# The Mechanism of Ligand Exchange with $B_{10}H_{12}$(ligand)$_2$ Species

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Abstract: The kinetics of the ligand-exchange reaction which produces $B_{10}H_{12}[(C_2H_5)_3N](C_5H_5N)$ from pyridine and $B_{10}H_{12}[(C_2H_5)_3N]_2$ has been examined along with the competing formation of the $B_{10}H_{10}^{-2}$ ion. Kinetic data were collected at 100° in acetonitrile solution and the results interpreted in terms of a common $B_{10}H_{12}[(C_2H_5)_3N]$ intermediate in both reactions

Ligand-exchange reactions involving the $B_{10}H_{12}$-(ligand)$_2$ derivatives of decaborane(14) were first reported[2] in 1958. At that time it was shown that triphenylphosphine would displace both acetonitrile and

$$B_{10}H_{12}(\text{ligand})_2 + 2\text{Ligand} \longrightarrow B_{10}H_{12}(\text{Ligand})_2 + 2\text{ligand}$$
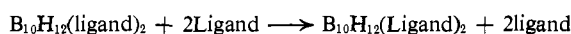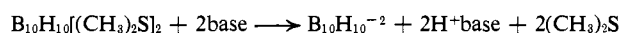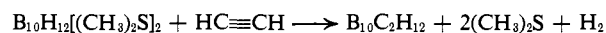
diethylcyanamide ligands and that diethylcyanamide would displace acetonitrile ligand. Later work[3] expanded this displacement reaction series to include a much larger array of ligands which included dialkyl sulfides, amides, amines, phosphite and phosphinate esters, thiophosphite esters, and arsines. The general utility of the ligand-exchange reaction is thus well established on a qualitative basis with dialkyl sulfides and alkyl nitriles appearing as weakly bound and easily displaced ligands, and amines, phosphines, etc., appearing as tightly bonded ligands capable of displacing dialkyl sulfides and nitriles.

The structures of $B_{10}H_{12}$(ligand)$_2$ derivatives have been determined in which the ligand was acetonitrile,[4] dimethyl sulfide,[5] and 2-bromopyridine,[6] and these structures are generalized in Figure 1. Since both $B_{10}H_{12}(CH_3CN)_2$ and $B_{10}H_{12}[(CH_3)_2S]_2$ have the general structure shown in Figure 1 and since the former compound may be prepared[3a] from the latter compound by treatment with acetonitrile, it is apparent that the ligand-exchange reaction proceeds with retention of configuration at the displacement center. Thus, any mechanism proposed for the ligand-exchange reaction must account for this stereochemical observation and the known qualitative displacement sequence[3] shown in the ligand series.

The formation of $B_{10}H_{12}(CH_3)_2S$ from the corresponding bisligand derivative,[7] the formation of 1,2-dicarbaclovododecaborane(12),[8] and the formation of

the $B_{10}H_{10}^{-2}$ ion from $B_{10}H_{12}$(ligand)$_2$ derivatives are,[9,10] in all probability, closely related to the ligand-exchange reaction. In fact, the study of the mecha-

$$B_{10}H_{12}[(CH_3)_2S]_2 \xrightarrow{\text{heat}} B_{10}H_{12}(CH_3)_2S + (CH_3)_2S$$

$$B_{10}H_{12}[(CH_3)_2S]_2 + HC{\equiv}CH \longrightarrow B_{10}C_2H_{12} + 2(CH_3)_2S + H_2$$

$$B_{10}H_{10}[(CH_3)_2S]_2 + 2\text{base} \longrightarrow B_{10}H_{10}^{-2} + 2H^+\text{base} + 2(CH_3)_2S$$

nism of $B_{10}H_{10}^{-2}$ formation which was reported in the preceding paper[11] could only be interpreted in terms of competing ligand exchange and $B_{10}H_{10}^{-2}$ formation involving a $B_{10}H_{12}$(ligand) intermediate. In order to further substantiate this result a kinetic system was devised which allowed the simultaneous and direct measurement of the ligand-exchange reaction and $B_{10}H_{10}^{-2}$ formation from the same reactants. The results of that study comprise the body of this paper.

