

Boronic Ester Neighboring Groups

DONALD S. MATTESON

Department of Chemistry, Washington State University, Pullman, Washington 99163

Received November 10, 1969

What effects might a neighboring metal atom have on organic reactions such as nucleophilic or electrophilic displacements? To answer this question experimentally, the first problem is to synthesize compounds which contain both a carbon-metal bond and another reactive functional group. Among organometallic compounds, boronic esters, $\text{RB}(\text{OR}')_2$, appeal to the cautious chemist. They do not spontaneously start fires or cause accidental poisonings, and they are stable enough to withstand preparation and isolation by ordinary organic techniques, though they do need protection from moisture and oxygen to preserve purity. Boron supplies three typical properties of metal atoms: lower electronegativity than carbon, a vacant orbital which can coordinate with nucleophiles, and the ability to function as an electrofuge (leaving atom) in displacement or elimination reactions.

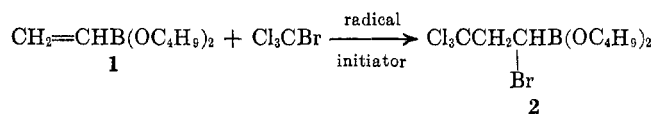
The classical synthesis of boronic acids from the Grignard reagent¹ is incompatible with reactive neighboring groups. Much of the effort of my research group has centered on finding new syntheses of carbon-functional boronic esters. We have studied mechanisms of reactions of each new class of compounds as soon as the synthetic work provided the opportunities. Hydroboration,² the best known branch of organoboron chemistry, has solved only one of our synthetic problems, but it has lent timeliness to some of our studies. For example, we reported alkyl migration from boron to carbon with displacement of bromide in α -bromoalkylboron compounds in 1963,³ and similar rearrangements are now being used in some of the most promising synthetic sequences based on hydroboration.⁴

In the discussion which follows, the effect of the $-\text{B}(\text{OR})_2$ group on nucleophilic displacement at the α carbon will be described first, β elimination next. In the second section, simple and transannular electrophilic displacements of boron by mercury(II) will be discussed, followed by the chemistry of $\text{C}[\text{B}(\text{OCH}_3)_2]_4$ and related compounds, in which various useful replacements of one or two boron atoms are greatly facilitated by the remaining neighbors.

Neighboring Boron in Nucleophilic Displacements

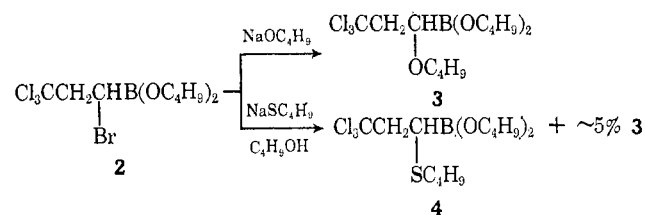
The Bromotrichloromethane-Vinylboronic Ester Adduct. The first α -haloalkaneboronic esters were made by radical-catalyzed additions to the double bond of

dibutyl vinylboronate (**1**).⁵ These radical reactions,



the products which can be obtained from them, and the stabilizing influence of the boron atom on the adjacent carbon radical have been reviewed in detail elsewhere.^{6,7}

The α -bromoalkaneboronic ester **2** proved to be a stable compound with some unusual patterns of reactivity. Most compounds containing the $\text{Cl}_3\text{CCH}_2\text{CHBr}$ group are dehydrobrominated by bases, but **2** yielded only the nucleophilic displacement product **3** with sodium butoxide.³ Butoxide even competes with butyl



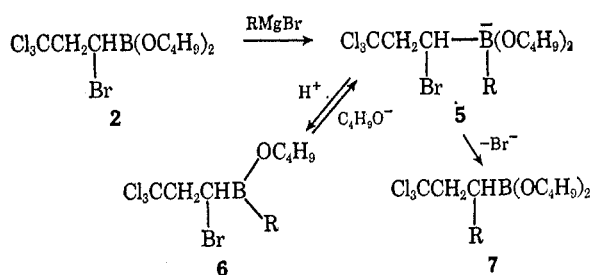
mercaptide in displacing bromide from **2**, contaminating the thioether **4** with the ether **3**, a result which seemed questionable until we confirmed it later with other α -bromo boronic esters. Reaction of **2** with sodium iodide in acetone to yield $\text{Cl}_3\text{CCH}_2\text{CHIB}(\text{OC}_4\text{H}_9)_2$ is hundreds of times faster than analogous reaction of the carboxylic ester, $\text{Cl}_3\text{CCH}_2\text{CHBrCO}_2\text{C}_2\text{H}_5$.³

The general mechanism of displacement of bromide from the α -bromo boronic ester **2** was clarified by the reaction with Grignard reagents, which permitted trapping of the boron-alkylated (or arylated) intermediate **5**.³ Prompt treatment of the anion **5** with acid at -70° removes a butoxy group to yield the boronic ester **6**. Structure **6** was confirmed by an alternative synthesis from Cl_3CBr and $\text{CH}_2=\text{CHB}(\text{OC}_4\text{H}_9)\text{R}$.⁸ The anion **5** rearranges at room temperature with intramolecular displacement of bromide by R, which migrates from electron-rich boron to electron-deficient carbon. Relative migration rates are mesityl > 2,5-dimethylphenyl > phenyl > ethyl.

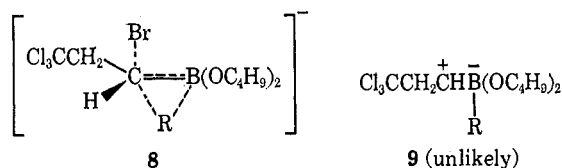
Our postulated transition state (**8**) is typical of intramolecular alkyl or aryl migrations to electron-deficient atoms. We argued that unassisted ionization of bromide to leave an intermediate zwitterion (**9**) is

(1) E. Khotinsky and M. Melamed, *Chem. Ber.*, **42**, 3090 (1909).
 (2) H. C. Brown, *Accounts Chem. Res.*, **2**, 65 (1969); H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.
 (3) D. S. Matteson and R. W. H. Mah, *J. Amer. Chem. Soc.*, **85**, 2599 (1963).
 (4) H. C. Brown, M. M. Rogié, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 818, 1911 (1968).

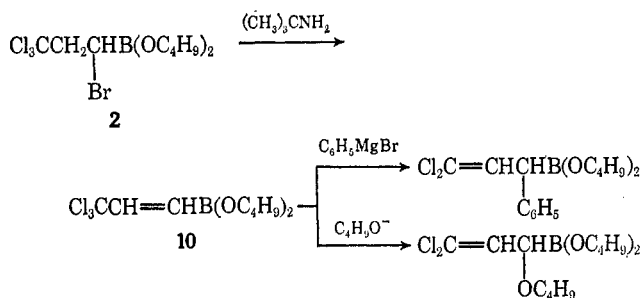
(5) D. S. Matteson, *ibid.*, **82**, 4228 (1960).
 (6) D. S. Matteson, *Organometal. Chem. Rev.*, **1**, 1 (1966).
 (7) D. S. Matteson, *Progr. Boron Chem.*, **3**, 117 (1970).
 (8) D. S. Matteson and R. W. H. Mah, *J. Org. Chem.*, **28**, 2171 (1963).



