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AN ELECTROPHILIC DISPLACEMENT ASSISTED BY NEIGHBORING BORON*

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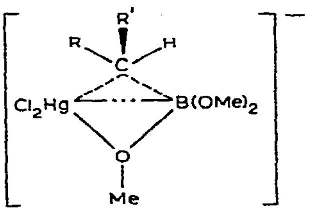
SUMMARY

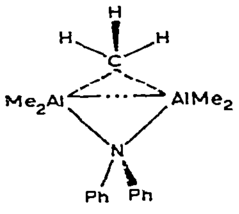
The mercuri-deboronation of (dimethoxyboryl)methanes $XCH_2B(OMe)_2$ with mercuric chloride in methanol at 30° to form XCH_2HgCl has the following relative rates with different substituents X: C_6H_5, 0.36; H, 1.0; ClHg, 3.0; $(MeO)_2B$, 98. The rate law in the presence of acetate buffer is $-d[HgCl_2]/dt = k\cdot[XCH_2B(OMe)_2]\cdot[HgCl_2]\cdot[NaOAc]/[HOAc]$. It appears that the vacant orbital of the neighboring boron or mercury atom plays an essential part in the rate acceleration. The results can be satisfactorily interpreted on the basis of cyclic three-center and four-center electron-pair bonding in the transition state.

INTRODUCTION

Electrophilic displacements at tetrahedral carbon which proceed with retention of configuration appear generally to involve some degree of direct bonding between the attacking and leaving groups in the transition state[2,3]. A reasonable model for the transition state (I) of a typical electrophilic displacement, mercuri-deboronation[3a,4], is provided by the analogous stable methyl-bridged compound μ-(diphenylamino)pentamethyldialuminum (II), which has been characterized by X-ray diffraction[5].



(I) (Transition state)



(II) (Stable)

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The mercury–oxygen–boron linkage drawn in transition state (I) is analogous to numerous examples in the literature[3], including the cyclic interactions which influence the stereochemistry of transition states involving considerable carbanion character[3c]. The three-center electron-pair bond[2] clearly must link the mercury, carbon, and boron in (I). However, the theoretically attractive direct boron–mercury interaction in (I) is difficult to establish experimentally, since there is no way to construct an analogous system in which such interaction can be proved to be absent.

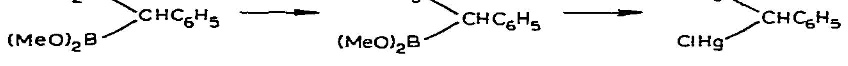
Neighboring group effects may provide indirect but useful information about these types of interactions. We have now found that a neighboring metal atom can markedly accelerate an electrophilic displacement, as if there is a significant amount of direct metal–metal or metal–ligand–metal interaction between the neighboring group and the attacking electrophile. Although our present results seem to point toward metal–metal bonding, the available evidence does not rule out all other possible interpretations.

RESULTS

Suitable compounds for studying neighboring-group effects in electrophilic displacements of boron have become available from the recently discovered method for attaching two or more boron atoms to the same carbon[6]. We initially chose to study the reaction of α,α-bis(dimethoxyboryl)toluene, $[(MeO)_2B]_2CHPh$ (III), with mercuric chloride, since kinetic data were already available for a series of α-(dialkoxyboryl)toluenes, $(RO)_2BCH_2Ar$[4], and the α-methyl homolog, $(RO)_2BCH(Me)Ph$[7], and the latter had been used to establish predominant retention of configuration at carbon on conversion to $ClHgCH(Me)Ph$[8].

Although it was immediately apparent that the α,α-bis(dialkoxyboryl)toluene reacts several times faster than α-(dialkoxyboryl)toluene with mercuric chloride in aqueous ethanol/glycerol under the conditions previously used for kinetic studies[4], the kinetic plots were badly curved and the points somewhat scattered. A search for better conditions was made, and good plots were obtained when the solvent was pure methanol buffered with acetic acid and sodium acetate, with sodium chloride added to repress the ionization of $HgCl_2$ to $HgCl^+$ and Cl^-. At 40°, the rate ratio $[(MeO)_2B]_2CHPh/(MeO)_2BCH_2Ph$ was found to be 22.

We failed to isolate the expected initial mercuri-deboronation product, α-(chloromercuri)-α-(dimethoxyboryl)toluene (IV), but obtained a solid having nearly the composition expected for α,α-bis(chloromercuri)toluene (V). The statistically corrected rate enhancement by the neighboring boronic ester group would be a factor of 11 if only one boron is replaced under the conditions of measurement, or somewhat less than if an appreciable amount of disubstitution occurs from the start.



(III) (IV) (Not isolated) (V)

We next turned to the study of bis(dimethoxyboryl)methane, $[(MeO)_2B]_2CH_2$ (VI), and immediately ran into further difficulties. The base-catalyzed reaction of (VI) with mercury(II) turned out to be so fast that it could not be suppressed by sodium EDTA, the reagent we had been using to stop the reaction and analyze for mercury(II)[4]. Various other methods for complexing mercury(II) in basic solution also failed. Success in complexing the mercury(II) was finally achieved by adding aliquots of the reaction mixture to carbon tetrachloride solutions of dithizone, which forms a soluble complex with mercury(II)[9]. Sodium acetate interferes with the analysis and must be removed at once by shaking with water, but if the water is added before the aliquot is mixed with the carbon tetrachloride solution of dithizone the mercury(II) continues to react with the boronic ester (VI). Two molecules of dithizone per $HgCl_2$ and one per RHgCl are complexed. The free dithizone was estimated spectrophotometrically at 625 nm.

A useful feature of the dithizone method is that it works best with relatively low concentrations of mercury(II). We gladly abandoned the tedious plotting of the complex rate law[4] in favor of pseudo-first-order or, where required, second-order plots. A typical plot is shown in Fig. 1.