Results and Discussion

The displacement of triethylamine by pyridine from $B_{10}H_{12}[(C_2H_5)_3N]_2$ was investigated in acetonitrile solution at 100°. Subsequent reaction of $B_{10}H_{12}$-

$$B_{10}H_{12}[(C_2H_5)_3N]_2 + py \longrightarrow B_{10}H_{12}[(C_2H_5)_3N]py + (C_2H_5)_3N$$
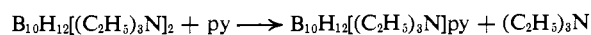
$[(C_2H_5)_3N]$py with pyridine to produce $B_{10}H_{12}(py)_2$ was avoided by employing the initial rate method and thereby following the reaction to 5% completion or less. The actual nature of the reaction products was determined by the use of thin-layer chromatographic analysis. After 5% conversion of $B_{10}H_{12}[(C_2H_5)_3N]_2$ to products, the nonvolatile species present were found to be $B_{10}H_{10}^{-2}$, $B_{10}H_{12}[(C_2H_5)_3N]py$, and $B_{10}H_{12}[(C_2H_5)_3N]_2$. Since $B_{10}H_{10}^{-2}$ was observed as a by-product, its rate of formation was measured[11] as well as that of the ligand-exchange product. Analysis for $B_{10}H_{12}[(C_2H_5)_3N]py$ was accomplished by making use of the 380-mμ absorption band of this compound.

The collected rate data are presented in Table I along with the initial concentrations of reagents present in each rate run. The variation of k_s and k_e (the observed first-order rate constants associated with $B_{10}H_{10}^{-2}$ formation and ligand exchange, respectively) with pyridine concentration in the absence of added triethylamine is illustrated in Figure 2. Above 0.4 M pyridine concentration the values of k_s and k_e become inde-

(1) Alfred P. Sloan Research Fellow, 1963–1966.
(2) M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **80**, 6685 (1958).
(3) (a) R. J. Pace, J. Williams, and R. L. Williams, *J. Chem. Soc.*, 2196 (1961); (b) R. J. Polak and T. L. Heying, *J. Org. Chem.*, **27**, 1483 (1962); (c) H. Schroeder, J. R. Reiner, and T. L. Heying, *Inorg. Chem.*, **1**, 618 (1962); (d) L. I. Zakharkin, V. I. Stanko, and A. I. Klimova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 917 (1964).
(4) J. Reddy and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 610 (1959); *J. Am. Chem. Soc.*, **81**, 754 (1959).
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(6) E. W. Hughes and C. Fritchie, Jr., Abstracts, American Crystallographic Association, Villanova, Pa., June 18–22, 1962, Paper F-9.
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(9) M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **81**, 5519 (1959).
(10) E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).
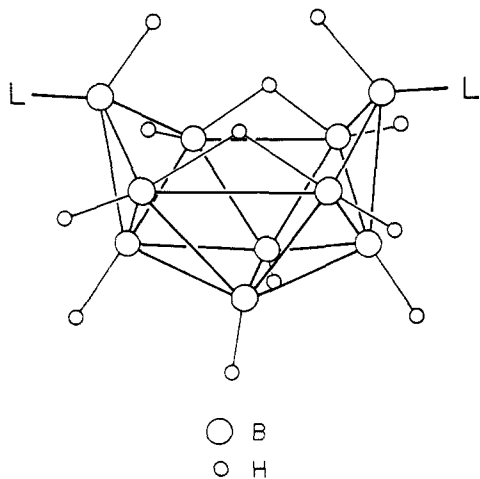(11) M. F. Hawthorne, R. L. Pilling, and R. N. Grimes, *J. Am. Chem. Soc.*, **89**, 1067 (1967).

○ B

○ H

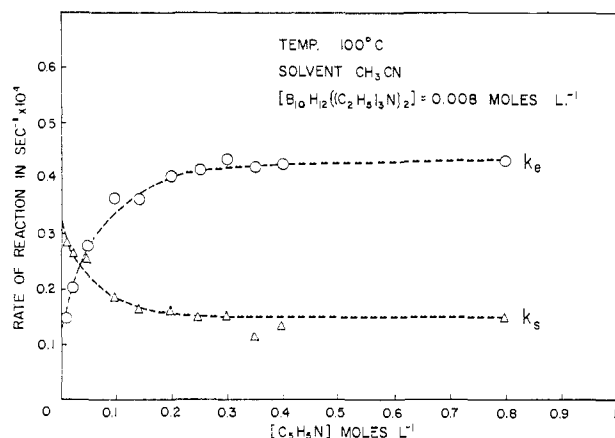Figure 1. Generalized structure of $B_{10}H_{12}(ligand)_2$ derivatives with L = ligand.