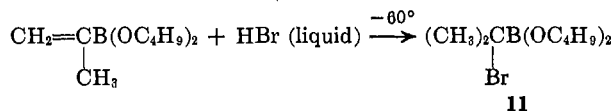
unlikely, since rearrangement of analogous carbonium ions is often concerted with their formation and there is no obvious energy barrier to the highly exothermic rearrangement of **9**.³ We would have liked to prove the stereospecificity but could imagine no practical way to do so. All subsequent evidence supports transition states analogous to **8** as being the general path of boron-assisted nucleophilic displacements.



After trying several other bases without success, we found that *t*-butylamine dehydrobrominates the α -bromo boronic ester **2**. The unsaturated product **10** undergoes facile S_N2' displacements with phenylmagnesium bromide or sodium butoxide.⁹

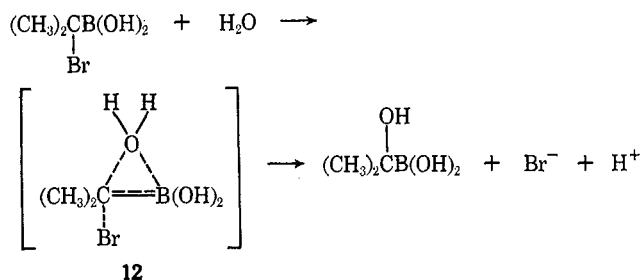


Simple α -Haloalkaneboronic Esters. The trichloromethyl group of **2** was an extraneous structural leftover from the synthetic method, and we naturally wanted to examine displacement reactions of simpler α -halo boronic esters as soon as we could find a way to make them. Ionic addition of hydrogen bromide or iodide to unsaturated boronic esters led to the desired compounds, though substantial proportions of unwanted β -halo isomers were obtained in some cases. Dibutyl 2-bromopropane-2-boronate (**11**) was the



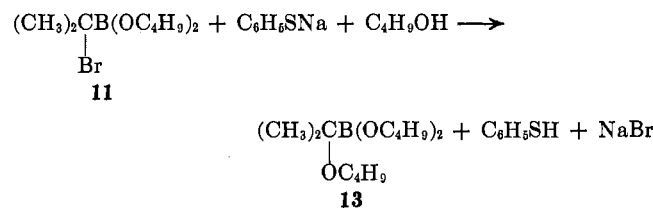
easiest of the series to make.¹⁰ We examined a variety of displacements on this halide (**11**) and measured ki-

netics of solvolysis in aqueous ethanol.¹¹ Bromide is displaced from **11** by hydroxide ion so rapidly that no stable titration end point above pH 4 can be reached without consuming the bromo compound, and the solvolysis was therefore followed by estimating the liberated hydrobromic acid with a pH meter. All evidence points toward a concerted displacement of bromide ion by water with assistance from the boronic acid group. (Dissolving the butyl ester in aqueous ethanol yields an equilibrium mixture of boronic acid



and esters.) The transition state **12** is closely related to that proposed for intramolecular rearrangements (**8**), though **12** probably has some carbonium ion character and weaker bonding. The Grunwald-Winstein dependence m of $\log k$ on a solvent composition parameter is 0.7, less than that of typical carbonium ion formation ($m = 1.0$) but more than typical values for concerted displacements ($m \sim 0.3$).¹² In 50% ethanol ΔS^\ddagger for the boronic ester **11** is -15 eu, significantly more negative than the -1 eu reported for *t*-butyl chloride solvolysis.¹³

Participation by the boron atom in the transition state is clearly indicated by the peculiar behavior of dibutyl 2-bromopropane-2-boronate (**11**) toward sodium



thiophenolate in butanol.¹¹ Similar behavior was observed with $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)\text{BrB}(\text{OC}_4\text{H}_9)_2$.¹⁴ The observed exclusive formation of the butoxy derivative **13** must overcome two seemingly impossible obstacles. The concentration of $\text{C}_6\text{H}_5\text{S}^-$ is probably $>10^3$ times that of $\text{C}_4\text{H}_9\text{O}^-$, because thiophenol is much more acidic than butanol, and $\text{C}_6\text{H}_5\text{S}^-$ would be ten times more reactive than $\text{C}_4\text{H}_9\text{O}^-$ in a typical nucleophilic displacement on carbon. However, boron forms much stronger bonds to oxygen than to sulfur, and the equilibrium concentration of the butoxide complex anion **14** might easily exceed that of the sulfur analog **15**. Departure of the bromide ion is probably directly

(11) D. S. Matteson and G. D. Schaumberg, *J. Org. Chem.*, **31**, 726 (1966).

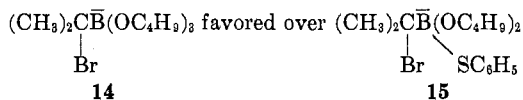
(12) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948); S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951).

(13) S. Winstein and A. H. Fainberg, *ibid.*, **79**, 5937 (1957).

(14) D. S. Matteson, R. A. Bowie, and G. Srivastava, *J. Organometal. Chem.*, **16**, 33 (1969).

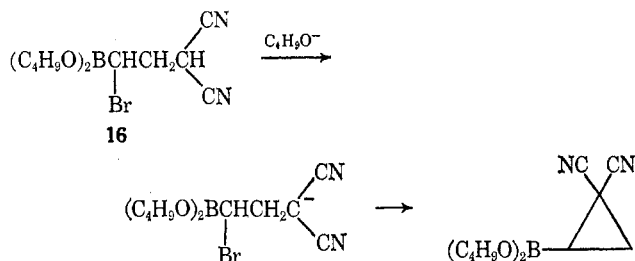
(9) D. S. Matteson and R. W. H. Mah, *J. Org. Chem.*, **28**, 2174 (1963).