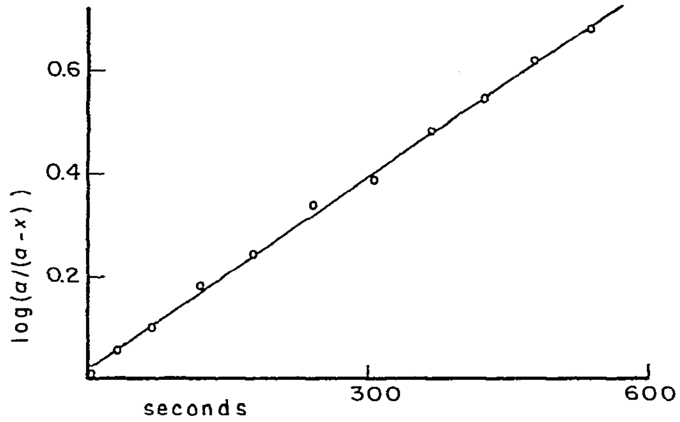


Fig. 1. Pseudo-first-order plof of $\log_{10}[a/(a-x)]$ *vs.* time for the reaction of $HgCl_2$ with $CH_2[B(OMe)_2]_2$, where a is $[HgCl_2]_0$ and x is the amount reached.

By adding a limited amount of sodium hydroxide to mercuric chloride and bis(dimethoxyboryl)methane (VI), we were able to isolate crystalline (chloromercuri)-(dihydroxyboryl)methane on concentration of the solution. Treatment with methanol and 2,2-dimethoxypropane yielded (chloromercuri)(dimethoxyboryl)methane (VII), which must be the direct product in anhydrous methanol. Bis(chloromercuri)-methane (VIII) was obtained when (VI) and mercuric chloride reacted with a sufficient amount of sodium hydroxide.

$$\underset{(VI)}{(MeO)_2BCH_2B(OMe)_2} \xrightarrow[NaOAc]{HgCl_2} \underset{(VII)}{ClHgCH_2B(OMe)_2} \rightarrow \underset{(VIII)}{ClHgCH_2HgCl}$$

The stoichiometry of the mercuri-deboronation in an acetate buffer is

$$RB(OMe)_2+HgCl_2+NaOAc+MeOH \rightarrow RHgCl+B(OMe)_3+NaCl+ +HOAc \quad (1)$$

The rate law was verified to be

$$-\mathrm{d}[\mathrm{HgCl_2}]/\mathrm{d}t = k \cdot \frac{[\mathrm{RB(OMe)_2}]\cdot[\mathrm{HgCl_2}]\cdot[\mathrm{NaOAc}]}{[\mathrm{HOAc}]} \tag{2}$$

with a series of fifteen runs in which the mercuric chloride was initially 10^{-3} *M* and the concentrations of $[(MeO)_2B]_2CH_2$, NaOAc, HOAc, and NaCl were each varied over an eight-fold range. The average *k* found was 0.169 ± 0.019 $l \cdot mol^{-1} \cdot sec^{-1}$, maximum deviation 0.039, at 30°. When $[HgCl_2]_0$ was increased to 4×10^{-3} *M*, the apparent *k* fell slightly to 0.131 ± 0.007 (four runs). No measurable effects on the rate resulted from addition of 1% or 10% water to the solvent, or from the presence of 0.04 *M* sodium nitrate.

Rate constants found for the series of boronic esters examined are summarized in Table 1. In order to avoid any systematic errors that might arise from analytical errors or deviations from the rate law, the initial concentrations used for obtaining the tabulated *k* values were confined to $[HgCl_2]_0 = 0.004$ *M*, $[RB(OMe)_2]_0 =$ 0.004–0.004 *M*, $[NaOAc]_0 = 0.06$ *M*, $[HOAc]_0 = 0.025$–0.1 *M*, and $[NaCl]_0 = 0.05$ *M*. These ranges best accommodate the most difficult compound to measure, $ClHgCH_2B(OMe)_2$ (see following paragraphs). The rough *k* for $C_4H_9B(OMe)_2$ is an exception, having been measured under non-standard conditions in an early phase of the work, and it is included here only because it is useful to know its order of magnitude.

TABLE 1

RATE CONSTANTS FOR REACTIONS OF BORONIC ESTERS WITH $HgCl_2$ IN ACETATE-BUFFERED METHANOL AT 30°[a]

Compound	*k* ($l \cdot mol^{-1} \cdot sec^{-1}$)	k/k_0 *per boron*[b]
$CH_3B(OMe)_2$	6.7×10^{-4}	1.0
$CH_2[B(OMe)_2]_2$	0.131	98
$ClHgCH_2B(OMe)_2$	2.0×10^{-3}	3.0
$C_6H_5CH_2B(OMe)_2$	2.1×10^{-4}	0.36
$HC[B(OMe)_2]_3$	0.27–0.60	135–300
$C[B(OMe)_2]_4$	0.016	6
$n\text{-}C_4H_9B(OMe)_2$	$3\text{–}8 \times 10^{-4}$	0.5–1.2

[a] Based on the expression rate $= k \cdot [HgCl_2] \cdot$ [boronic ester] $\cdot$ [NaOAc]/[HOAc], with approx. 0.05 *M* NaCl present to repress ionization of $HgCl_2$. [b] The observed *k* is divided by the number of boron atoms in the molecule, and k_0 refers to $CH_3B(OMe)_2$.

The analytical method does not permit accurate measurements where the mercuric chloride concentration considerably exceeds that of the boronic ester. Because the conversion of $HgCl_2$ to RHgCl only reduces the apparent mercury(II) concentration by half, with a 4/1 ratio of $HgCl_2$ to $RB(OMe)_2$ a reasonable 1% error in determining mercury(II) is an 8% error in $RB(OMe)_2$. Erratic results were naturally obtained in the few runs tried under such conditions.

A second limitation on the measurable range of the rate law is the apparent trend toward slightly lower *k*'s as $[HgCl_2]_0$ is increased, for example, the 25% decrease in *k* noted for $CH_2[B(OMe)_2]_2$ when $[HgCl_2]_0$ was increased four-fold. Perhaps the mercuric chloride interferes with the buffering by complexing with acetate, or there could be other interactions in this complex system. The linearity of pseudo-first-order (or pseudo-second-order) plots to >75% consumption of the mercuric chloride confirms that the reaction is first-order in this reactant.

For consistent results, spectrophotometric readings should be made within a few minutes of taking each aliquot. When dithizone solutions were stored several hours from the slow reactions of $CH_3B(OMe)_2$, *k*'s ranged from +10% to −40% deviation from the "correct" value and plots were erratic. With four promptly analyzed runs, reproducibility was ±5%.