Figure 2. Variation of k_s and k_e with pyridine concentration in the absence of added triethylamine.

pendent of pyridine concentration which indicates that the rate-controlling step of either reaction does not involve pyridine at high pyridine concentrations. However, at lower pyridine concentrations, the observed values of k_s and k_e are quite dependent upon pyridine concentration and in such a manner as to suggest that a common intermediate is partitioned between $B_{10}H_{10}^{-2}$ formation and the formation of the exchange reaction product. This interdependence of k_s and k_e is clearly shown in Table I since the value $(k_s + k_e)$ is constant within experimental error and independent of pyridine and triethylamine concentrations.

A plot of k_s/k_e vs. $[(C_2H_5)_3N]/[py]$ is presented in Figure 3. The equation of the resulting straight line is $k_s/k_e = 54[(C_2H_5)_3N]/[py] + 0.2$. This linear relationship is typically obtained in systems in which two reagents (triethylamine and pyridine) are competing for a common intermediate in reactions of the same order.

Straight lines which passed through the same origin (within experimental error) were obtained by plotting k_e^{-1} vs. $[py]^{-1}$ at constant triethylamine concentrations. The slopes of a series of such lines determined at a variety of triethylamine concentrations were then plotted vs. $[(C_2H_5)_3N]$, and the linear relationship shown in Figure 4 was obtained with no discernible
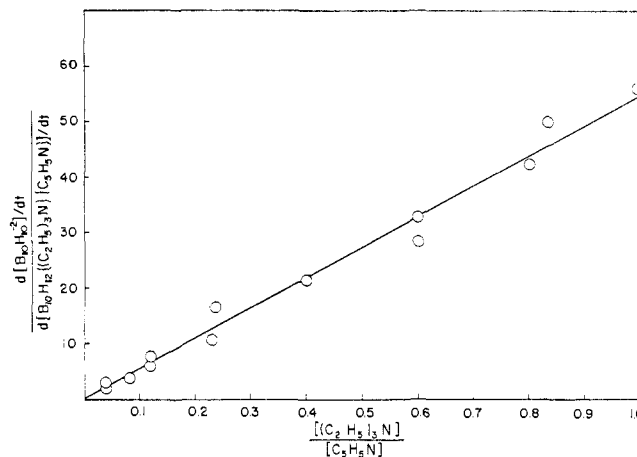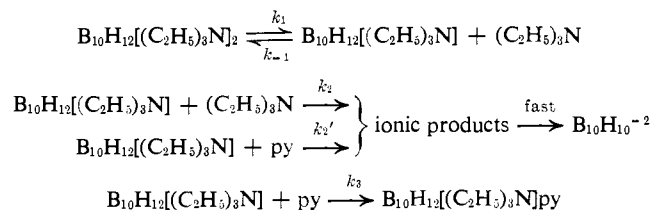
Figure 3. Plot of k_s/k_e vs. $[(C_2H_5)_3N)/[py]$ giving least-squares fit of $k_s/k_e = 54[(C_2H_5)_3N]/[py] + 0.2$.

intercept. The experimental form of the ligand-exchange reaction is therefore of the form

$$1/k_e = A[(C_2H_5)_3N]/[py] + B$$

The experimental results are in agreement with the mechanism shown below.

$$B_{10}H_{12}[(C_2H_5)_3N]_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B_{10}H_{12}[(C_2H_5)_3N] + (C_2H_5)_3N$$

$$\left. \begin{array}{l} B_{10}H_{12}[(C_2H_5)_3N] + (C_2H_5)_3N \overset{k_2}{\underset{k_2'}{\longrightarrow}} \\ B_{10}H_{12}[(C_2H_5)_3N] + py \longrightarrow \end{array} \right\} \text{ionic products} \overset{fast}{\longrightarrow} B_{10}H_{10}^{-2}$$

$$B_{10}H_{12}[(C_2H_5)_3N] + py \overset{k_3}{\longrightarrow} B_{10}H_{12}[(C_2H_5)_3N]py$$

