{10}H_{12}[(C_2H_5)_3N]$ intermediate, if formed, would be common to both systems.

Table II presents the rate data collected at 0.0, 20.0, and 29.9° with the unsymmetrical system, and Figure 2 indicates the profiles of the observed first-order rate

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(15) B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, 1, 622 (1962).

constant, k_i *vs.* triethylamine concentration. Meaningful data could not be obtained at 0.0° with triethylamine concentrations below 2.5×10^{-3} *M* owing to the very low reaction rate. At 20.0 and 29.9° the hyperbolic shapes of the rate-profile curves were established, and a series of 29.9° runs with varying initial substrate concentrations established the first-order dependence of k_i upon substrate concentration at all initial triethylamine concentrations. Plots of k_i^{-1} *vs.* $[(C_2H_5)_3N]^{-1}$ were linear in accordance with the equation $k_i^{-1} = A[(C_2H_5)_3N]^{-1} + B$. The values of *A* and *B* determined at 20.0 and 29.9° and the value of *B* estimated from the 0.0° data are presented in Table V.

Table II. The Rates of Reaction of $B_{10}H_{12}[(C_2H_5)_3N](CH_3CN)$ with Triethylamine at 0, 20, and 29.9° in Acetonitrile Solution

Temp, °C	$[B_{10}H_{12}$-$[(C_2H_5)_3N]$-$(CH_3CN)]$, $M \times 10^3$	$[(C_2H_5)_3N]$, $M \times 10^3$	Pseudo-first-order rate constant, k_i, sec^{-1} $\times 10^5$	Method of calcn
0.0	10.0	2.5	0.98	2
	10.0	5.0	0.97	2
	10.0	10.0	1.00	2
	10.0	20.0	0.98	2
	10.0	40.0	1.03	2
	10.0	80.0	1.01	2
20.0	10.0	0.40	1.48	4
	10.0	1.00	2.18	4
	10.0	2.00	2.97	4
	10.0	2.50	3.10	2
	10.2	5.00	3.18	2
	10.0	10.0	3.28	2
	10.0	20.0	3.32	2
29.9	9.83	0.236	3.05	3
	10.1	0.512	3.42	3
	9.95	0.473	3.81	3
	5.20	0.965	6.00	2
	10.1	1.00	6.35	4
	10.1	1.02	6.79	3
	9.86	0.946	7.11	3
	20.8	2.41	10.3	2
	10.0	2.00	11.0	4
	10.0	4.00	13.7	4
	10.0	5.00	13.4	4
	5.00	9.65	16.3	2
	10.0	10.0	16.2	4
	10.0	20.0	18.7	2
	10.0	40.0	18.7	2
	10.0	60.0	18.7	2
	5.20	80.0	18.8	2
	10.0	80.0	18.7	2
	20.8	80.0	18.7	2
	29.9	80.0	18.8	2
	29.9	100	18.7	2

In a separate series of experiments, the yield of $B_{10}H_{10}^{-2}$ from 1×10^{-2} *M* $B_{10}H_{12}[(C_2H_5)_3N](CH_3CN)$ was determined as a function of initial triethylamine concentration. Below 1.5×10^{-2} *M* triethylamine the yields obtained were of the order of 90–100%. Initial amine concentrations greater than 1.5×10^{-2} *M* resulted in a steady decrease in $B_{10}H_{10}^{-2}$ yield to a value of approximately 65% of the theoretical at 8×10^{-2} *M* amine. Although this change in $B_{10}H_{10}^{-2}$ yield with changing initial triethylamine concentration was apparent in infinite time runs, the clean correlation of k_i values obtained from initial reaction rates indicates that the diminution of $B_{10}H_{10}^{-2}$ yields was a result of side reactions between amine and substrate which only become important at high amine concentrations. An over-all second-order reaction of amine with substrate to give an unidentified product is suggested.

Table III. The Rates of Reaction of $B_{10}H_{12}[(CH_3)_2S]_2$ with Triethylamine at 0, 20, and 29.9° in Toluene Solution with Added $(CH_3)_2S$

Temp, °C	$[B_{10}H_{12}$-$[(CH_3)_2S]_2]$, $M \times 10^3$	$[(C_2H_5)_3N]$, $M \times 10^3$	$[(CH_3)_2S]$, $M \times 10^3$	Pseudo-first-order rate constant, k_i, sec^{-1} $\times 10^5$
0.0	11.8	4.87		0.084
	11.7	9.5		0.12
	47.5	24.4		0.139
	11.8	36.2		0.14
	47.5	47.6		0.145
20.0	15.7	4.87		2.53
	7.85	4.87		2.57
	3.92	4.87		2.53
	10.0	4.87		2.24
	9.75	9.52		3.32
	9.95	24.4		4.34
	9.72	47.7		4.66
	9.84	36.2		4.37
	8.54	167		4.87
	9.12	11.1	4.83	1.71
	9.12	16.6	4.83	2.12
	9.15	22.2	4.83	2.36
	9.12	33.2	4.83	2.80
	9.15	55.6	4.83	3.36
	9.15	111	4.83	3.87
	9.12	11.1	9.66	1.22
	9.16	16.6	9.66	1.65
	9.12	22.2	9.66	1.98
	9.16	33.2	9.66	2.47
	9.12	55.6	9.66	2.91
	9.16	111	9.66	3.52
	9.15	11.1	38.6	0.47
	9.24	16.6	38.6	0.68
	9.15	22.2	38.6	0.90
	9.24	33.2	38.6	1.20
	9.15	55.6	38.6	1.66
	9.24	111	38.6	2.47
29.9	9.7	4.8		4.17
	9.6	9.5		7.81
	9.1	18.2		11.9
	9.9	24.4		13.1
	9.7	36.2		13.9
	9.4	47.6		13.8

The Reaction of $B_{10}H_{12}[(CH_3)_2S]_2$ and $B_{10}H_{12}[(C_2H_5)_2S]_2$ Substrates with Triethylamine. The reaction of $B_{10}H_{12}[(CH_3)_2S]_2$[16] with triethylamine was examined in toluene solution at 0.0, 20.0, and 29.9°. The similar reaction of $B_{10}H_{12}[(C_2H_5)_2S]_2$[17] was restricted to a study at 0.0° due to the great rapidity of $B_{10}H_{10}^{-2}$ formation at higher temperatures. The rate data collected for these systems are presented in Tables III and IV. As in the case of the $B_{10}H_{12}[(C_2H_5)_3N](CH_3CN)$ substrate, the dialkyl sulfide systems were examined using the initial rate method (method 2). This was necessary owing to the less than quantitative yields of $B_{10}H_{10}^{-2}$ obtained.