(10) D. S. Matteson and J. D. Liedtke, *Chem. Ind. (London)*, 1241 (1963).



assisted by the migrating butoxide or mercaptide, but with some development of carbonium ion character at the carbon so that relative concentrations of anions **14** and **15**, not nucleophilicities of migrating groups, dominate the outcome. Structural changes which would increase the sensitivity to nucleophilicity reverse the outcome, and thus $\text{CH}_3\text{CHBrB}(\text{OC}_3\text{H}_7)_2$ yields the thioether, $\text{CH}_3\text{CH}(\text{SC}_6\text{H}_5)\text{B}(\text{OC}_3\text{H}_7)_2$.¹¹

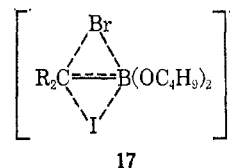
We were unable to alkylate malonic ester with the α -bromo boronic esters discussed so far, apparently because boron promotes competing displacement of bromide by alkoxide so effectively. We decided to take advantage of this tendency in planning a synthesis of a boron-substituted pyrimidine to be tested as a possible agent for the therapy of brain tumors by the nuclear reaction $^{10}\text{B} + ^1_0\text{n} \rightarrow ^7\text{Li} + ^4\text{He}$. Radical-catalyzed addition of bromomalononitrile to dibutyl vinylboronate gave dibutyl 1-bromo-3,3-dicyanopropane-1-borinate (**16**), and we hoped that alkoxide would replace the bromide first, allowing base-catalyzed condensation of the malononitrile function with urea to form a pyrimidine. Nature can be frustrating, and it turned out that bases close **16** to a cyclopropane by an intramolecular malononitrile alkylation.¹¹



Except for the foregoing example, the strong preference shown by α -bromo boronic esters for displacement of bromide by alkoxide rather than by other nucleophiles was an impediment to our synthetic objectives. Our reactivity trends implied that nucleophilicity might predominate over basicity in attack on a halomethaneboronic ester, $\text{XCH}_2\text{B}(\text{OR})_2$, making possible substitutions by amines, malonic ester anion, and other synthetically useful nucleophiles. However, a totally new synthetic approach had to be devised in order to make a halomethaneboronic ester. Chlorination of di-*t*-butyl methaneboronate with *t*-butyl hypochlorite yielded tantalizing but impractically small amounts of $\text{ClCH}_2\text{B}(\text{OR})_2$.¹⁵ The practical solution began with ICH_2HgI , a "novel" organometallic first reported in 1880,¹⁶ which reacts with boron tribromide to form ICH_2BBr_2 and related halides. These are converted to $\text{ICH}_2\text{B}(\text{OC}_4\text{H}_9)_2$ with butanol and sodium iodide.¹⁷ In accord with our expectations, ICH_2B -

$(\text{OC}_4\text{H}_9)_2$ gave the desired replacement of iodide by a variety of nucleophiles, including amines, mercaptopyrimidines, malononitrile, malonic ester, acetamidomalonic ester, and enamines.¹⁷ None of these derivatives showed any useful tendency to accumulate in brain tumors.

Because it is a good nucleophile but an extremely weak base, iodide ion displaces bromide from α -boronic esters without interfering side reactions, and semiquantitative measurements of relative rates of this displacement are easy to make. From competition experiments with allyl bromide and literature values for other alkyl halides, we have estimated the rate ratios $(\text{CH}_3)_2\text{CBBr}(\text{OC}_4\text{H}_9)_2/(\text{CH}_3)_2\text{CHBr} = 1600$ and $\text{CH}_3\text{CHBrB}(\text{OC}_4\text{H}_9)_2/\text{CH}_3\text{CH}_2\text{Br} = 150$.¹¹ The ratio for the two boronic esters is 1:4, which shows a very small steric retardation as a result of chain branching, and their reactivities are close to that of allyl bromide. The postulated transition state (**17**) is fundamentally similar to those for alkyl migration (**8**) and hydrolysis (**12**).



Both halides are shown as interacting with boron because if both were identical (isotopic exchange) the principle of microscopic reversibility would require that they be equivalent, at least in the statistical average, as pointed out by Bartlett and Trachtenberg for analogous carbonyl-activated halide exchange.¹⁸ Because the bonding of halide to boron is weak, these reactions are probably much less accelerated than those involving attack of strong bases on α -bromo boronic esters, and it is unlikely that the transition state **17** is preceded by an anionic intermediate, $\text{R}_2\text{CBBr}(\text{OC}_4\text{H}_9)_2\text{I}^-$.

We still have not proved the stereochemistry of migrations from boron to carbon, but this has now been done with boranes derived from hydroborations. Migrating hydride displaces halide with inversion,¹⁹ and the stereochemistry of certain complex halogenation-rearrangement-elimination sequences starting from alkenylboranes also requires inversion.²⁰ Migrating alkyl groups retain their configuration.²¹

The future synthetic importance of alkyl migrations from boron to carbon is suggested by the alkylation of ethyl bromoacetate with trialkylboranes derived from hydroboration (Scheme I).^{4,22} Many more examples of this very promising approach to organic synthesis could be cited, but Professor Brown can speak for himself in his own reviews.

β Eliminations. Radical-catalyzed addition of HBr to

(18) P. D. Bartlett and E. N. Trachtenberg, *J. Amer. Chem. Soc.*, **80**, 5808 (1958).

(19) D. J. Pasto and J. Hickman, *ibid.*, **89**, 5608 (1967).

(20) G. Zweifel, H. Arzoumanian, and C. C. Whitney, *ibid.*, **89**, 3652 (1967).

(21) H. C. Brown, M. M. Rogi, M. W. Rathke, and G. W. Kabalka, *ibid.*, **91**, 2150 (1969).

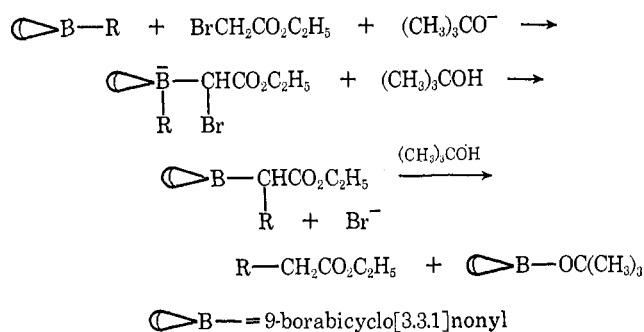
(22) H. C. Brown and M. M. Rogi, *ibid.*, **91**, 2146 (1969).

(15) D. S. Matteson, *J. Org. Chem.*, **29**, 3399 (1964).

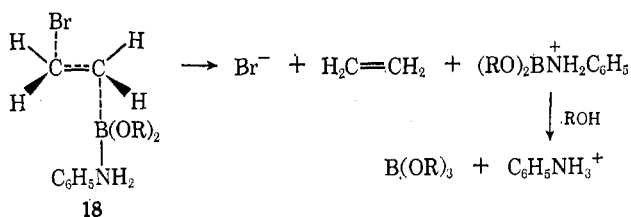
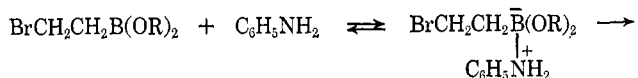
(16) J. Sakurai, *J. Chem. Soc.*, **37**, 658 (1880).

(17) (a) D. S. Matteson and T. C. Cheng, *J. Organometal. Chem.*, **6**, 100 (1966); (b) D. S. Matteson and T. C. Cheng, *J. Org. Chem.*, **33**, 3055 (1968).