Taking $d[B_{10}H_{12}[(C_2H_5)_3N]]/dt = 0$, the following expressions may be deduced from the proposed mechanism.

$$\frac{k_s}{k_e} = \frac{k_2[(C_2H_5)_3N]}{k_3[py]} + \frac{k_2'}{k_3}$$

$$\frac{1}{k_e} = \frac{(k_{-1} + k_2)[(C_2H_5)_3N]}{k_1k_3[py]} + \frac{k_2' + k_3}{k_1k_3}$$

$$k_s + k_e = \frac{k_1k_3[py] + k_1k_2'[py] + k_1k_2[(C_2H_5)_3N]}{k_3[py] + k_2'[py] + (k_{-1} + k_2)[(C_2H_5)_3N]}$$

The first equation is identical with that obtained from Figure 3, and the second equation agrees with the linear plots of k_e^{-1} vs. $[py]^{-1}$ and the data of Figure 4. The third relationship is in agreement with the experimental data if $k_{-1} \ll k_2$. The values for the various rate constant ratios obtained from experimental slopes and intercepts are $k_2/k_3 = 54$ (slope, Figure 3), $k_2'/k_3 = 0.2$ (intercept, Figure 3), $k_2'/k_3 = 0.35$ (limiting values of k_s and k_e, Figure 2), $(k_2' + k_3)/k_1k_3 = 2.6 \times 10^4$ sec (intercept of k_e^{-1} vs. $[py]^{-1}$), $(k_{-1} + k_2)/k_1k_3 = 1.0 \times 10^6$ sec (slope, Figure 4), and $k_1 = 5.4 \times 10^{-5}$ sec^{-1} (average value of $k_s + k_e$). The value of $k_1 = k_s + k_e$ compares favorably with the limiting rate of $B_{10}H_{10}^{-2}$ formation determined[11] under similar conditions.

As in the previous study[11] of $B_{10}H_{10}^{-2}$ formation, the k_1/k_{-1} equilibrium provides a reactive intermediate which returns to reactant $B_{10}H_{12}(ligand)_2$ in the absence of added basic or nucleophilic reagents. Qualitative evidence which supports this reasoning is the fact that

Table I. Rate Data for Ligand Exchange and $B_{10}H_{10}^{-2}$ Formation Using 7.67×10^{-3} M $B_{10}H_{12}[(C_2H_5)_3N]_2$ in Acetonitrile Solution at $100°$

$[C_5H_5N]$, M	$[(C_2H_5)_3N]$, M	k_e, sec^{-1} $\times 10^4$	k_s, sec^{-1} $\times 10^4$	$k_e + k_s$, sec^{-1} $\times 10^4$
0.0125	...	0.149	0.280	0.429
0.025	...	0.202	0.262	0.464
0.050	...	0.279	0.251	0.530
0.100	...	0.365	0.182	0.547
0.142	...	0.362	0.164	0.526
0.200	...	0.403	0.161	0.564
0.250	...	0.416	0.150	0.566
0.300	...	0.435	0.150	0.585
0.350	...	0.421	0.111	0.532
0.400	...	0.428	0.132	0.560
0.800	...	0.432	0.147	0.580
...	0.100	...	0.536	0.536
0.060	0.0024	0.169	0.358	0.527
0.050⎫	0.0120	0.032	0.540	0.572
0.100⎬	0.0120	0.060	0.478	0.538
0.300⎭	0.0120	0.130	0.400	0.530
0.180	0.0216	0.072	0.434	0.506
0.040⎫	0.0240	0.020	0.576	0.596
0.100⎬	0.0240	0.043	0.471	0.514
0.300⎭	0.0240	0.112	0.452	0.564
0.0300	0.0300	0.011	0.587	0.598
0.0600	0.0500	0.091	0.456	0.547
0.1500	0.0600	0.023	0.489	0.512
0.0900⎫	0.0720	0.012	0.533	0.545
0.120 ⎭	0.0720	0.016	0.522	0.538
0.100	0.100	0.009	0.486	0.495
			Av	0.538

$B_{10}H_{12}$(ligand)$_2$ derivatives may be repeatedly recrystallized from solution without significant loss. The k_2' process accounts for the formation of $B_{10}H_{10}^{-2}$ observed in the absence of added triethylamine at high pyridine concentrations. The k_3 process is identical with the k_{-1} process except for the interchange of ligands. In the presence of added triethylamine the increased rate of $B_{10}H_{10}^{-2}$ formation is accounted for by the k_2 process.