At 20.0°, the maximum yield of $B_{10}H_{10}^{-2}$ from $B_{10}H_{12}[(CH_3)_2S]_2$ (1×10^{-2} *M* solution in toluene in all cases)

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[16] W. H. Knoth and E. L. Muetterties, *J. Inorg. Nucl. Chem.*, 20, 71 (1961).

[17] B. M. Graybill, J. K. Ruff, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 2669 (1961).

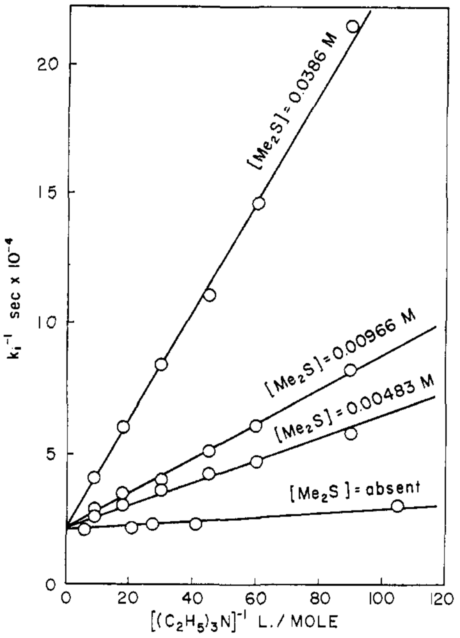

Figure 3. Plot of k_i^{-1} *vs.* $[(C_2H_5)_3N]^{-1}$ for the $B_{10}H_{12}[(CH_3)_2S]_2$ system at 20.0° in toluene solution with added dimethyl sulfide.

was 80% when the initial triethylamine concentration was 8×10^{-2} *M*. At lower initial amine concentrations the yield based upon available amine fell to 50% at 1×10^{-2} *M* amine. At initial amine concentrations greater than 8×10^{-2} *M*, the yield of $B_{10}H_{10}^{-2}$ slowly decreased to 70% at 0.20 *M*. Preparative-scale product studies were carried out with the dimethyl sulfide substrate at 20°. After 4.5 days, 0.02 *M* $B_{10}H_{12}[(CH_3)_2S]_2$ and 0.15 *M* triethylamine had produced 70% $B_{10}H_{10}^{-2}$, 15% $B_{10}H_{12}[(C_2H_5)_3N]_2$, and 15% unidentified oil.

Table IV. The Rates of Reaction of $B_{10}H_{12}[(C_2H_5)_2S]_2$ with Triethylamine at 0° in Toluene Solution with Added $(C_2H_5)_2S$

$[B_{10}H_{12}[(C_2H_5)_2S]_2]$, $M \times 10^3$	$[(C_2H_5)_3N]$, $M \times 10^3$	$[(C_2H_5)_2S]$, $M \times 10^3$	First-order rate constant, k_i, sec⁻¹ × 10⁶
50.0	5.0		1.72
50.0	10.0		2.22
50.0	20.0		2.33
50.0	40.0		2.34
50.0	40.0		2.32
50.0	120		2.37
25.0	40.0		2.32
25.0	80.0		2.33
100.0	40.0		2.25
100.0	80.0		2.33
50.0	5.0	50.0	0.57
50.0	10.0	50.0	1.10
50.0	20.0	50.0	1.49
50.0	40.0	50.0	1.95
50.0	80.0	50.0	2.24
50.0	160	50.0	2.31
50.0	10.0	100	0.70
50.0	20.0	100	1.10
50.0	40.0	100	1.63
50.0	80.0	100	2.10
50.0	160	100	2.34
50.0	250	100	2.34
50.0	20	160	0.90
50.0	40	160	1.42
50.0	80	160	1.87
50.0	20	200	0.75
50.0	40	200	1.25
50.0	80	200	1.69
50.0	20	400	0.45
50.0	40	400	0.81
50.0	80	400	1.25
50.0	160	400	1.72

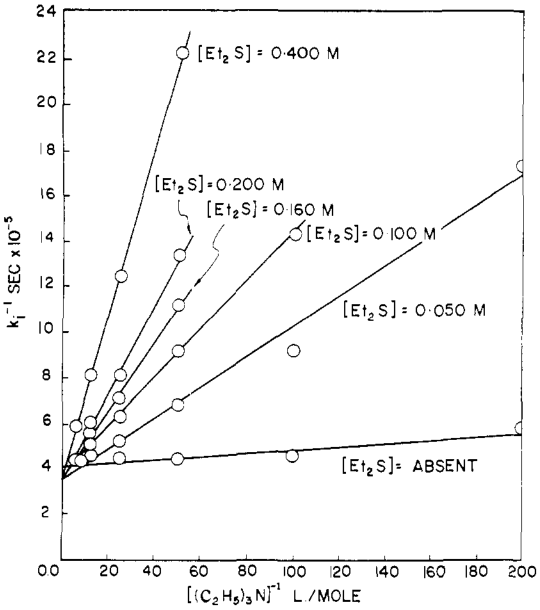

Figure 4. Plot of k_i^{-1} *vs.* $[(C_2H_5)_3N]^{-1}$ for the $B_{10}H_{12}[(C_2H_5)_2S]_2$ system at 0.0° in toluene solution with added diethyl sulfide.