Scheme I

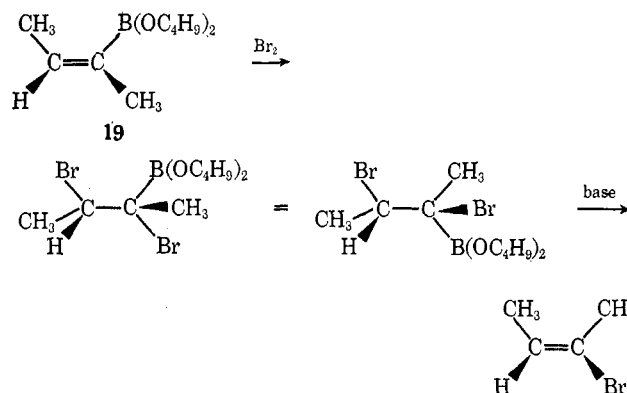


dibutyl vinylboronate furnished $\text{BrCH}_2\text{CH}_2\text{B}(\text{OC}_4\text{H}_9)_2$, and the β -boronic ester group accelerates somewhat the reaction with sodium iodide in acetone to form $\text{ICH}_2\text{CH}_2\text{B}(\text{OC}_4\text{H}_9)_2$.²³ Other than that, all slightly basic nucleophiles tested gave synthetically useless β elimination of boron and bromide. "Because it was there," we undertook a mechanistic study of deboronobromination.²⁴ For amine-catalyzed deboronobromination in ethanol, transition state **18** is supported by kinetics, deviation of $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ from a Brønsted correlation of $\text{XC}_6\text{H}_4\text{NH}_2$ rates, and lack of any solvent deuterium isotope effect in $\text{C}_2\text{H}_5\text{OD}$. The mechanism of solvolytic deboronobromination appears similar, with



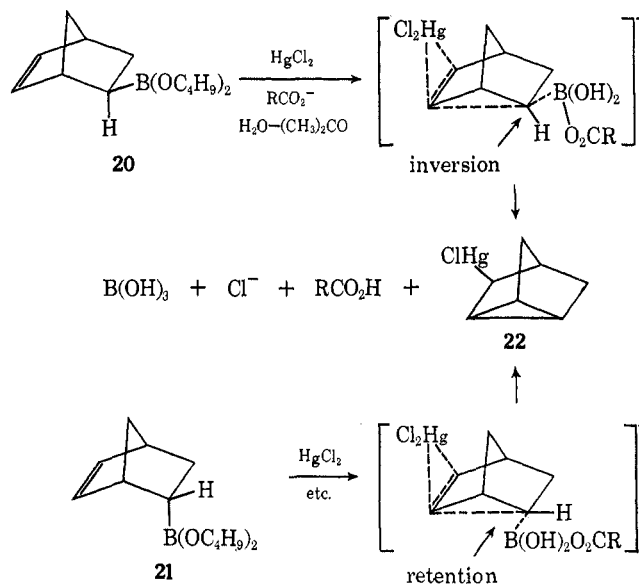
a molecule of solvent taking the place of the amine so that the leaving electrophilic group is $(\text{RO})_2\text{B}(\text{OHR})^+$. The rate is very sensitive to the basicity of the solvent and the Grunwald-Winstein m is low, 0.4. With strong bases such as hydroxide the rate of deboronobromination is extremely rapid, in this respect resembling displacement reactions of α -bromo boronic esters. The nature of the boron-containing leaving group in elimination reactions is consistent with our interpretations both of the activating influence of boron in displacements at the α carbon and of the leaving groups found in electrophilic displacements of boron, to be discussed in the following section.

The *trans* stereochemistry of the β elimination was supported by a bromination-elimination sequence starting from dibutyl *trans*-2-butene-2-boronate (**19**).²⁴ The *cis* isomer of **19** led to 2-bromo-*trans*-2-butene. Evidence for acid- and base-catalyzed *trans* eliminations in hydroboration sequences has been reported, with *cis* elimination occurring in uncatalyzed reactions.²⁶



Electrophilic Displacement of Boron

Transannular Displacements. Boron is a good leaving electrophile, whether the experimenter likes it or not, and there is a constant temptation to join the thermodynamic trend and study deboronation mechanisms. Dibutyl *exo*- and *endo*-5-norbornene-2-boronate (**20** and **21**), the Diels-Alder adducts of dibutyl vinylboronate with cyclopentadiene,²⁶ seemed likely candidates for transannular electrophilic displacements. The thought of ruining good boronic esters was ameliorated by choosing another metal for the attacking electrophile. Mercuric chloride smoothly converted either isomer (**20** or **21**) to the same crystalline product, nortricycylmercuric chloride (**22**).²⁷



Reaction of the *exo* isomer **20** inverts the carbon from which the boron departs and is 400 times faster than reaction of the *endo* isomer **21** (retention) in 75% acetone at 25°. This preference for inversion in an electrophilic displacement was unexpected on the basis of most previous literature, though one prior example in a cyclopropane opening had been reported.²⁹

The attacking electrophile in the ring closure of **20** or

(23) D. S. Matteson and J. D. Liedtke, *J. Org. Chem.*, **28**, 1924 (1963).

(24) D. S. Matteson and J. D. Liedtke, *J. Amer. Chem. Soc.*, **87**, 1526 (1965).

(25) D. J. Pasto and R. Snyder, *J. Org. Chem.*, **31**, 2777 (1966).

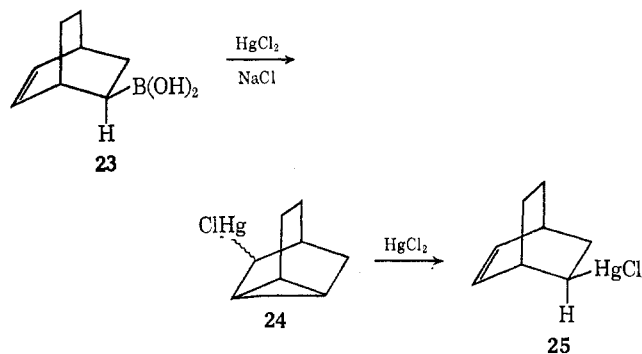
(26) D. S. Matteson and J. O. Waldbillig, *ibid.*, **28**, 366 (1963).

(27) D. S. Matteson and J. O. Waldbillig, *J. Amer. Chem. Soc.*, **85**, 1019 (1963); **86**, 3778 (1964).

(28) D. S. Matteson and M. L. Talbot, *ibid.*, **89**, 1119 (1967).

(29) S. J. Cristol and R. T. LaLonde, *ibid.*, **80**, 4355 (1958).