The availability and high reactivity of the $B_{10}H_{12}$-(ligand) intermediate suggests that it may be a precursor in the formation of $B_{10}H_{12}[(CH_3)_2S]^{7,11}$ and 1,2-dicarbaclovododecaborane(12).[8] In addition, its presence is similarly indicated in the solvolytic degradation of $B_{10}H_{12}$(ligand)$_2$ derivatives to B_9H_{13}(ligand) species.[12]

In 1,2-dicarbaclovododecaborane(12) formation the acetylene probably attacks the $B_{10}H_{12}$(ligand) intermediate at a point between the 6 and 9 boron atoms (those boron atoms which bear ligands in $B_{10}H_{12}$-(ligand)$_2$ derivatives) and eventually closes the icosahedron. The proton-removal step postulated to occur in the formation of $B_{10}H_{10}^{-2}$ may also take place via attack of a base molecule on a proton located between the 6 and 9 boron atoms of the $B_{10}H_{12}$(ligand) intermediate. However, in the k_{-1} and k_3 processes of the ligand-exchange reaction, one accounts for retention of stereochemical integrity by envisioning external attack by the entering ligand along a line joining the 6 and 9 boron atoms. Thus it may be possible to classify reactions of the $B_{10}H_{12}$(ligand) intermediate as endo (internal) or exo (external) with respect to the 10 boron atom icosahedral fragment which comprises the structure of the $B_{10}H_{12}$(ligand) intermediate.

(12) B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, 1, 626 (1962).
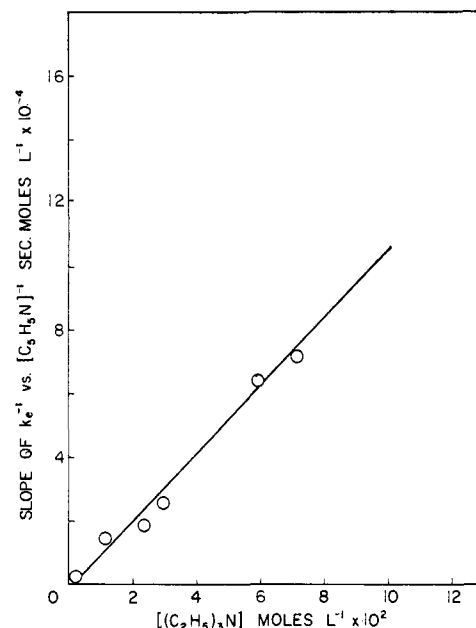

Figure 4. Slopes of k_e^{-1} vs. $[py]^{-1}$ lines plotted vs. triethylamine concentration.

Experimental Section

Materials. Solvent grade acetonitrile was purified and dried using the method described by Hawthorne, Pilling, and Grimes.[11]

Reagent grade pyridine and triethylamine were freshly distilled from calcium hydride before use.

Preparation of $B_{10}H_{12}$ (ligand)$_2$ Derivatives. Both $B_{10}H_{12}[(C_2H_5)_3N]_2$ and $B_{10}H_{12}(py)_2$ were prepared using the method described by Pace, Williams, and Williams.[3a]

The preparation of $B_{10}H_{12}[(C_2H_5)_3N]py$ employed the method of Graybill, Pitochelli, and Hawthorne[13] as follows. To 70 ml of a tetrahydrofuran solution containing 4.28 g (15 mmoles) of freshly recrystallized and dried pyridinium chloride was added 4.42 g (15 mmoles) of $(CH_3)_4NB_{10}H_{13}[(C_2H_5)_3N]$. The reaction mixture was refluxed under nitrogen and with stirring for 4 hr during which time hydrogen gas was evolved. The solution was filtered and the solvent removed under pressure. The resulting solid was recrystallized to constant melting point from methylene chloride–pentane mixtures. The product consisted of well-formed bright yellow needles, mp 169°.

Anal. Calcd for $B_{10}H_{12}[(C_2H_5)_3N](C_5H_5N)$: B, 35.99; C, 43.95; H, 10.73; N, 9.32. Found: B, 35.49; C, 43.76; H, 10.54; N, 10.04.