All the foregoing sources of error are enhanced in the case of $ClHgCH_2B(OMe)_2$, which itself complexes with one mole of dithizone. Measurements cannot be made far from the optimum 1/1 ratio of boronic ester and mercuric chloride, which produces only a 33% change in measured mercury(II) concentration at 100% reaction. To make matters worse, this compound yields cloudy solutions with dithizone, which must be allowed to settle one hour before spectrophotometric readings of the uncomplexed dithizone can be made. In spite of these problems, we obtained an unbroken series of five runs agreeing to ±7% in which $[ClHgCH_2B(OMe)_2]_0$ was varied by a factor of 2. Four of five earlier runs in which the other reactants were varied by factors of 2 to 8 yielded *k*'s within ±35% of the "correct" value.

Since the observed *k* for $ClHgCH_2B(OMe)_2$ is only 1/60 that for $CH_2[B(OMe)_2]_2$, the successive displacements of the two borons atoms are fully separated in the kinetic measurements. We verified separately that the reaction of $CH_2[B(OMe)_2]_2$ slows drastically when the first boron is replaced by mercury. We also showed that $ClHgCH_2B(OMe)_2$ is stable in the absence of $HgCl_2$, with *k* for the self-condensation to $ClHgCH_2HgCH_2B(OMe)_2$ and $B(OMe)_3$ being less than 5×10^{-5}.

Special problems were encountered with $HC[B(OMe)_2]_3$. This compound is degraded rapidly to methanediboronic acid or ester in the presence of water or methanolic sodium methoxide[6]. Evidently it survives for a while in acetate-buffered methanol, since the observed *k*'s are several times higher than could be produced by derived $CH_2[B(OMe)_2]_2$. Initial *k*'s under a given set of conditions were reproducible to ±10%, but the plots generally showed a shallow S-shape, with the initial *k* falling off by 30–50% after 20–40% reaction, then rising again. With excess $HgCl_2$ it appears that more than one but less than two boron atoms are displaced at a fairly rapid rate. The apparent *k* falls with decreasing initial $HC[B(OMe)_2]_3$ concentration. Because it appeared possible that methanolysis might be competing with the reaction with $HgCl_2$, we gave up attempting to verify the rate law with this compound. The highest reproducible *k*, $0.6\ l \cdot mol^{-1} \cdot sec^{-1}$ with $HC[B(OMe)_2]_3$ at 0.01 *M*, is probably the closest approach to the true value.

With $C[B(OMe)_2]_4$ good straight lines could be obtained up to consumption of about half the $HgCl_2$ (initially 0.004 *M*), provided special precautions were taken in drying the methanol. Later in the reaction, precipitation of insoluble products began to interfere with the analyses. By reducing the amount of $C[B(OMe)_2]_4$ it was shown that more than one boron is replaced at about the same rate, but the problem with insoluble products prevented complete investigation. From other work it is known that $C[B(OMe)_2]_4$ is stable in methanol with a little acetic acid, that it is degraded to methanediboronic ester or acid slowly by methanolic sodium methoxide and rapidly by water[6], that mercuric acetate replaces all four boron atoms of $C[B(OMe)_2]_4$ to form $C(HgOAc)_4$, and that $C(HgCl)_4$ is insoluble in water or alcohols[10].

Temperature dependences were measured for $[(MeO)_2B]_2CH_2$, $CH_3B(OMe)_2$, and $C_6H_5CH_2B(OMe)_2$. The k values found for $[(MeO)_2B]_2CH_2$ were 0.031 and 0.033 at 0.3°, 0.088 at 20°, 0.137 at 30°, and 0.262 and 0.295 at 40°, yielding $\Delta H^{\neq} = 8.8\ (\pm 1.5)$ kcal·mol^{-1} and $\Delta S^{\neq} = -33$ cal·mol^{-1}·K^{-1}, or if only the range 20–40° is considered for comparison with the other compounds, $\Delta H^{\neq} = 9.9$ kcal·mol^{-1} and $\Delta S^{\neq} = -29$ cal·mol^{-1}·K^{-1}. For $CH_3B(OMe)_2$, k is 2.85×10^{-4} at 20°, 6.7×10^{-4} at 30°, and 16.4×10^{-4} at 40° yielding $\Delta H^{\neq} = 15.4$ kcal·mol^{-1} and $\Delta S^{\neq} = -22$ cal·mol^{-1}·K^{-1}. For $C_6H_5CH_2B(OMe)_2$, k is 1.06×10^{-4} at 20° and 6.63×10^{-4} at 40°, yielding $\Delta H^{\neq} = 16.2$ kcal·mol^{-1} and $\Delta S^{\neq} = -21$ cal·mol^{-1}·K^{-1}.

Because the reactions involve base catalysis, the pK_a's of the three boronic esters which are stable in basic solution were measured. In methanol containing 0.048 M sodium chloride and 5×10^{-4} M boronic ester, potentiometric titration with lithium methoxide under nitrogen yielded apparent pK_a values shown in Table 2. The equilibrium measured is $RB(OMe)_2 + MeOH \rightleftharpoons RB(OMe)_3^- + H^+$. Because the observed values are at the upper end of the measurable range, the pK_a's were also determined in the presence of 4% ethylene glycol, which lowers all the figures by 0.4–0.7 but leaves the relationships between compounds unchanged.

TABLE 2

APPARENT pK_a's OF BORONIC ESTERS IN METHANOL

Compound	*pK_a in pure MeOH*	*pK_a in 4% $HOCH_2CH_2OH$*
$CH_2[B(OMe)_2]_2$	10.87, 10.78	10.11
$CH_3B(OMe)_2$	10.62	10.24
$C_6H_5CH_2B(OMe)_2$	9.72	9.02
$B(OMe)_3$	8.98	8.54

The difference in pK_a values between $CH_3B(OR)_2$ and $C_6H_5CH_2B(OR)_2$, 0.9–1.2 pK units, is comparable with the 1.47 pK unit difference found previously between the corresponding boronic acids in water[11].