21 is a carbon atom made electrophilic by the mercuric chloride when it complexes with the double bond. The stereochemistry of the mercury attack has not been proved in this case, but *exo* addition is expected. The $^{10}\text{B}/^{11}\text{B}$ isotope effect provides evidence that carbon-boron bond breaking takes place in the rate-determining step.³⁰ Further support for the proposed mechanism



was obtained with the bicycloocteneboronic acids. The *exo* isomer **23** again reacts much faster than the *endo*, but in this case the tricyclooctylmercuric chloride **24** initially formed is less stable than its bicyclic isomer (**25**), which therefore cannot be an intermediate.³¹

Other examples of inversion in cyclopropane ring openings by electrophilic displacement have been reported,³² but my current opinion is that cyclopropyl systems may be governed mainly by their own peculiar orbital arrangement and are not valid models for electrophilic displacements in general.³³ Recently observed examples of inversion in the replacement of lithium by bromine may have more general significance.³⁴

Unassisted Displacements. The unexpected preference for inversion in the transannular displacement reactions of **20** and **21** prompted us to examine the stereochemistry of an ordinary mercurideboronation. We resolved dibutyl 1-phenylethaneboronate (**26**) by way of the chelate with bisdemethylbrucine and showed that mercuric chloride displaces the boronic ester group with predominant retention.³⁵ The reaction is first order in boronic ester, mercuric chloride, and hydroxide ion in the presence of sodium chloride, which represses ionization of HgCl_2 , and glycerol, which catalyzes the reaction by forming a reactive cyclic boronic ester.³⁶ Studies on a series of substituted benzylboronic esters have indicated that electronic and steric effects are small.^{14,36} The Hammett correlation found with four benzylboronic esters is shown in Figure 1.

(30) D. S. Matteson, J. O. Waldbillig, and S. W. Peterson, *J. Amer. Chem. Soc.*, **86**, 3781 (1964).

(31) D. S. Matteson and M. L. Talbot, *ibid.*, **89**, 1123 (1967).

(32) (a) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *ibid.*, **88**, 3354 (1966); (b) C. H. DePuy, F. H. Breitbeil, and K. R. DeBruin, *ibid.*, **88**, 3347 (1966).

(33) D. S. Matteson, *Organometal. Chem. Rev.*, **A**, **4**, 263 (1969).

(34) (a) D. E. Applequist and G. N. Chmurny, *J. Amer. Chem. Soc.*, **89**, 875 (1967); (b) W. H. Glaze and C. M. Selman, *J. Organometal. Chem.*, **11**, P3 (1968).

(35) D. S. Matteson and R. A. Bowie, *J. Amer. Chem. Soc.*, **87**, 2587 (1965).

(36) D. S. Matteson and E. Krämer, *ibid.*, **90**, 7261 (1968).

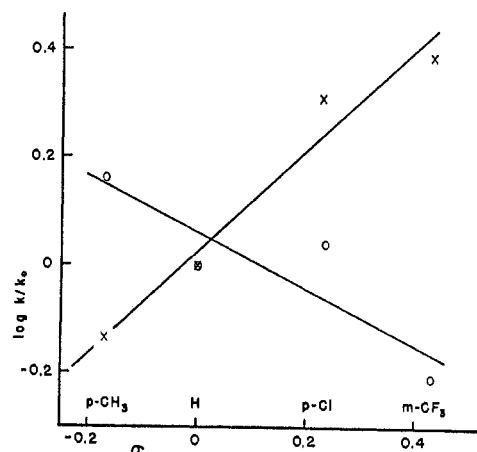
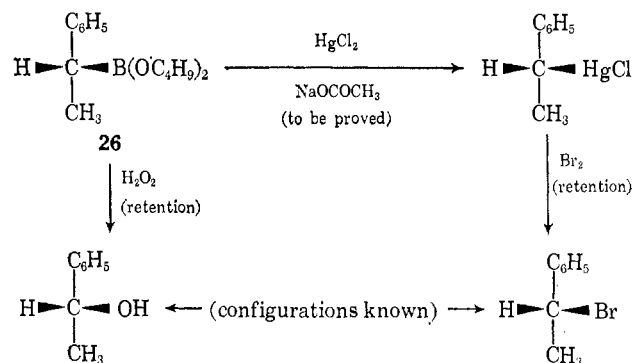


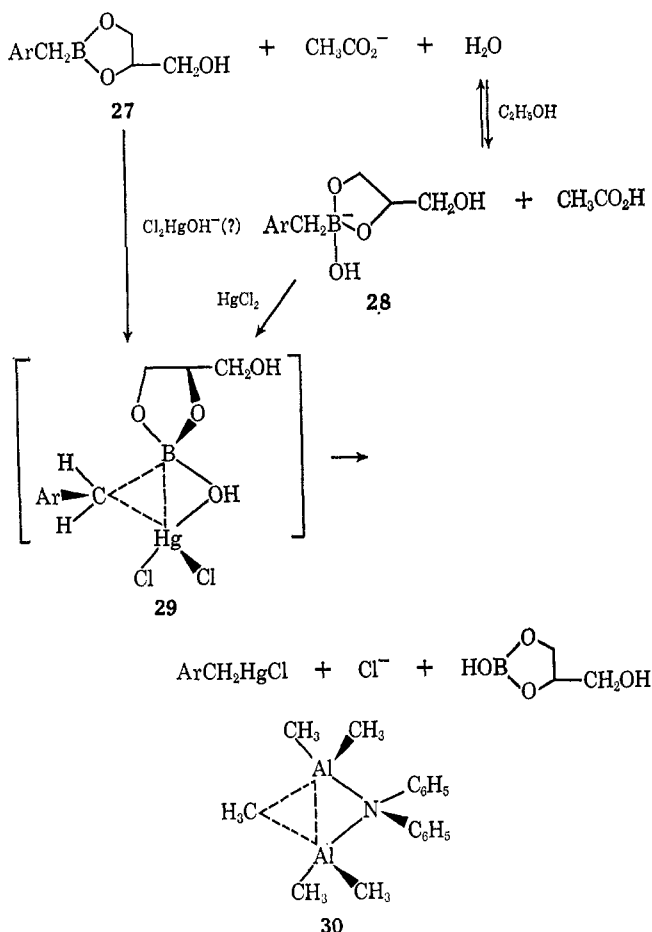
Figure 1. Hammett correlation of rates of reaction of benzylboronic esters with mercuric chloride. X, measured k values; O, k values derived by taking pK_a values into account.³⁶



The electron density at the site of displacement is slightly higher in the transition state than in the starting boronic ester **27** ($\rho = +0.9$) but somewhat lower than in the possibly intermediate sodium salt **28** ($\rho = -0.5$). An α -methyl substituent reduced the rate only by a factor of 2 and appeared to make the overall ρ become negative, but instability of the products $\text{ArCH}(\text{CH}_3)\text{-HgCl}$ interfered with obtaining accurate rates so that the results are only qualitative.¹⁴ The structure we postulated for transition state **29**³⁶ resembles the stable compound $\text{Al}_2(\text{CH}_3)_5\text{N}(\text{C}_6\text{H}_5)_2$ (**30**) recently characterized by X-ray crystallography.³⁷

Quantum mechanical symmetry rules require the three-center bonds drawn in the transition state model **29** and the methyl-bridged dialuminum compound **30**. In **30**, each aluminum atom and the bridging carbon contribute one sp^3 orbital to the three-center molecular orbital, to which only one electron pair can be assigned. The Al-Al orbital overlap cannot be zero, and the occupied molecular orbital has bonding character between each pair of the three atoms.³³ The bonding energy that can be attributed to direct Al-Al interaction is only a few kilocalories per mole, much smaller than the C-Al energy, because the electron density in the aluminum orbitals is relatively low.³⁷ In contrast, the Al-N-Al bridge on the other side of the molecule (**30**) is assigned two electron pairs, and quantum mechanical symmetry

(37) V. R. Magnuson and G. D. Stucky, *ibid.*, **91**, 2544 (1969).