The yields of $B_{10}H_{10}^{-2}$ obtained with 5×10^{-2} *M* $B_{10}H_{12}[(C_2H_5)_2S]_2$ and triethylamine in toluene at 0.0° were of the order of 50–65% and independent of amine concentration. A preparative-scale experiment which employed these reagents at 25° produced 88% $B_{10}H_{10}^{-2}$ and 9% $B_{10}H_{12}[(C_2H_5)_3N]_2$ after 2 days with initial reactant concentrations of 0.17 *M* $B_{10}H_{12}[(C_2H_5)_2S]_2$ and 0.50 *M* triethylamine.

The rate data collected for the dialkyl sulfide systems are of two types. The first type of data was obtained by conducting a series of rate runs in the absence of added dialkyl sulfide ligand and with varying initial concentrations of substrate and amine. The k_i values obtained in these runs were successfully correlated with the corresponding triethylamine concentration by the use of the equation $k_i^{-1} = A[(C_2H_5)_3N]^{-1} + B$, where *A* and *B* are constants which correspond to the similar constants obtained with the $B_{10}H_{12}[(C_2H_5)_3N](CH_3CN)$ system in acetonitrile solution. The values of *A* and *B* are presented in Table V. The second type of data presented in Tables III and IV were obtained by adding known initial concentrations of the corresponding dialkyl sulfide ligand to the dimethyl sulfide system at 20.0° and to the diethyl sulfide system at 0.0°. Thus, a group of runs was made at each fixed dialkyl sulfide ligand concentration with substrate and amine concentrations as variables. The k_i values obtained were correlated as before at each dialkyl sulfide concentration. In this manner it was apparent that *A* was dependent upon added ligand concentration and given by $A = C[\text{ligand}] + D$. Representative plots of k_i^{-1} *vs.* $[(C_2H_5)_3N]^{-1}$ are presented in Figures 3 and 4 for the dimethyl sulfide system at 20.0° and the diethyl sulfide system at 0.0°, respectively. Figures 5 and 6 present plots of the *A* values obtained from Figures 3

Table V. Kinetic Analysis of Reaction Rate Data

Substrate	Temp, °C	Solvent	Concn of added ligand, [L], $M \times 10^3$	$A = (k_{-1}[L] + k_4)/k_1k_2$, sec mole l.$^{-1}$	$B = (k_2 + k_3)/k_1k_2$, sec $\times 10^{-4}$
$B_{10}H_{12}[(C_2H_5)_2N](CH_3CN)$	0.0	CH_3CN	19.1×10^3		9.9
	20.0	CH_3CN	19.1×10^3	15.9	2.80
	29.9	CH_3CN	19.1×10^3	10.9	0.49
$B_{10}H_{12}[(CH_3)_2S]_2$	0.0	$C_6H_5CH_3$		2660	61.5
	20.0	$C_6H_5CH_3$		121	1.89
	20.0	$C_6H_5CH_3$	4.83	402[a,b]	2.30
	20.0	$C_6H_5CH_3$	9.66	659[a,b]	2.14
	20.0	$C_6H_5CH_3$	38.6	2120[a,b]	2.01
	29.9	$C_6H_5CH_3$		93.5	0.413
$B_{10}H_{12}[(C_2H_5)_2S]_2$	0.0	$C_6H_5CH_3$		749	41.1
	0.0	$C_6H_5CH_3$	50.0	7645[a,b]	34.5
	0.0	$C_6H_5CH_3$	100	10810[a,b]	37.6
	0.0	$C_6H_5CH_3$	160	15280[a,b]	34.0
	0.0	$C_6H_5CH_3$	200	19660[a,b]	33.7
	0.0	$C_6H_5CH_3$	400	37220[a,b]	34.5

[a] $C = k_{-1}/k_1k_2 = 5.15 \times 10^4$ and 9.00×10^4 sec in the dimethyl sulfide and diethyl sulfide systems, respectively. [b] $D = k_4/k_1k_2 = 145$ and 1500 sec mole l.$^{-1}$ in the dimethyl sulfide and diethyl sulfide systems, respectively.

and 4, respectively, plotted *vs.* ligand concentration. Figures 5 and 6 thus provide the values of *C* and *D* for the dimethyl sulfide system at 20.0° and the diethylsulfide system at 0.0°.

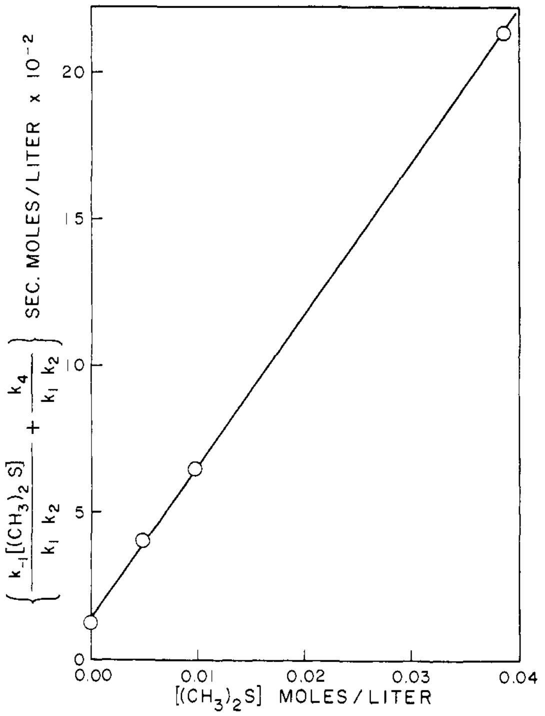

Figure 5. Slopes of lines from Figure 3 plotted *vs.* corresponding dimethyl sulfide concentrations.