DISCUSSION

The rate law established by this work for the reaction of $CH_2[B(OMe)_2]_2$ with mercuric chloride in buffered methanol [see Results, eqn. (2)] is analogous to that previously found for the reaction of benzylboronic ester with mercuric chloride in buffered ethanol/water/glycerol[4]. The available data, though limited in scope, support the same rate law for the other boronic esters used in this study. The direct dependence on acetate ion and inverse dependence on acetic acid corresponds to catalysis by methoxide ion, the concentration of which is governed by the equilibrium in eqn. (3). Other equilibria which might be involved are shown in eqns. (4)–(6).

$$OAc^- + MeOH \rightleftharpoons HOAc + MeO^- \qquad (3)$$

$$\mathrm{MeO^- + HgCl_2 \rightleftarrows MeOHgCl_2^-} \tag{4}$$

$$\mathrm{OAc^- + HgCl_2(MeOH)_n \rightleftarrows MeOHgCl_2(MeOH)_{n-1}^- + HOAc} \text{ where } n = 1\text{–}4 \tag{5}$$

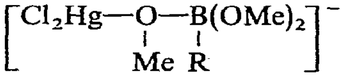
$$\mathrm{MeO^- + RB(OMe)_2 \rightleftarrows RB(OMe)_3} \tag{6}$$

Omitting solvation, the two most likely pathways to the transition state (T.S.) are given by eqns. (7) and (8).

$$\mathrm{MeOHgCl_2^- + RB(OMe)_2 \rightarrow (T.S.) \rightarrow RHgCl + B(OMe)_3 + Cl^-} \tag{7}$$

$$\mathrm{HgCl_2 + RB(OMe)_3^- \rightarrow (T.S.) \rightarrow RHgCl + B(OMe)_3 + Cl^-} \tag{8}$$

Inasmuch as mercury(II) complexes strongly with chloride and hydroxide ions[12], perhaps $\mathrm{MeOHgCl_2^-}$ [eqn. (7)] is more abundant than $\mathrm{RB(OMe)_3^-}$ [eqn. (8)], but the two paths are kinetically indistinguishable and the undecidable choice between them is irrelevant to the question of the structure of the transition state. It is likely that the two paths converge on a reversibly formed B–O–Hg linked intermediate (IX) prior to the transition state. An analogy to this energy relationship is provided by μ-(tert-butoxy)pentamethyldialuminum, in which the Al–C–Al linkage can open while the Al–O–Al bridge remains intact[13].



$$\left[\mathrm{Cl_2Hg{-}\underset{Me}{\underset{|}{O}}{-}\underset{R}{\underset{|}{B}}(OMe)_2}\right]^-$$

(IX)

The 200 times faster rate with $\mathrm{CH_2[B(OMe)_2]_2}$ than with $\mathrm{CH_3B(OMe)_2}$ is highly significant in a reaction which is only slightly sensitive to the usual structural influences. Inductive effects are small. We have previously shown that in a set of four arylmethaneboronic esters, electron-withdrawing substituents have a small accelerating effect (Hammett $\rho = +0.9$)[4]. Put another way, the more acidic boronic esters react faster, but the total range of rates $[\log(k_4/k_1) = 0.5]$ is less than the range of acidities $[\log(K_4/K_1) = 0.9]$. If intermediates having structure (IX) are involved, the rates must be very nearly proportional to the concentration of the intermediate, with almost no electronic influence on the actual step of displacement of boron by mercury. The previous study used a different solvent (and different alkoxy ligands on boron), but the Grunwald–Winstein Y value[14] (index of effective polarity) of 88% ethanol/4% glycerol/8% water should be within 0.3 unit of that of 100% methanol, the rate of reaction of $\mathrm{CH_2[B(OMe)_2]_2}$ is unaffected by 10% water ($\Delta Y \approx 0.7$), the absolute rates for the benzylboronic ester in the two different media are only about a factor of four apart at 40°, and there is no reason to expect any significant change in the Hammett plot with the change in solvent. Structure has some influence, the α-methylbenzylboronic ester series appearing to have a slightly negative Hammett ρ on the basis of very limited data[7], but the inductive effect remains small.

Steric effects are also small. The rate with $\mathrm{C_4H_9B(OMe)_2}$ is at least half that with $\mathrm{CH_3B(OMe)_2}$, and when corrected for the non-standard conditions of its determination, the former is probably equal or a little faster. This lack of sensitivity to the alkyl substituent is typical of electrophilic displacements with retention of configuration at carbon[15,16]. If $\mathrm{C_4H_9B(OMe)_2}$ reacted much slower than $\mathrm{CH_3B(OMe)_2}$, there might be reason to worry about a possible inversion mechanism[16].

The α-methylbenzylboronic ester series reacts somewhat slower than the benzylboronic ester series[4,7], but the change is not gross.

This does not mean that steric effects are zero. If the rate/acidity correlation held, $CH_3B(OMe)_2$ should react 1/3 as fast as $C_6H_5CH_2B(OMe)_2$. Instead, it reacts 3 times as fast. This 10-fold, 1 $kcal \cdot mol^{-1}$ shift toward a faster rate may well be steric in origin, as may be the slow reaction of the very hindered $C[B(OMe)_2]_4$ compared to $CH_2[B(OMe)_2]_2$.

To challenge the reality of the alleged neighboring group effect as strongly as possible, one would ignore possible steric effects and plot log (k/k_0) *vs.* pK_a for $CH_3B(OMe)_2$ and $C_6H_5CH_2B(OMe)_2$. Then the statistically corrected pK_a for $CH_2[B(OMe)_2]_2$ is 0.5(±0.1) units greater than for $CH_3B(OMe)_2$, and the statistically corrected rate constant is "predicted" to be almost 3 times greater for $CH_2[B(OMe)_2]_2$. This is a factor of 30 or 40 short of the actual ratio, 100. To be as realistic as possible, one would compare $CH_2[B(OMe)_2]_2$ directly with the sterically more equivalent $C_6H_5CH_2B(OMe)_2$, making the apparent statistically corrected acceleration a factor of 300, or taking the observed[4] pK_a/rate correlation into account, a factor of 1000–2000. There is no doubt that this is a real neighboring group effect.

Several other observations support the conclusion that this rate acceleration is caused by a direct interaction of the neighboring (non-displaced) boron atom with the attacking electrophile. The difference between the $\Delta H^{\neq}$ values for $CH_3B(OMe)_2$ and $CH_2[B(OMe)_2]_2$, ≈ 6 $kcal \cdot mol^{-1}$, represents a reasonable strength for a weak bond of some sort, and the $\Delta S^{\neq}$ difference of ≈ -9 $cal \cdot mol^{-1} \cdot K^{-1}$ is appropriate for the formation of an additional small ring in the case of $CH_2[B(OMe)_2]_2$. The approximate rate constant for $HC[B(OMe)_2]_3$ verifies that it reacts faster than $CH_2[B(OMe)_2]_2$, but the statistically corrected effect on the departing boron per neighboring boron remains roughly constant, as if only a 1/1 interaction can be utilized. If an electronic effect were involved, each boron atom ought to contribute a roughly equal increment of energy, and $HC[B(OMe)_2]_3$ would probably react hundreds of times faster than $CH_2[B(OMe)_2]_2$, which is clearly contrary to fact.