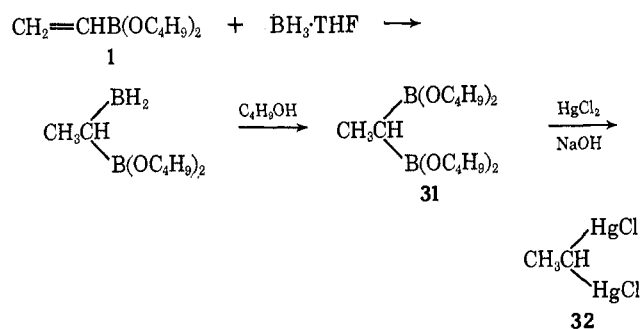


rules factor the filled orbitals into two localized bonds with no net direct Al-Al bonding.

Winstein, Traylor, and Garner in 1955 pointed out the likelihood of three-center bonding in transition states for electrophilic displacement.³⁸ All our experimental evidence regarding **29** is consistent with this interpretation.³⁸ However, the inherent impossibility of constructing any real analog of **29** or **30** which lacks the metal-metal bond (just as "localized benzene" is an artificial concept) makes experimental estimation of the magnitude of metal-metal bonding elusive. Anyone not committed to faith in quantum theory (especially its simplified versions) may doubt that such bonding is real. We hope that accelerations of electrophilic displacements by neighboring metal atoms, to be discussed in the next section, may provide further support for the simple quantum mechanical interpretation.

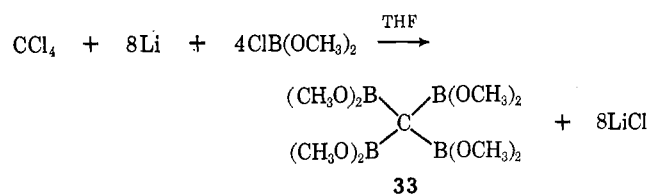
Methanetetraboronic and Methanediboronic Esters.

The first *gem*-diboronic ester was synthesized from dibutyl vinylboronate (**1**) by hydroboration.^{39,40} Conversion of tetrabutyl ethane-1,1-diboronate (**31**) to 1,1-bis(chloromercuri)ethane (**32**) with mercuric chloride and sodium hydroxide at 0° was very rapid.³⁹ Unsubstituted boronic esters appeared to react slowly or not



at all with mercury(II),^{14,27} and these results therefore implied that displacement of the first boron was accelerated by the presence of the second, and displacement of the second boron was aided by the α -chloromercuri group.

We next found a synthesis of methanediboronic acid, $\text{CH}_2[\text{B}(\text{OH})_2]_2$, from $\text{CH}_2(\text{HgI})_2$.¹⁷ The more boron the better, and Castle suggested that the synthesis of $\text{C}[\text{Si}(\text{CH}_3)_3]_4$ by Merker and Scott⁴¹ might be adapted to boron compounds. After a considerable search for the right conditions, we found that reaction of carbon tetrachloride, lithium dispersion, and dimethoxyboron chloride in tetrahydrofuran at -30° yielded crystalline octamethyl methanetetraboronate (**33**).⁴² Similarly,



chloroform has been converted to $\text{HC}[\text{B}(\text{OCH}_3)_2]_3$ and other corresponding halides to $\text{CH}_2[\text{B}(\text{OCH}_3)_2]_2$, $\text{C}_6\text{H}_5\text{-C}[\text{B}(\text{OCH}_3)_2]_3$, $\text{C}_6\text{H}_5\text{CH}[\text{B}(\text{OCH}_3)_2]_2$, and $\text{CH}_3\text{C}[\text{B}(\text{OCH}_3)_2]_3$.⁴² All our current research on boronic esters naturally centers on these novel compounds.

Methanetetraboronic ester (**33**) reacts with bases in aprotic media to form tris(dimethoxyboryl)methide ion (**34**) or, if **34** is not actually liberated, an anionic species which readily transfers **34** to attacking electrophiles.⁴² For example, triphenyltin chloride and **34** yield triphenylstannyltris(dimethoxyboryl)methane (**35**). Treatment of **35** with base evidently removes another boron, and disproportionation to bis(triphenylstannyl)-bis(dimethoxyboryl)methane (**36**) follows.⁴³

Alkylation of the triborylmethide ion **34** tends to be followed by boron transfer between the initial product (**37**) and unconsumed carbanion (**34**), which leads to dialkylation.^{42,44} With methyl iodide a mixture of 1,1,1-tris(dimethoxyboryl)ethane (**37**) and 2,2-bis(dimethoxyboryl)propane (**38**) results, and we have not found any way to obtain one product without the other or to separate the mixture without resort to gas chromatography.

(38) S. Winstein, T. G. Traylor, and C. S. Garner, *J. Amer. Chem. Soc.*, **77**, 3741 (1955).

(39) D. S. Matteson and J. G. Shdo, *ibid.*, **85**, 2684 (1963); *J. Org. Chem.*, **29**, 2742 (1964).