Discussion

Two features of the kinetic results presented above point to a mechanism for $B_{10}H_{10}^{-2}$ formation which requires a reversible ligand dissociation step followed by a reaction of the $B_{10}H_{12}$(ligand) intermediate with triethylamine. These features are (1) the zero-order dependence of $B_{10}H_{10}^{-2}$ formation upon triethylamine concentration at high amine concentrations or, in the special case of $B_{10}H_{12}[(C_2H_5)_3N]_2$ substrate, at all amine concentrations; and (2) the depression of the rate of $B_{10}H_{10}^{-2}$ formation which accompanies the addition of ligand to the reaction mixture. Product analysis and many examples in the literature[6b,c] require the concurrent operation of ligand displacement reactions, and the intercepts which are distinctly seen in Figures 5 and 6 require the loss of the $B_{10}H_{12}$(ligand) intermediate by a pathway which does not involve the ligand or triethylamine. These observations may be combined to produce the following set of reactions (where L = ligand) which appear to describe the sequence of events when $B_{10}H_{12}$(ligand)$_2$ substrates are allowed to react with bases such as triethylamine. The $B_{10}H_{11}^-$ intermediate could well be an edge-protonated $B_{10}H_{10}^{-2}$ ion in which an apex-equatorial edge bears a proton. A steady-state

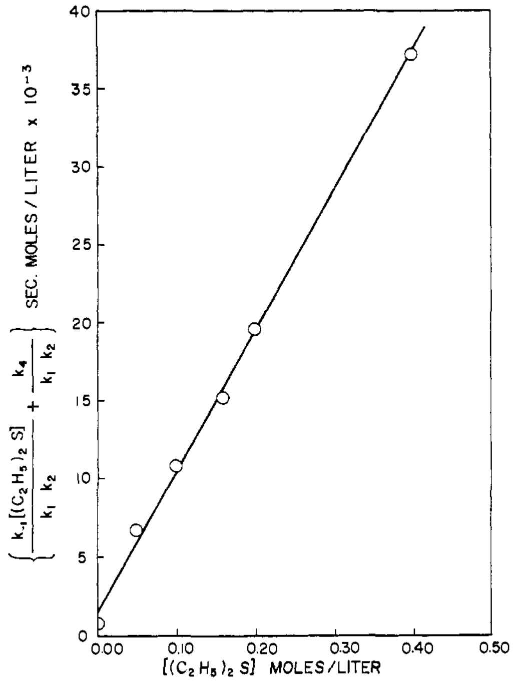

Figure 6. Slopes of lines from Figure 4 plotted *vs.* corresponding diethyl sulfide concentrations.

$$B_{10}H_{12}L_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B_{10}H_{12}L + L$$

$$B_{10}H_{12}L + \text{base} \xrightarrow{k_2} B_{10}H_{11}^- + H^+\text{base} + L$$

$$B_{10}H_{11}^- + \text{base} \xrightarrow{\text{very fast}} B_{10}H_{10}^{-2} + H^+\text{base}$$

$$B_{10}H_{12}L + \text{base} \xrightarrow{k_3} B_{10}H_{12}L(\text{base})$$

$$B_{10}H_{12}L \xrightarrow{k_4} \text{unidentified products}$$

approximation for [$B_{10}H_{12}L$] gives the following rate expression

$$d[B_{10}H_{10}^{-2}]/dt = \frac{k_1k_2[\text{base}][B_{10}H_{12}L_2]}{(k_2 + k_3)[\text{base}] + k_{-1}[L] + k_4} \qquad (1)$$

since the experimentally observed pseudo-first-order rate constant, k_i, is given by ($d[B_{10}H_{10}^{-2}]/dt$)/[$B_{10}H_{12}L_2$], eq 1 may be rearranged to yield

$$1/k_i = \frac{1}{[\text{base}]}\left\{\frac{k_{-1}[L] + k_4}{k_1k_2}\right\} + \frac{(k_2 + k_3)}{k_1k_2} \qquad (2)$$

In the case of the $B_{10}H_{12}[(C_2H_5)_3N]_2$ substrate, very high yields of $B_{10}H_{10}^{-2}$ were obtained, and the k_4 term would appear to be relatively insignificant. The identity of the base and ligand in this system requires $k_{-1} = k_3$, and the over-all rate equation (1) reduces to the observed rate expression with $k_i = k_1k_2/(k_{-1} + k_2)$.

The unsymmetrical substrate, $B_{10}H_{12}[(C_2H_5)_3N](CH_3CN)$, was examined in acetonitrile solution, and assuming that the weakly bound acetonitrile ligand dissociates in the k_1 step, [L] = [CH_3CN] = 19.1 *M*. Equation 2 then provides the observed linear plot of k_i^{-1} *vs.* [base]$^{-1}$ with the slope, $A = (k_{-1}[CH_3CN] + k_4)/k_1k_2$ and the intercept $B = (k_2 + k_3)/k_1k_2$.

Figures 3 and 4 are plots of k_i^{-1} *vs.* [base]$^{-1}$ taken from the data obtained with the $B_{10}H_{12}[(CH_3)_2S]_2$ and $B_{10}H_{12}[(C_2H_5)_2S]_2$ systems, respectively. In addition, the corresponding dialkyl sulfide ligand was initially present in these runs, and the dependence of the *A* term upon added ligand concentration is clearly illustrated. Plots of the values of *A* obtained from Figures 3 and 4 *vs.* the concentration of the added dialkyl sulfide ligand are shown in Figures 5 and 6 for dimethyl sulfide and diethyl sulfide, respectively. The linearity of these plots firmly supports eq 2 and allows the slope, *C*, and the intercept, *D*, to be identified as k_{-1}/k_1k_2 and k_4/k_1k_2, respectively. Table V summarizes all values of *A*, *B*, *C*, and *D* available from this study.