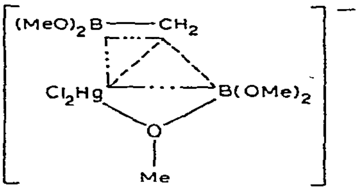
The relative reactivities $(MeO)_2B\text{–}CH_2B(OMe)_2 > ClHg\text{–}CH_2B(OMe)_2 > H\text{–}CH_2B(OMe)_2 > C_6H_5\text{–}CH_2B(OMe)_2$ strongly suggest that the vacant *p* orbital of the neighboring boron or mercury becomes involved in the interaction. The series $CH_2[B(OMe)_2]_2 > C_6H_5CH[B(OMe)_2]_2 > C_6H_5CH_2B(OMe)_2$, though less accurately documented, also supports the importance of the vacant orbital. If mere π bonding interaction between the neighboring group and the carbon at the displacement site were involved, several things should be different. Phenyl should be as good or better than dimethoxyboryl in such interactions, and mercury should be ineffective because of the large size and diffuseness of its *p* orbitals.

For related reasons, any rationalization involving carbanion character at the displacement site can be ruled out. (Free carbanion intermediates are of course ruled out by the rate law.) Neither the low[4] Hammett ρ, the failure of phenyl to accelerate the reaction, the ability of chloromercuri to do so, nor the failure of $HC[B(OMe)_2]_3$ to react orders of magnitude faster than $CH_2[B(OMe)_2]_2$ can be reconciled with carbanion character. In this regard, carbanions can be readily generated from $HC[B(OMe)_2]_3$ and $C[B(OMe)_2]_4$ under conditions where $R_2C[B(OMe)_2]_2$ is inert[17], in contrast to the rate patterns observed in this work.

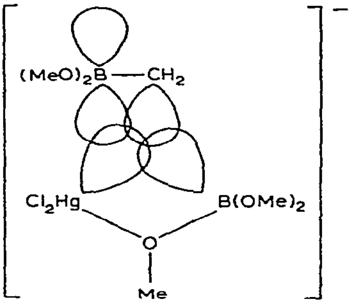
Another possible explanation is that the transition state for reaction of

$CH_2[B(OMe)_2]_2$ may be similar in structural features to that for $CH_3B(OMe)_2$, but that $CH_2[B(OMe)_2]_2$ itself is somehow destabilized. There is no good reason for believing this to be correct. First, it ignores the difference between the entropies of activation. Second, the available data on the hydroboration of acetylenes and vinylboronic esters indicates a slight preference for formation of $CH_3CH(BX_2)_2$ over $X_2BCH_2CH_2BX_2$[18]. These results may be kinetically controlled and do not prove the thermodynamic question in a rigorous way, but they do not suggest any gross destabilization of $CH_3CH(BX_2)_2$. Indeed, when one considers the stabilities of carboranes, clustering several boron atoms around one carbon should tend to increase stability instead of decreasing it. The interpretation to be developed in the following paragraphs will be somewhat analogous to saying that the transition state for reaction of $CH_2[B(OMe)_2]_2$ is more carborane-like than $CH_2[B(OMe)_2]_2$ itself, and that this is the fundamental reason for the rate acceleration.

An interpretation which does fit the experimental facts follows. The neighboring boron has a vacant* *p* orbital which can overlap simultaneously with the vacant orbital of the attacking mercury electrophile and with the (approximately) sp^3 carbon orbital which is the displacement site. Thus, the three-center electron-pair bond of transition state model (I) is extended to include a fourth center, as illustrated by the partial-bond structure (X) or the stylized orbital picture (XI). It is readily apparent that this additional bonding to the fourth center is allowed by quantum mechanical symmetry rules. The one electron pair occupies only that four-center molecular orbital which is totally symmetric (all lobes positive) in the region of effective orbital overlap. Therefore the energy of the system is lowered and transition state (X) is stabilized. In the terminology of the Woodward–Hoffmann rules[19], the introduction of the fourth center corresponds to an allowed [0+2] cyclization. Simple Hückel calculations provide another description that is essentially based on orbital symmetry. The energy for one electron pair in a symmetrical cyclic three-center orbital is $2\alpha+4\beta$, and addition of the fourth center to one side of the triangle yields a more favorable $2\alpha+5.12\beta$.



(X)



(XI)

Structure (X) does not necessarily add any angle strain to transition state (I). Assuming that the B–C–B angle in $CH_2[B(OMe)_2]_2$ is approximately tetrahedral

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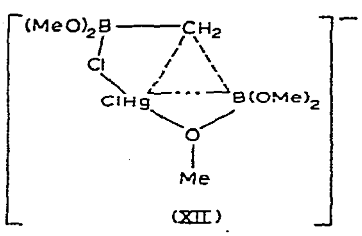
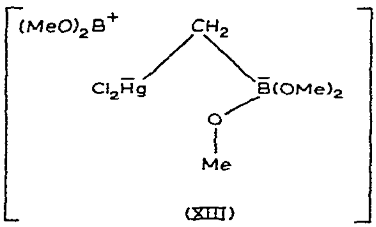
* Back-bonding delocalizes this vacancy to some extent, but this does not change the essential nature of the description.

and that the mercury atom approaches in or near the B–C–B plane, interaction with the vacant *p* orbital of the non-displaced boron is inevitable. In this connection, it should be remembered that the actual contours of electron density for *p* orbitals and sp^3 or *sp* hybrids[20] cover much wider angles than the stylized orbital representation (XI) suggests. The mercury *sp* (or other hybrid) orbital covers a particularly broad front. If the B–C–Hg angle at the reacting center is 80° [similar to μ-(diphenylamino)pentamethyldialuminum[5] (II)], and if the line bisecting that angle is 110° from the stationary B–C bond, a reasonable guess for the transition state geometry, then considerable neighboring group interaction is still possible (based on inspection of rough drawings with the right orbital shapes). There is no basis for quantitative treatment.