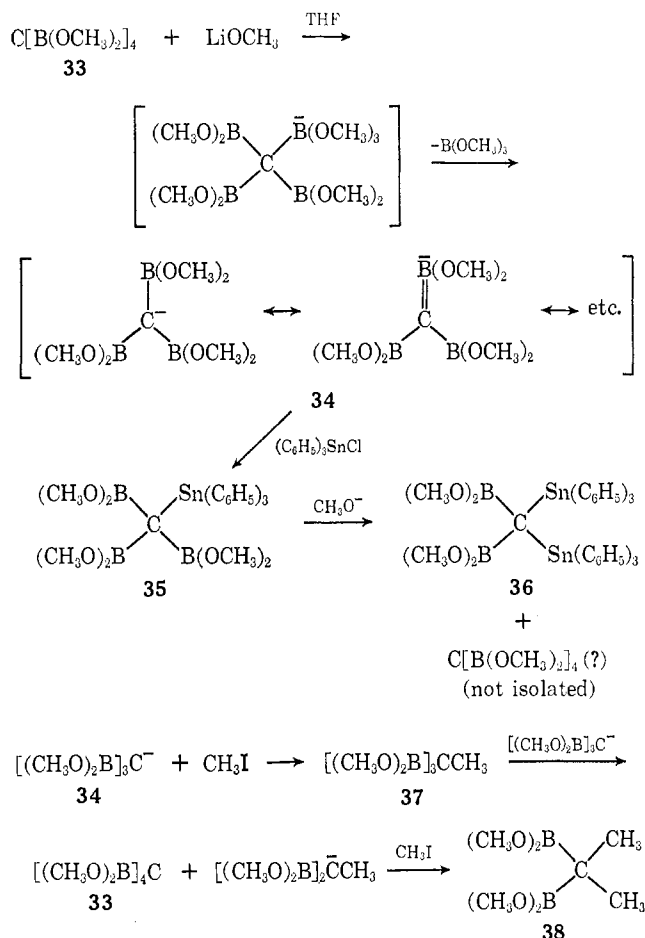
(40) B. M. Mikhailov and P. M. Aronovich, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1233 (1963).

(41) R. L. Merker and M. J. Scott, *J. Org. Chem.*, **29**, 953 (1964).

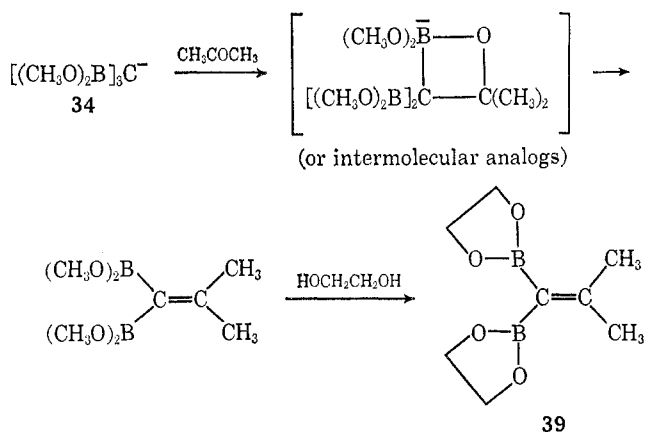
(42) R. B. Castle and D. S. Matteson, *J. Amer. Chem. Soc.*, **90**, 2194 (1968); *J. Organometal. Chem.*, **20**, 19 (1969).

(43) D. S. Matteson and G. L. Larson, *J. Amer. Chem. Soc.*, **91**, 6541 (1969).

(44) D. S. Matteson and J. R. Thomas, *J. Organometal. Chem.*, submitted for publication.



Reaction of the carbanion **34** with ketones or aldehydes yields 1,1-bis(dimethoxyboryl)alkenes. The product from acetone is most easily isolated as the crystalline ethylene glycol ester (**39**).⁴⁵



Prior to our work on methanetetra-boronic ester (**33**), the conversion of 1,1-diborylalkanes, $(\text{R}_2\text{B})_2\text{CHCH}_2\text{R}'$, with butyllithium to α -lithio boranes, $\text{R}_2\text{BCHLiCH}_2\text{R}'$, had been described.^{46,47} These α -lithio boranes undergo reactions analogous to those of the triborylmethide ion **35**, for example, condensation with aldehydes or ketones to form olefins.⁴⁶

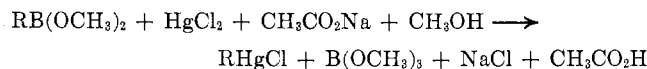
(45) D. S. Matteson and T. B. Tripathy, *J. Organometal. Chem.*, **21**, P6 (1970).

(46) G. Cainelli, G. Dal Bello, and G. Zubiani, *Tetrahedron Lett.*, 4329 (1965); 4315 (1966).

(47) G. Zweifel and H. Arzoumanian, *ibid.*, 2535 (1966).

The triborylmethide ion **34** bears obvious analogy to the carbanion from malonic ester, but an essential difference between carboxylic and boronic ester chemistry should be noted. It is always easier to abstract the unit $(\text{CH}_3\text{O})_2\text{B}^+$ than H^+ where a choice is available. For example, treatment of $\text{HC}[\text{B}(\text{OCH}_3)_2]_3$ with alkyl-lithium gives the anion $[(\text{CH}_3\text{O})_2\text{B}]_2\text{CH}^-$, not $[(\text{CH}_3\text{O})_2\text{B}]_3\text{C}^-$, and alkylation with benzyl bromide yields $\text{C}_6\text{H}_5\text{CH}_2\text{CH}[\text{B}(\text{OCH}_3)_2]_2$,⁴⁴ not the mixture of $\text{C}_6\text{H}_5\text{CH}_2\text{C}[\text{B}(\text{OCH}_3)_2]_3$ and $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}[\text{B}(\text{OCH}_3)_2]_2$ which results from analogous reaction of $\text{C}[\text{B}(\text{OCH}_3)_2]_4$.⁴² Sodium methoxide in methanol degrades $\text{C}[\text{B}(\text{OCH}_3)_2]_4$ irreversibly to $\text{CH}_2[\text{B}(\text{OCH}_3)_2]_2$, with no evidence of accumulation of the intermediate $\text{HC}[\text{B}(\text{OCH}_3)_2]_3$.⁴²

Concerted electrophilic displacement of boron by mercury(II) has been described earlier in this review. We have recently begun a quantitative study of neighboring-group effects in such displacements, comparing the reactivities of $\text{CH}_2[\text{B}(\text{OCH}_3)_2]_2$ and other newly available boronic esters with that of $\text{CH}_3\text{B}(\text{OCH}_3)_2$.⁴⁸ The reactions proceed at convenient rates in methanol buffered with sodium acetate and acetic acid. We



followed the kinetics by estimating the remaining HgCl_2 with dithizone spectrophotometrically and have found that the rate law is

$$-d[\text{HgCl}_2]/dt =$$

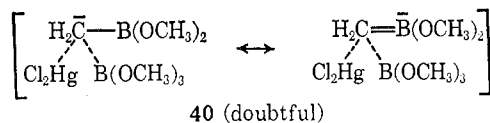
$$k[\text{RB}(\text{OCH}_3)_2][\text{HgCl}_2][\text{CH}_3\text{CO}_2\text{Na}]/[\text{CH}_3\text{CO}_2\text{H}]$$

Relative rates at 30° are summarized in Table I.