Enthalpies and Entropies of Activation. The temperature dependence of $k_1k_2/(k_2 + k_3) = B^{-1}$ was obtained with the $B_{10}H_{12}[(C_2H_5)_3N](CH_3CN)$ and $B_{10}H_{12}[(CH_3)_2S]_2$ substrates in acetonitrile and toluene solvents, respectively. The $\Delta H^{\ddagger}$ values obtained from these data were, within experimental error, independent of temperature, and virtually identical values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained for the two systems ($\Delta H^{\ddagger}$ = 28 ± 1 and 27 ± 1 kcal/mole for $B_{10}H_{12}[(C_2H_5)_3N](CH_3CN)$ and $B_{10}H_{12}[(CH_3)_2S]_2$ systems, respectively, while $\Delta S^{\ddagger}$ was 14 ± 3 eu for both systems). Since each of these substrates formed $B_{10}H_{10}^{-2}$ in high yield, it appears that $k_2 >> k_3$, and the activation parameters may be taken as those of the k_1 process. The positive $\Delta S^{\ddagger}$ values which were observed are in agreement with the proposed inclusion of a dissociation step in the rate-determining process.

Effect of Leaving Group Identity. Comparison of the available rate data suggests that diethyl sulfide is a more facile leaving group than the sterically less encumbered dimethyl sulfide. This effect could be attributed to the larger release of B strain which accompanies the dissociation of a diethyl sulfide molecule during the k_1 process. This is not a large effect and amounts to a factor of about 1.8 in the $k_1k_2/(k_2 + k_3)$ terms of the two reactions at 0°.

Using the available $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values obtained with the $B_{10}H_{12}[(C_2H_5)_3N](CH_3CN)$ system, a $k_1k_2/(k_2 + k_3)$ value was calculated for the reaction of this substrate with triethylamine in acetonitrile solution at 100°. Assuming no great dependence of the activation parameters upon temperature, one obtains a $k_1k_2/(k_2 + k_3)$ value of 1.8 sec^{-1}. Since the k_3 process of the $B_{10}H_{12}[(C_2H_5)_3N](CH_3CN)$ reaction is identical with the k_{-1} process in the $B_{10}H_{12}[(C_2H_5)_3N]_2$ reaction, a direct comparison of this value with the $k_1k_2/(k_{-1} + k_2)$ value of the latter system is possible. Such a comparison indicates that acetonitrile is approximately 3×10^4 more efficient as a leaving group than is triethylamine. This conclusion is in qualitative agreement with previously reported studies[6b,c] of the related ligand displacement reaction (k_3 process).

Attempts were made to block the formation of $B_{10}H_{10}^{-2}$ by slowing the k_2 process. Accordingly, the unsymmetrical substrate, $B_{10}H_{12}[(n\text{-}C_4H_9)_3P](CH_3CN)$ was prepared by a known method[15] and examined in its reaction with 0.15 *M* triethylamine at 100° in acetonitrile solution. After 1000 min only 5.5% of the substrate had been converted to $B_{10}H_{10}^{-2}$. This result suggests that the k_2 process was diminished in rate owing to the strong bonding of the tri-*n*-butylphosphine in the $B_{10}H_{12}[(n\text{-}C_4H_9)_3P]$ intermediate which would arise from the dissociation of acetonitrile in the k_1 process.

The k_4 Process and the Nature of $B_{10}H_{12}L$ Intermediates. The existence of a process which consumes the $B_{10}H_{12}L$ intermediate without producing $B_{10}H_{10}^{-2}$ and without dependence upon triethylamine concentration is suggested by the intercepts of Figures 5 and 6. Such a process would account for the decrease in $B_{10}H_{10}^{-2}$ yield commonly observed at very low amine concentrations with the bis(dialkyl sulfide) substrates. Using the values of k_4/k_1k_2, k_{-1}/k_1k_2, and $(k_2 + k_3)/k_1k_2$ terms available for both bis(dialkyl sulfide) substrates (Table V), the relative importance of the k_4 process may be evaluated with respect to the k_{-1} and $k_2 + k_3$ processes. In addition, similar manipulations yield the ratio of the k_{-1} process to the sum of the k_2 and k_3 processes. These ratios are presented in Table VI.

The proposed $B_{10}H_{12}L$ intermediate formally resembles the $B_{10}H_{13}^-$ ion for which two topological structures have been suggested.[18] In addition, Knoth and Muetterties[16] have reported the preparation of $B_{10}H_{12}(CH_3)_2S$, which was formed by the dissociation of dimethyl sulfide from $B_{10}H_{12}[(CH_3)_2S]_2$ at high temperature. That the compound of Knoth and Muetterties is not the $B_{10}H_{12}L$ intermediate involved in $B_{10}H_{10}^{-2}$ formation was shown by the fact that this monoligand derivative formed $B_{10}H_{10}^{-2}$ at a rate which was slower by a factor of more than 10^3 than the reaction of $B_{10}H_{12}[(CH_3)_2S]_2$ under the same conditions. The slow formation of $B_{10}H_{10}^{-2}$ from the $B_{10}H_{12}(CH_3)_2S$ of Knoth

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(18) W. N. Lipscomb, *J. Nucl. Inorg. Chem.*, 11, 1 (1959).

Table VI. Rate Constant Ratios Obtained with $B_{10}H_{12}(R_2S)_2$ Substrates

Substrate in toluene	Temp, °C	$k_4/k_{-1}[L]$	$k_4/(k_2 + k_3)[(C_2H_5)_3N]$	$k_{-1}[L]/(k_2 + k_3)[(C_2H_5)_3N]$
$B_{10}H_{12}[(CH_3)_2S]_2$	20.0	$2.8 \times 10^{-3}/[(CH_3)_2S]$	$7 \times 10^{-3}/[(C_2H_5)_3N]$	$2.5[(CH_3)_2S]/[(C_2H_5)_3N]$
$B_{10}H_{12}[(C_2H_5)_2S]_2$	0.0	$1.7 \times 10^{-2}/[(C_2H_5)_2S]$	$5 \times 10^{-3}/[(C_2H_5)_3N]$	$0.27[(C_2H_5)_2S]/[(C_2H_5)_3N]$

and Muetterties may involve the tautomerization of this more stable isomer to the reactive intermediate suggested by this study. Conversely, the k_4 process may involve the first-order rearrangement of the $B_{10}H_{12}L$ reaction intermediate to the more stable isomer which cannot produce $B_{10}H_{10}^{-2}$ by a direct pathway.