Two other types of neighboring group interaction need to be considered. A ligand on the attacking mercury electrophile could coordinate with the vacant orbital on the neighboring boron, as in transition state (XII). Second, hyperconjugation electron donation from the neighboring carbon–boron bond[21], depicted by resonance structure (XIII), might stabilize the transition state. These interactions are not necessarily exclusive of that depicted in (X), though they would tend to populate a non-bonding four-center orbital. If ligand bridging (XII) were especially important, the ClHg neighboring group ought to be more effective than $(MeO)_2B$, contrary to observation, since the Hg–Cl–Hg ligand bridge should be stronger than an Hg–Cl–B or Hg–(MeOH)–B bridge. However, it would require study of many more compounds than presently available to rule out a fortuitous combination of Hg–Cl–Hg ligand bridging and Hg–Hg steric repulsion as governing the rate. The evidence does not particularly support the hyperconjugation hypothesis, since electron-donation does not normally aid the reaction[4], and it is not likely that boron would be better than mercury in such interactions.



(XII)



(XIII)

[for possible inclusion in a resonance description of (X)]

Other variations in transition state model (X) are conceivable. The positions of the attacking and leaving electrophiles might be interchanged. The planar structure might be bent toward a tetrahedron, with some boron–boron bonding (Hückel energy $2\alpha+6\beta$), but this would probably introduce too much strain to be viable. The mechanism might shift to inversion[16] with the aid of the neighboring group, since interactions of the type discussed would still be symmetry allowed even though much modified in detail, though there is no reason to expect such a change in mechanism.

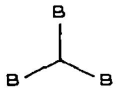
Previous literature which might be reinterpreted on the basis of a transition state analogous to (X) includes a study of acid and halogen cleavages of $(Me_3SiCH_2)_2$-SnR_2 compounds, in which preferential cleavage of Me_3SiCH_2 rather than a plain alkyl group from the tin was observed[22]. The vacant *d* orbital of silicon could assist electrophilic displacement. A second example is the mercuration of acetic acid by mercuric acetate[23]. The reaction is obviously aided by the neighboring carboxyl group and fails in its absence, the isotope effect requires that the proton be displaced in the rate-determining step, there is no H–D exchange, and the rate is first-order in mercuric acetate. An enol intermediate cannot be involved, and the results seem quite weird until they are interpreted in terms of a transition state analogous to (X).

NOTE ON SYMBOLISM

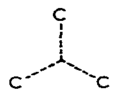
Three-center bonds are a common feature of organometallic[5,24,25] and carbonium ion[26,27] chemistry. There is no general agreement on symbolism. We have used our own modification of the symbolism favored by Winstein[26]. The three-center bond is indicated by a broken line (---) triangle written within the triangle of linked atoms. Where one exchange integral is obviously smaller than the others [such as the Hg–B link in (X)] we have written a dotted line (...) somewhat arbitrarily.

Calculations suggest that metal–metal interactions can contribute significantly to the energy of the three-center bond[5,25]. In any event, leaving off one leg of the triangle because one interaction is supposedly weaker than the rest implies an incorrect symmetry operation, adding a node to the wave function where there can be none. It is common practice among chemists to write some sort of bond between adjacent atoms for each occupied molecular orbital in excess of the number of antibonding nodes in these orbitals, even though it is usually done with no conscious effort. This approach can be justified by advanced calculations, as in the case of conjugated polyenes[28]. Even though there is no such thing as a localized electron pair, localized bonds work in practice because they correctly relate to the fundamental symmetry of the molecular wave function[28]. Correctly chosen delocalized bonds, written with broken lines or sets of resonance structures, likewise must obey symmetry rules in any serious discussion of bonding. The cyclic three-center bond is an indivisible unit which cannot be factored further.

The alternative symbols (XIV) and (XV) have been used in boron hydride[24] and carbonium ion[27] representations. These have three disadvantages. (1) They are not useful in organic line structures, since the line junction can be misread as a carbon atom. (2) They emphasize arbitrary factoring of the wave function into orbitals, rather than the more fundamental total number and placement of nodes. (3) Cumbersome resonance structures[24] are required in order to represent such simple extensions as structure (X). However, it should be emphasized that representations such as (XIV) or (XV) do not differ in any real meaning or implication from the triangular symbol we prefer.



(XIV)



(XV)

EXPERIMENTAL

(Dihydroxyboryl)(chloromercuri)methane

A solution of 0.517 g (12.9 mmol) of sodium hydroxide in 50 ml of water was added dropwise for 45 min to 7.1 g (26 mmol) of mercuric chloride and 2.1 g (13.1 mmol) of bis(dimethoxyboryl)methane[6] in approx. 75 ml of water and 25 ml of methanol (to dissolve the mercuric chloride) stirred at 0° under nitrogen. The precipitate was filtered and the filtrate was concentrated under vacuum. The residue was recrystallized from 60 ml of water. The NMR spectrum (DMSO-d_6) showed the CH_2 peak at δ 0.85 with the ^{199}Hg satellites, J 302 Hz, and the broad OH peak at δ 7.2. (Found: C, 4.37; H, 1.51; B, 3.89; Cl, 12.03; Hg, 68.28. $CH_4BClHgO_2$ calcd.: C, 4.06; H, 1.35; B, 3.66; Cl, 12.2; Hg, 68.0%.)