The electronic spectrum of the compound consisted of three bands: 217 mμ (ϵ 10,600), 240 (9050), and 380 (3100).

Analytical Methods. Analyses for $B_{10}H_{10}^{-2}$ were obtained using the method described by Hawthorne, Pilling, and Grimes,[11] which is based on the azo dye formed between the phenyl diazonium and $B_{10}H_{10}^{-2}$ ions.

Analyses for $B_{10}H_{12}[(C_2H_5)_3N]py$ were carried out spectrophotometrically using the absorption band at 380 mμ. For concentrations of product below about 1.5×10^{-4} M, 4-cm path-length silica cells were used; above 1.5×10^{-4} M, 1-cm path-length cells were used and appropriate dilutions were made.

The Kinetic Method. In all kinetic runs initial rates were measured and the reaction followed to 5% completion or less.

Kinetic solutions were prepared at room temperature and contained weighed quantities of the reagents in purified acetonitrile. In a typical kinetic run the prepared solution was divided up into ten Pyrex tubes. The tubes were then cooled in liquid nitrogen, evacuated, degassed, and sealed off under vacuum. The kinetic run was started by heating the tubes to 100° in steam. At known time intervals, tubes were withdrawn and the reaction was quenched by cooling to 0°. The contents of the tubes were then removed and analyzed separately for $B_{10}H_{10}^{-2}$ and $B_{10}H_{12}[(C_2H_5)_2N]py$.

(13) B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *ibid.*, 1, 622 (1962).

Data Treatment. The experimental results gave the concentration of $B_{10}H_{10}^{-2}$ and $B_{10}H_{12}[(C_2H_5)_3N]$py at known time intervals. The slope of plots of these concentrations *vs.* time gave values for k_s and k_e when divided by the initial substrate concentration. No significant intercepts were observed for the individual rate runs.

$$k_s = \frac{d[B_{10}H_{10}^{-2}]}{dt} \Big/ [B_{10}H_{12}[(C_2H_5)_3N]_2]$$

$$k_e = \frac{d[B_{10}H_{12}[(C_2H_5)_5N](py)]}{dt} \Big/ [B_{10}H_{12}[(C_2H_5)_3N]_2]$$

Product Determination. The products present after 5% reaction were determined by thin-layer chromatographic analysis. A solution containing 0.100 M pyridine, 0.0240 M triethylamine, and 7.67×10^{-3} M $B_{10}H_{12}[(C_2H_5)_3N]_2$ was placed in two tubes which were degassed and sealed under vacuum. The tubes were heated at 100° in a steam bath. The first tube was removed after 15 min and the second tube after 32 min. Samples from the two tubes were analyzed as follows. Mixtures of either 80 parts (by volume) of chloroform with 20 parts of pentane, or 60 parts of acetone with 40 parts of chloroform, were found to be good eluents. With either of these eluents, known mixtures of $B_{10}H_{12}[(C_2H_5)_3N]_2$,

$B_{10}H_{10}^{-2}$ salts, $B_{10}H_{12}(py)_2$, and $B_{10}H_{12}[(C_2H_5)_3N]$py were completely separated when silica gel was used as the stationary phase. The R_f values were in the order $B_{10}H_{12}[(C_2H_5)_3N]_2 > B_{10}H_{12}[(C_2H_5)_3N]$py $> B_{10}H_{12}(py)_2 > B_{10}H_{10}^{-2}$ salts $= 0$. Triethylammonium and pyridinium salts of $B_{10}H_{10}^{-2}$ were used. Analysis of the experimental samples was carried out by placing a spot of the unknown mixture between spots of a known synthetic mixture on the plate and eluting. After developing the plates with iodine vapor, visual inspection showed that the unknown samples contained $B_{10}H_{12}[(C_2H_5)_3N]_2$, $B_{10}H_{10}^{-2}$ salts, and $B_{10}H_{12}[(C_2H_5)_3N]$py; no spot could be seen in a position corresponding to $B_{10}H_{12}(py)_2$. Both eluents gave the same results.

A second product determination in which the sample solution contained 0.300 M pyridine, 0.0120 M triethylamine, and 7.67×10^{-3} M $B_{10}H_{12}[(C_2H_5)_3N]_2$ was heated at 100° for 40 min and then analyzed as described above. Again no spot corresponding to $B_{10}H_{12}(py)_2$ was observed; the material present was $B_{10}H_{12}[(C_2H_5)_3N]_2$ with smaller quantities of $B_{10}H_{10}^{-2}$ and $B_{10}H_{12}[(C_2H_5)_3N]$py.