Table I
Relative Rates per Boron of Reaction with HgCl_2 in Methanol

Compound	k/k_0
$\text{CH}_3\text{B}(\text{OCH}_3)_2$	1
$\text{CH}_2[\text{B}(\text{OCH}_3)_2]_2$	98
$\text{ClHgCH}_2\text{B}(\text{OCH}_3)_2$	3.0
$\text{C}_6\text{H}_5\text{CH}_2\text{B}(\text{OCH}_3)_2$	0.4
$\text{HC}[\text{B}(\text{OCH}_3)_2]_3$	~135
$\text{C}[\text{B}(\text{OCH}_3)_2]_4$	~6

Can the 100-fold rate increase caused by a neighboring boron be attributed to electron delocalization from an electron-rich displacement site to the boron in transition state **40**? This interpretation appears in-

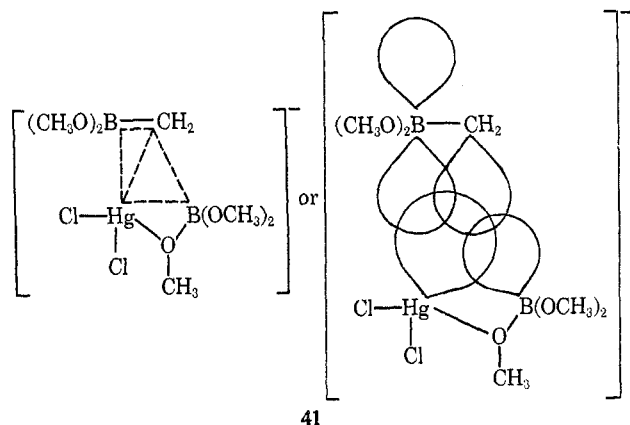


adequate for several reasons. The chloromercuri group, a poor π -bonding substituent, activates the boron toward displacement, while phenyl, a good π -bonding group, deactivates (Table I). There appears to be little charge density at the displacement site anyway, according to our Hammett correlation.³⁶ The rate law excludes any free carbanion intermediate. If in spite of these observations there were an anomalously

(48) D. S. Matteson and P. G. Allies, *J. Amer. Chem. Soc.*, **92**, 2672 (1970).

high degree of carbanion character in the reaction of $\text{CH}_2[\text{B}(\text{OCH}_3)_2]_2$, then $\text{HC}[\text{B}(\text{OCH}_3)_2]_3$ and $\text{C}[\text{B}(\text{OCH}_3)_2]_4$, which are normally much better carbanion sources,⁴³⁻⁴⁵ ought to be many times more reactive than observed.

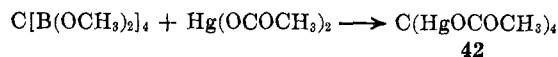
The three-center bonded transition-state model **29** discussed earlier appears satisfactory for interpretation of these new results. The vacant p orbital of the neighboring boron could further delocalize the electron pair from the three-center bond in transition state **41**.



Simple molecular orbital calculations suggest significant stabilization from such delocalization. Ligand bridging ($\text{Hg}-\text{Cl}-\text{B}$) may also contribute. The neighboring mercury in $\text{ClHgCH}_2\text{B}(\text{OCH}_3)_2$ could provide analogous though weaker stabilization, but the phenyl in $\text{C}_6\text{H}_5\text{CH}_2\text{B}(\text{OCH}_3)_2$ could not. Transition state **41** does not require moving the neighboring $(\text{CH}_3\text{O})_2\text{B}$ group from its initial position, but does freeze out its rotation. In accord with this requirement, a brief study of temperature dependence has indicated that ΔS^* is about 10 eu more negative for $\text{CH}_2[\text{B}(\text{OCH}_3)_2]_2$ than for $\text{CH}_3\text{B}(\text{OCH}_3)_2$.

The somewhat lowered reactivity of $\text{C}[\text{B}(\text{OCH}_3)_2]_4$ (compared with $\text{HC}[\text{B}(\text{OCH}_3)_2]_3$) toward mercury(II) is

consistent with the concerted displacement mechanism and is attributed to steric hindrance. All four boron atoms are replaced by mercuric acetate in refluxing ethanol.⁴⁹ Tetrakis(acetoxymethyl)mercuric methane (**42**) is



soluble in aqueous acetic acid. It yields a white hydroxide precipitate, which clearly distinguishes it from mercurous or mercuric salts, and with stannous chloride it forms white $\text{C}(\text{HgCl})_4$, which is not reduced. The bromide $\text{C}(\text{HgBr})_4$ reacts with bromine vapor to form carbon tetrabromide.

There is enough room around the central carbon to pack four mercury atoms. A carbon-mercury distance of 2.07 Å⁵⁰ leaves 3.4 Å between mercury atoms, which exceeds the van der Waals distance by 0.1-0.3 Å.⁵⁰ This does not leave much space for squeezing out the last boron simultaneously with the attack of the last mercury. The transition-state model we have proposed (**41**), with electron delocalization to neighboring mercury, would permit the necessary close packing and narrow B-C-Hg bond angle.

Most salts of $\text{C}(\text{Hg}^+)_4$ are extremely insoluble. The nitrate precipitates slowly but does not redissolve in concentrated nitric acid, as if it were an oxygen-bridged cationic polymer. The yellow iodide, $\text{C}(\text{HgI})_4$, shows some solubility in sodium iodide solutions in water or aprotic solvents. By undermining the previous record established in 1881 with $\text{HC}(\text{HgI})_3$,⁵¹ the 0.9% carbon content of $\text{C}(\text{HgI})_4$ sets a new low for organic chemistry.

I thank the National Science Foundation (Grant GP-9320 and predecessors) and the National Cancer Institute (Grant CA-05513) for financial support and the Alfred P. Sloan Foundation for a fellowship (1966-1968).

(49) D. S. Matteson, R. B. Castle, and G. L. Larson, *J. Amer. Chem. Soc.*, **92**, 231 (1970).

(50) D. Grdenić, *Quart. Rev. Chem. Soc.*, **19**, 303 (1965).

(51) J. Sakurai, *J. Chem. Soc.*, **39**, 485 (1881).

X-Ray Photoelectron Spectroscopy

JACK M. HOLLANDER AND WILLIAM L. JOLLY

Nuclear Chemistry Division and Inorganic Materials Research Division of the Lawrence Radiation Laboratory and the Department of Chemistry of the University of California, Berkeley, California 94720

Received January 13, 1970

As far as most chemists are concerned, atomic core electrons are as inaccessible and inert as the nucleus, neither contributing to nor being affected by chemical bonding. However the recent development of X-ray photoelectron spectroscopy is rapidly changing this view, and these "forgotten electrons" are playing an important and growing role in chemistry.

X-Ray photoelectron spectroscopy (also called "ESCA" and "XPS") is the study of the energy distri-

bution of the electrons emitted from X-ray-irradiated compounds. In principle all electrons, from the core to the valence levels, can be studied. In this respect the technique differs from ultraviolet photoelectron spectroscopy, in which only the valence electrons can be studied.¹ In this Account we describe this new technique and discuss some of its chemical applications.

(1) A. D. Baker, *Accounts Chem. Res.*, **3**, 17 (1970).