(Dimethoxyboryl)(chloromercuri)methane

Crude (dihydroxyboryl)(chloromercuri)methane (0.05 mol) was dissolved in

TABLE 3

RATE CONSTANTS FOR REACTION OF $CH_2[B(OMe)_2]_2$ WITH $HgCl_2$ IN ACETATE-BUFFERED METHANOL, AT 30° EXCEPT WHERE NOTED OTHERWISE

Run No.	*Molarity* $\times 10^3$					k_{obs}
	$HgCl_2$	*$CH_2[B(OMe)_2]_2$*	*NaOAc*	*HOAc*	*NaCl*	
47	0.97	10.0	7.55	10.48	11.85	0.165
48	0.97	10.0	7.55	20.96	11.85	0.151
49	0.97	10.0	7.55	41.92	11.85	0.149
50	0.97	10.0	7.55	83.84	11.85	0.149
51	0.97	10.0	7.55	41.0	5.92	0.177
52	0.97	10.0	7.55	41.0	11.84	0.156
53	0.97	10.0	7.55	41.0	23.68	0.139
54	0.97	10.0	7.55	41.0	47.36	0.131
55	0.97	10.0	7.55	41.92	11.85	0.123[a]
56	0.97	10.0	7.55	41.92	11.85	0.155[a]
57	0.97	10.0	15.10	41.0	47.36	0.208
58	0.97	10.0	30.2	41.0	47.36	0.182
59	0.97	10.0	60.4	41.0	47.36	0.195
61	0.97	10.0	7.55	41.0	5.92	0.182[b]
64	0.97	10.0	61.0	41.7	48.0	0.194
65	0.97	5.0	61.0	41.7	48.0	0.179
66	0.97	0.476	61.0	41.7	48.0	0.169[c]
70	1.005	3.00	61.0	6.99	48.0	0.184
76	0.957	10.0	30.7	167	47.8	0.108
93	3.99	3.99	60.8	25.2	48.1	0.121
96	4.05	4.05	61.2	25.2	48.0	0.126
104	4.02	4.02	60.7	25.2	48.1	0.139
112	4.05	4.05	61.4	101.2	48.7	(0.088, 20°)
113	4.00	4.00	60.6	99.6	48.1	0.137
114	4.14	4.14	62.8	103.2	49.8	(0.033, 0.3°)
115	3.95	3.95	59.9	98.8	47.5	(0.295, 40°)
124	3.64	3.64	55.4	90.8	43.6	0.135[d]
125	4.14	4.14	63.0	103.2	49.5	(0.031, 0.3°)
126	3.95	3.95	60.1	98.8	47.2	(0.262, 40°)

[a] Solvent 99% methanol, 1% water. [b] 42×10^{-3} M sodium nitrate added. [c] Unfavorable mercuric chloride/boronic ester ratio for analysis, points scattered. Two other runs under similar conditions yielded plots too poor to record, but verified that reaction stops after $CH_2[B(OMe)_2]_2$ consumes one mole of $HgCl_2$. [d] Solvent 90% methanol, 10% water (v/v).

anhydrous methanol (50 ml), 10 ml of 2,2-dimethoxypropane was added to remove water, and the methanol was distilled. After removal of the last traces of solvent under vacuum at 25°, the syrupy residue was dissolved in a small amount of methanol, filtered, and cooled to crystallize. Recrystallization from methanol yielded 4 g (25%) of (dimethoxyboryl)(chloromercuri)methane (VII). NMR (DMSO-d_6) δ 0.86 (s, 2, CH_2) with ^{199}Hg satellites, J 312 Hz, 3.52 (s, 6, OCH_3). Rates obtained with the dihydroxy and dimethoxy compounds in methanol were similar. (Found: C, 11.11; H, 2.87; B, 3.64; Cl, 11.58; Hg, 65.5. $C_3H_8BClHgO_2$ calcd.: C, 11.14; H, 2.48; B, 3.35; Cl, 10.98; Hg, 62.10%.)

Bis(chloromercuri)methane

A solution of 0.48 g (13 mmol) of sodium hydroxide in 50 ml of water was

TABLE 4

RATE CONSTANTS FOR REACTION OF $CH_3B(OMe)_2$ WITH $HgCl_2$ IN ACETATE-BUFFERED METHANOL, AT 30° EXCEPT WHERE NOTED OTHERWISE

Run No.	*Molarity* × 10^3					k_{obs} × 10^4
	$HgCl_2$	*$CH_3B(OMe)_2$*	*NaOAc*	*HOAc*	*NaCl*	
60	0.97	9.05	7.55	41.0	47.4	7.3[a]
63	0.97	9.05	60.5	40.6	47.4	4.8[a]
95	4.05	8.10	61.2	25.6	48.0	3.7[a]
116	4.02	37.2	61.0	25.1	48.4	7.0
117	4.02	37.2	61.0	25.1	48.4	6.4
118	3.95	36.5	59.9	24.7	47.5	(16.4, 40°)
120	4.05	37.2	61.0	25.1	48.4	(2.85, 20°)
122	4.02	37.2	61.2	25.1	48.1	7.0
123	4.02	9.30	61.2	25.1	48.1	6.4

[a] These data were taken before it was realized that prompt spectrophotometric readings are essential, and the points are considerably scattered.

TABLE 5

RATE CONSTANTS FOR REACTION OF $PhCH_2B(OMe)_2$ [AND $BuB(OMe)_2$] WITH $HgCl_2$ IN ACETATE-BUFFERED METHANOL AT 30° EXCEPT WHERE OTHERWISE NOTED

Run No.	*Molarity* × 10^3					k_{obs} × 10^4
	$HgCl_2$	*$PhCH_2B(OMe)_2$*	*NaOAc*	*HOAc*	*NaCl*	
109	4.00	38.7	60.3	25.0	47.8	2.40
119	3.95	38.0	59.7	24.7	47.8	(6.63, 40°)
121	4.02	38.7	61.2	25.1	48.1	(1.06, 20°)
78	0.94	10.1	61.7	1.05	48.2	(0.89)[a]
73	0.94	(10.0)[b]	61.7	1.05	48.2	(3.3)[c]

[a] Conditions inadequate for accuracy; HOAc concn. too low for pseudo-first-order plot, spectrophotometric readings not prompt enough. [b] $BuB(OMe)_2$. [c] Only data available for $BuB(OMe)_2$, conditions comparable to run 78. Comparison of run 78 with run 109 suggests that the k found in run 73 is 1/3 to 1/2 the true value.

added with stirring in 40 min to 5.4 g (20 mmol) of mercuric chloride and 0.96 g (6 mmol) of bis(dimethoxyboryl)methane[6] in 100 ml of water. The precipitate was filtered, washed with water, dried, dissolved in dimethyl sulfoxide, and reprecipitated with water, then washed with acetone and dried. NMR (DMSO-d_6) δ 1.52 (s, CH_2) with ^{199}Hg satellites, J 173 Hz. (*Found*: C, 2.46; H, 0.89; Cl, 14.60; Hg, 82.48. $CH_2Cl_2Hg_2$ calcd.: C, 2.47; H, 0.41; Cl, 14.58; Hg, 82.5%.)