At the present time it is impossible to propose a precise structure for the $B_{10}H_{12}L$ intermediate or to define the exact mechanistic role of the base molecule. It is apparent, however, that the dissociation of a ligand molecule from $B_{10}H_{12}L_2$ would generate a highly reactive species which contains an unfilled orbital at the 6-boron atom. Abstraction of a proton from a 7–8 B–H–B bridge would generate an electron pair which, in turn, could be shared with the empty orbital in a "twist-collapse" process[12] which initiates polyhedron formation. This overly simplified proposal ignores the possible motion of hydrogen atoms during the dissociation reaction.

Experimental Section

Materials. Technical grade acetonitrile was purified and dried as follows. The solvent was passed through a 60-cm Dowex 50 ion-exchange column in the acid form, shaken with silica gel, distilled from benzenediazonium tetrafluoroborate, dried by shaking with P_2O_5, and distilled under reduced pressure from fresh P_2O_5.

Reagent grade benzene and toluene were refluxed for 30 min over calcium hydride and distilled from calcium hydride using a 50-cm Vigreux fractionation column.

Reagent grade triethylamine was distilled from benzoyl chloride to remove primary and secondary amines, distilled from calcium hydride, and finally distilled under reduced pressure on a 100-cm spinning-band column.

Reagent grade dimethyl sulfide and diethyl sulfide were redistilled using a 100-cm spinning-band column.

Compounds of the type $B_{10}H_{12}L_2$, where L is $(C_2H_5)_3N$ or $(CH_3)_2S$, were prepared using a method previously described[16] for $B_{10}H_{12}[(C_2H_5)_2S]_2$.

Compounds of the type $B_{10}H_{12}L'L''$, where L′ and L″ = CH_3CN, $(C_2H_5)_3N$, $(n\text{-}C_4H_9)_3P$, were prepared from the appropriate $B_{10}H_{13}$(ligand) anions[15] as described below.

$B_{10}H_{12}[(CH_3)_2S)]_2$. In a 250-ml, three-necked, round-bottom flask, equipped with a condenser, were placed 10 g of sublimed decaborane (0.082 mole), 20 ml of dry benzene, and 20 g of dimethyl sulfide (0.322 mole). The mixture was refluxed under nitrogen for 5 hr with stirring, during which time, hydrogen was evolved. The solution was cooled to room temperature and the product precipitated from solution by the addition of 50 ml of pentane. The pale yellow solid was filtered and recrystallized twice. The first recrystallization was carried out by dissolving the compound in a minimum volume of acetonitrile at 0° and adding an ice-cold methanol–water mixture dropwise to the solution. The compound was recrystallized a second time from a benzene–pentane mixture. There was obtained 16.9 g (84%) of white crystals, mp 124–126° (lit.[16] 122–124°).

$B_{10}H_{12}[(C_2H_5)_2S)]_2$. This compound was prepared as previously described.[17]

$B_{10}H_{12}[(C_2H_5)_3N)]_2$. The preparation of this compound has been previously described by Pace, *et al.*[6c]

$B_{10}H_{12}(CH_3CN)[(C_2H_5)_3N]$. The compound $B_{10}H_{12}(CH_3CN)[(C_2H_5)_3N]$ was prepared from the previously described[15] compound $[(CH_3)_4N]B_{10}H_{13}[(C_2H_5)_3N]$. A slow stream of dry hydrogen chloride was passed over a stirred solution containing 16.8 g (56.8 mmoles) of $[(CH_3)_4N]B_{10}H_{13}[(C_2H_5)_3N]$ in 300 ml of dry acetonitrile under nitrogen. The solution developed a yellow color, hydrogen was evolved, and white crystals were deposited. After 4 hr the solution was filtered and the solvent was removed under reduced pressure to obtain a second crop of solid. The two crops of solid were combined, dissolved in methylene chloride, and filtered. On adding pentane to the filtrate, an off-white solid was precipitated. The solid was recrystallized five times by dissolving it in acetonitrile at 0°, filtering, and adding water dropwise at 0° to the rapidly stirred acetonitrile solution. There was obtained 3.6 g (13.7 mmoles) of a white crystalline solid melting with decomposition at 142–143° (24% yield). *Anal.* Calcd for $B_{10}H_{12}(CH_3CN)[(C_2H_5)_3N]$: B, 41.21; C, 36.60; N, 10.67; H, 11.52. Found: B, 41.05; C, 35.61; N, 10.02; H, 11.53.

$B_{10}H_{12}(CH_3CN)[(n\text{-}C_4H_9)_3P]$. Starting from decaborane the compound $B_{10}H_{12}(CH_3CN)[(n\text{-}C_4H_9)_3P]$ was prepared as follows. To a stirred suspension of 4.40 g (0.185 mole) of sodium hydride in 50 ml of dry ether under nitrogen was added dropwise a solution of 10 g (0.082 mole) of decaborane in 80 ml of ether. After stirring for 1 hr at room temperature, during which time hydrogen was evolved, 16.4 g (0.081 mole) of tri-*n*-butylphosphine was added. After stirring for a further 3.5 hr, 350 ml of acetonitrile was added and dry hydrogen chloride gas was passed over the solution. Hydrogen gas was evolved and the reaction mixture developed an orange-yellow color. The acetonitrile solution was treated with a two-phase mixture of 500 ml of water and 100 ml of ether at 0°. The aqueous layer was discarded and the ether layer was washed twice with water. The washings were discarded. The red ethereal solution was dried with anhydrous sodium sulfate, and the solvent was removed under reduced pressure at room temperature to give a viscous red oil. Extraction of the oil with ethanol gave a red solution and a pale yellow solid. The solid was purified by four recrystallizations; each was carried out by dissolving the compound in acetonitrile at 0° and adding an ice-cold 50:50 mixture of methanol–water to the solution. After washing with methanol and drying at room temperature under vacuum, well-formed white crystals melting at 139–140° were obtained. *Anal.* Calcd for $B_{10}H_{12}(CH_3CN)[(n\text{-}C_4H_9)_3P]$: B, 29.75; C, 46.24; H, 11.65; N, 3.85; P, 8.51. Found: B, 30.07; C, 46.37; H, 11.68; N, 4.09; P, 8.39.