A control kinetic run in which $[(C_2H_5)_3NH]_2B_{10}H_{10}$ was used as substrate proved that, under the same conditions, no yellow products were formed from this material.

Observation of the Chelate Effect with a Bidentate Lewis Acid, F2BCH2CH2BF2

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Contribution from the Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois 60201. Received October 5, 1966

Abstract: Chelate adducts appear to form when $F_2BCH_2CH_2BF_2$ reacts with triphenylmethyl ethers. These adducts involve the coordination of both boron atoms of the Lewis acid to a central oxygen donor, *e.g.*

$$[(C_6H_5)_3C^+] \left[\begin{array}{c} CH_2-BF_2 \\ | \qquad\qquad \diagdown \\ CH_2-BF_2 \diagup \end{array} O-CH_3^- \right]$$
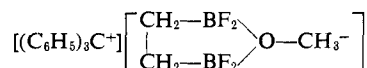
This is the converse of the usual situation where a central metal ion serves as an acceptor toward a difunctional base. The chelate effect appears to contribute to the stability of these adducts as evidenced by the displacement of BF_3 from $[(C_6H_5)_3C^+][H_3CO \cdot 2BF_3^-]$ by $F_2BCH_2CH_2BF_2$. In the course of these studies, a number of more conventional 2:1 donor–acceptor adducts were prepared by the interaction of a variety of oxygen-containing Lewis bases with the difunctional Lewis acids $F_2BCH_2CH_2BF_2$ and $Cl_2BCH_2CH_2BCl_2$.

It has been reported that the difunctional Lewis acid, 1,2-bis(dichloroboryl)ethane,[1] reacts with bases in a straightforward manner to produce 2:1 adducts,[2,3] *e.g.*

$$Cl_2BCH_2CH_2BCl_2 + 2(CH_3)_3N \longrightarrow$$
$$(CH_3)_3NBCl_2CH_2CH_2BCl_2N(CH_3)_3 \quad (1)$$
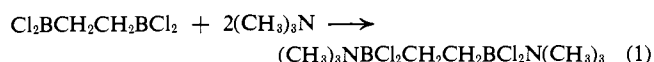
If the Lewis base contains a labile proton, however, B–Cl bond cleavage occurs,[3] *e.g.*

$$Cl_2BCH_2CH_2BCl_2 + 4MeOH \longrightarrow$$
$$(H_3CO)_2BCH_2CH_2B(OCH_3)_2 + 4HCl \quad (2)$$
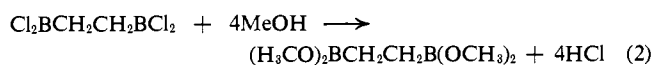
It is not surprising that the chloro acid reacts normally, with each boron atom acting as an electron-pair acceptor

toward a monofunctional Lewis base. However, the structure of the molecule suggests that a chelate adduct (1:1 stoichiometry of acid and base) could be achieved with a proper donor atom. This would be the analog of the well-known ethylenediamine–metal ion systems found in transition metal coordination chemistry. For such systems, it is known that the complex which contains a five- or six-membered chelate ring is generally more stable than a similar complex containing monofunctional ligands.[4] To a first approximation, this chelate effect has a simple statistical explanation;[4] so the chelate effect is expected for difunctional acids as well as difunctional bases.

In order to achieve a chelate adduct with the dihaloborylethanes, a base must be employed which contains at least two nonbonding electron pairs on a single atom. Furthermore, the dibasic donor atom must be of sufficient basicity to coordinate both boron atoms, yet of

(1) For brevity, 1,2-bis(dichloroboryl)ethane is referred to as the "chloro acid," and 1,2-bis(difluoroboryl)ethane is likewise termed "fluoro acid."

(2) G. Urry, J. Kerrigan, T. D. Parsons, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **76**, 5299 (1954).

(3) A. K. Holliday and A. G. Massey, *J. Chem. Soc.*, 43 (1960).

(4) C. G. Spike and R. W. Parry, *J. Am. Chem. Soc.*, **75**, 2726 (1953).