TABLE 6

RATE CONSTANTS FOR REACTION OF $ClHgCH_2B(OMe)_2$ WITH $HgCl_2$ IN ACETATE-BUFFERED METHANOL AT 30°

Run No.	*Molarity* × 10^3					k_{obs} × 10^3
	$HgCl_2$	*$RB(OMe)_2$*	*NaOAc*	*HOAc*	*NaCl*	
69	1.005	3.01	61.0	6.99	48.0	(3.7)[a]
71	1.005	3.01	61.0	6.99	48.0	(2.7)[a]
87	0.94	0.94	61.7	3.15	48.2	(1.4)[b]
88	None	2.30	62.0	1.05	None	(< 0.05)[c]
89	3.98	8.85	61.5	12.6	23.6	2.30
90	3.98	8.85	58.5	12.1	46.3	1.50
91	3.90	8.62	58.5	24.2	46.3	1.94
92	3.99	3.99	59.9	24.8	47.4	2.16
94	3.99	3.99	59.9	24.8	47.4	1.73
97	3.91	7.82	59.1	24.3	46.3	2.04
98	3.98	3.98	60.1	24.8	47.2	2.13

[a] Points scattered, accuracy doubtful. [b] Points scattered, two other runs with these low boronic ester and acetic acid concentrations were too poor to tabulate. [c] Sets an upper limit for k for the side reaction 2 $ClHgCH_2B(OMe)_2 \rightarrow ClHgCH_2HgCH_2B(OMe)_2$.

TABLE 7

RATE CONSTANTS FOR REACTION OF $HC[B(OMe)_2]_3$ WITH $HgCl_2$ IN ACETATE-BUFFERED METHANOL AT 30°

Run No.	*Molarity* × 10^3					k_{obs}
	$HgCl_2$	*$HC[B(OMe)_2]_3$*	*NaOAc*	*HOAc*	*NaCl*	
74	0.97	9.89	7.56	41.0	23.7	0.49
75	0.96	9.89	30.7	167	47.8	0.61
77	0.96	9.89	30.7	167	47.8	0.60
84	0.97	0.485	61.0	41.7	48.0	(0.10)[a]
85	0.96	9.90	4.17	41.7	48.5	0.49
106	4.02	2.01	60.7	50.4	48.1	(0.26)[b]
107	4.02	2.01	60.7	25.2	48.1	(0.27)[b]

[a] This value is of doubtful significance because of the low boronic ester concentration. [b] More than one but less than two moles of $HgCl_2$ reacted (smooth curve if appropriately plotted). These are initial slopes based on 1/1 ratio. The high initial mercuric chloride/boronic ester ratio decreases analytical accuracy.

TABLE 8

RATE CONSTANTS FOR REACTION OF $C[B(OMe)_2]_4$ WITH $HgCl_2$ IN ACETATE-BUFFERED METHANOL

Run No.	*Molarity* × 10^3					k_{obs}
	$HgCl_2$	$C[B(OMe)_2]_4$	*NaOAc*	*HOAc*	*NaCl*	
80	0.97	10.0	61.0	41.7	48.0	(0.02)[a]
82	0.93	0.234	61.0	1.05	1.2	(0.0027)[b]
102	3.97	8.90	60.0	24.7	47.1	0.029[c]
103	3.94	9.42	59.5	24.7	47.1	0.0201
105	4.00	2.48	60.4	25.1	47.8	0.0166
110	10.0	2.50	63.7	25.1	48.1	(0.004)[d]
111	3.96	9.94	59.7	24.8	47.3	0.0164

[a] Initial rate: curves upward to 0.04 as reaction proceeds, suggesting formation of more reactive boronic ester. [b] Low acetic acid and low boronic ester concentrations both contribute to low *k*'s. [c] Inadequate precautions in drying methanol make values in runs 102 and 80 questionable, *k*'s likely to be high. [d] Unfavorable mercuric chloride/boronic ester ratio; plot badly scattered, meaning doubtful.

Kinetics

Stock solutions containing the desired amounts of mercuric chloride, sodium chloride, anhydrous sodium acetate, and acetic acid in reagent grade anhydrous methanol were prepared. A solution of dithizone (diphenylthiocarbazone) was prepared by boiling a weighed amount of dithizone in carbon tetrachloride, filtering, treating the insoluble material with a second portion of carbon tetrachloride, and diluting the combined filtrates with carbon tetrachloride to a measured volume. If the initial concentration of mercuric chloride is 4×10^{-3} *M* and 1-ml aliquots are taken, the optimum dithizone concentration is 0.235 g/l. The stock solution of mercuric chloride, 25 ml, was placed in a flask connected to a source of nitrogen, which could be shut off by a stopcock once the air was flushed out of the system. The flask had a magnetic stirrer and a sidearm equipped with a rubber cap for transferring samples by syringe, and it was placed in a bath controlled to $\pm 0.02°$ (except the runs at 0.3°, which were controlled with ice to $\pm 0.1°$). A set of eleven 10-ml portions of dithizone solution was measured into 125-ml Erlenmeyer flasks (stoppered). An accurately measured amount of the boron compound (in solution if a solid) was injected into the reaction flask at t_0, and at appropriate intervals accurately measured 1-ml aliquots were removed by means of a syringe equipped with a Chaney adaptor to aid in maintaining constant sample size. Each aliquot was added to 10 ml of the dithizone solution and swirled to mix. Deionized water (100 ml) was added immediately and the flask was stoppered and shaken vigorously, then kept in the dark until the spectrophotometric readings could be taken. Readings were made after completion of the faster runs, within a few minutes of taking each aliquot for slow runs, or after the turbidity had had time to settle (1 h) in the case of $ClHgCH_2B(OMe)_2$. The carbon tetrachloride layer was pipetted into a cell having a 1-mm path length and the spectrum recorded from 750 to 615 nm with a Cary Model 15 spectrophotometer. The uncomplexed dithizone was estimated from the height h_t of the maximum at 625 nm and was compared with the t_0 value h_0 obtained from the stock solution of reagents without any boron compound and also with the absorbance h_a of the dithizone solution itself without mercury. Since $HgCl_2$ complexes two molecules of dithizone and RHgCl complexes one, the amount of remaining $HgCl_2$ is proportional to $\frac{1}{2}(h_0+h_a)-h_t$. Results of individual kinetic runs are summarized in Tables 3–8.

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