Determination of $B_{10}H_{10}^{-2}$ Yields. Yields of $B_{10}H_{10}^{-2}$ obtained under the experimental conditions of the kinetic runs were determined by continuing individual runs and sampling at time intervals of 6–12 hr until the concentration of $B_{10}H_{10}^{-2}$ (determined using the spectrophotometric method) was constant. The yield was then calculated from the known initial concentrations of reactants and the final $B_{10}H_{10}^{-2}$ concentration.

In the case of $B_{10}H_{12}[(CH_3)_2S]_2$ and $B_{10}H_{12}[(C_2H_5)_2S]_2$, the determined yields were checked by carrying out the reaction on a larger scale and isolating the products as described below.

Product Isolation for $B_{10}H_{12}(R_2S)_2$. (a) **$B_{10}H_{12}[(CH_3)_2S]_2$.** A solution, 0.0206 *M* in $B_{10}H_{12}[(CH_3)_2S]_2$ and 0.15 *M* in triethylamine, was prepared by dissolving 5.05 g of $B_{10}H_{12}[(CH_3)_2S]_2$ and 15.25 g of triethylamine in 1 l. of dry toluene. The solution was maintained at 20° for 108 hr. During this time a white precipitate was formed. The precipitate was separated by filtration, washed with hot benzene, and air-dried to give 5.35 g of white solid. The filtrate and washings were evaporated to dryness at room temperature and gave 1.25 g of white solid. The ^{11}B nmr and infrared spectra of the toluene-insoluble portion identified the material as $[(C_2H_5)_3NH]_2B_{10}H_{10}$ with a small percentage of impurity. The single ^{11}B resonance at −18.5 ppm due to the impurity suggested that it could be boric acid or ester. The purity of the $[(C_2H_5)_3NH]_2B_{10}H_{10}$ was estimated using the standard analytical method, and it was found to be 87.5% $B_{10}H_{10}^{2-}$ salt. Thus the total yield of $[(C_2H_5)_3NH]_2B_{10}H_{10}$ was 4.68 g or 70.5%, with 0.67 g of impurity. The toluene-soluble portion was recrystallized from a benzene–pentane mixture to give 1.16 g of a material identified as $B_{10}H_{12}[(C_2H_5)_3N]_2$ from its infrared spectrum. This represents 15.3% of the initial $B_{10}H_{12}[(CH_3)_2S]_2$ and a further 0.09 g of impurity.

The products of the reaction under the above conditions are therefore 70.5% $B_{10}H_{10}^{-2}$ salt, 15.3% covalent $B_{10}H_{12}[(C_2H_5)_3N]_2$, and 14.2% unidentified impurity.

(b) $B_{10}H_{12}[(C_2H_5)_2S]_2$. Product isolation for $B_{10}H_{12}[(C_2H_5)_2S]_2$ was carried out in the same manner as for $B_{10}H_{12}[(CH_3)_2S]_2$. A solution of 5.0 (16.6 mmoles) of $B_{10}H_{12}[(C_2H_5)_2S]_2$ and 5.1 g (50 mmoles) of triethylamine in 100 ml of toluene was kept at 25° for 24 hr. The concentrations of the reagents were $B_{10}H_{12}[(C_2H_5)_2S]_2$, 0.166 *M*, and triethylamine, 0.50 *M*. After 24 hr the white precipitate which formed was removed by filtration, washed with hot benzene, and air dried. There was obtained 5.12 g of white solid which was identified as $[(C_2H_5)_3NH]_2B_{10}H_{10}$ from its characteristic ^{11}B nmr and infrared spectra. The material was estimated to be 92% pure by using the standard analytical technique for $B_{10}H_{10}^{2-}$. Thus 4.70 g of the white solid was $[(C_2H_5)_3NH]_2B_{10}H_{10}$ (14.6 mmoles), or 88% of the substrate was converted to the $B_{10}H_{10}^{2-}$ salt. The toluene filtrate and the benzene washings were combined and evaporated to dryness at room temperature. The resulting solid was recrystallized from a minimum amount of a mixed benzene-pentane solvent. After drying, 0.48 g (1.49 mmoles) of the covalent material $B_{10}H_{12}[(C_2H_5)_3N]_2$ was obtained. The compound was identified by its infrared spectrum.

The products of the reaction under the above conditions were 88% $[(C_2H_5)_3NH]_2B_{10}H_{10}$, 9% $B_{10}H_{12}[(C_2H_5)_3N]_2$, and 3% unidentified impurity.

Analytical Method for $B_{10}H_{10}^{-2}$. The analytical method used for the determination of $B_{10}H_{10}^{-2}$ was based on the coupling reaction of $B_{10}H_{12}^{-2}$ with diazonium ion[14] to produce a highly colored product. Compounds which couple with diazonium ion interfere with the method, and for the estimation of $B_{10}H_{10}^{-2}$ in the presence of free amine it was essential to neutralize the amine with excess acid. Dry glassware and solvents were used throughout.

A stock solution of benzenediazonium tetrafluoroborate was prepared by dissolving 50 mg of the compound in 10 ml of dry acetonitrile. This solution was stored at 0° for 30 min before use and was kept at 0° during use.

The analysis was carried out as follows. A sample of the reacting solution containing approximately 5×10^{-3} mmole of $B_{10}H_{10}^{-2}$ was quenched by adding it to 2 ml of 0.1 *N* trifluoroacetic acid in dry acetonitrile contained in a 5-ml volumetric flask with the 0.1 *N* trifluoroacetic acid solution. In a second 5-ml volumetric flask 50 μl of the stock benzenediazonium tetrafluoroborate solution (representing $1-3 \times 10^{-2}$ mmole of compound) was added to 2 ml of 0.1 *N* trifluoroacetic acid in dry acetonitrile, 500 μl of the quenched solution was then added, and the volume was made up to 5 ml with the 0.1 *N* trifluoroacetic acid solution. With the addition of the quenched solution a color rapidly developed, the intensity of which was determined spectrophotometrically in solution. A Beckman DB spectrophotometer was used. The azo coupling product has ϵ 19,400 at 520 mμ.

This analytical method has been used with slight modification for the estimation of $B_{10}H_{10}^{-2}$ in concentrations as low as 1×10^{-5} *M*.

Kinetic Procedures. Kinetic runs have been carried out at 0, 20, 29.9, and 100°. At 0 and 100°, temperature control was provided by means of ice-water or water-steam baths, respectively. At 20 and 29.9° a Sargent Thermonitor controlled water bath was used to maintain the temperature within ±0.02°.

Runs at 100° were carried out in evacuated sealed tubes. To start the reaction a set of tubes was plunged into the steam bath. Single tubes were withdrawn at timed intervals and the reaction quenched by rapidly cooling the tube to 0°. The contents of the tubes were analyzed for $B_{10}H_{10}^{-2}$ (*vide supra*).

Runs at 0, 20, and 29.9° were carried out in volumetric flasks immersed in the thermostat or ice-water baths. The reaction was started by adding a known amount of triethylamine solution to a flask containing the other reactants. The flask was shaken and rapidly made up to volume. At measured time intervals samples of solution were withdrawn using a micropipet. The samples were quenched by adding them to a solution of trifluoroacetic acid in acetonitrile and analyzed for $B_{10}H_{10}^{-2}$.

Data Treatment for Obtaining k_i. The experimentally determined quantities k_i and $k_{i,obsd}$ are defined by the relationships

$$\left(\frac{d[B_{10}H_{10}^{-2}]}{dt}\right)_i = k_{i,\,obsd} \text{ and } k_i = \frac{k_{i,\,obsd}}{[\text{substrate}]_i}$$

(subscript "i" indicates values at time zero)

In all kinetic runs the experimental results gave values of $[B_{10}H_{10}^{-2}]$ at known times. These results were treated by one of the four methods outlined below to give k_i or $k_{i,obsd}$. The choice of method depended on such factors as the yield of the reaction under the experimental conditions and the limiting reagent.

Method 1. For the reaction of $B_{10}H_{12}[(C_2H_5)_3N]_2$ with triethylamine the displaced ligand is identical with the consumed base, and the concentration of triethylamine thus remains constant within any one run. Individual runs were found to be first order with respect to $B_{10}H_{12}[(C_2H_5)_3N]_2$ and proceeded to give $[B_{10}H_{10}^{-2}]$ in high yield. Under these conditions the experimental values of $[B_{10}H_{10}^{-2}]$ at known time were converted to $[B_{10}H_{12}[(C_2H_5)_3N]_2]$ at known time, *t*, using the expression

$$[B_{10}H_{12}[(C_2H_5)_3N]_2]_t = [B_{10}H_{12}[(C_2H_5)_3N]_2]_i - [B_{10}H_{10}^{2-}]_t$$

The data were then correlated with the integrated first-order rate expression

$$-\ln\,[B_{10}H_{12}[(C_2H_5)_3N]_2]_t = k_it + c$$

Method 2. For the substrates $B_{10}H_{12}[(CH_3)_2S]_2$ and $B_{10}H_{12}[(C_2H_5)_2S]_2$, where part of the active intermediate is consumed by the competing ligand displacement reaction, the effect of the competing reaction was minimized by using the initial rate method. Reactions were followed until about 5% of the substrate had been converted to $B_{10}H_{10}^{-2}$. Plots of $[B_{10}H_{10}^{-2}]$ *vs.* time were constructed and found to be linear. The slopes of these plots gave $k_{i,obsd}$ directly.

This method was also used for runs with $B_{10}H_{12}(CH_3CN)[(C_2H_5)_2N]$ as substrate, especially at high concentrations of triethylamine when the yields of $B_{10}H_{10}^{-2}$ fell below 90%.

Method 3. At low concentrations of triethylamine with the asymmetric substrate $B_{10}H_{12}(CH_3CN)[(C_2H_5)_3N]$, the base was the limiting reagent, and quantitative yields of $B_{10}H_{10}^{-2}$ were obtained. Under these conditions the experimental values of $[B_{10}H_{10}^{-2}]$ at known time were converted to values of $[(C_2H_5)_3N]$ at known time using the expression

$$[(C_2H_5)_3N]_t = [(C_2H_5)_3N]_i - [B_{10}H_{10}^{2-}]_t$$

Values of k_i were obtained from the initial slopes of plots of ln $[(C_2H_5)_3N]$ *vs.* time using the relationship

$$-k_i = \frac{d(\ln\,[(C_2H_5)_3N])}{dt}\,\frac{[(C_2H_5)_3N]_i}{[\text{substrate}]_i}$$

Method 4. As an alternative to method 3, where quantitative yields were obtained with the substrate $B_{10}H_{12}(CH_3CN)[(C_2H_5)_3N]$, plots of $[B_{10}H_{10}^{-2}]_t$ *vs.* time were made for data up to 50% reaction.

Normals to the resulting curves were drawn at different values of $[B_{10}H_{10}^{-2}]$, and the instantaneous rates of reaction at the known values of $[B_{10}H_{10}^{-2}]_t$ were estimated from the normals. These instantaneous rates were plotted *vs.* $[B_{10}H_{10}^{-2}]_t$ and $k_{i,obsd}$ obtained by extrapolation to $[B_{10}H_{10}^{-2}]_t = 0$.

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