$$\frac{1}{w} = \sigma_F^2 = 0.025 \left( \frac{C + (B/4)}{C - (B/2)} \right)$$

For counts C not greater than B/2, the weight was taken to be zero.

Although counting statistics is of course not the only source of error to be feared, all other sources such as absorption, extinction, and variations in primary beam intensity were ignored in this assignment of weights.

### TABLE II

#### BOND DISTANCES AND ANGLES

	Distance,				
Bond	Å.	σ	Angle	Degrees	ø
Fe-C <sub>1</sub>	1.757	0.009	$Fe-C_1-O_1$	177.1	0.8
$Fe-C_2$	1.771	0.010	$Fe-C_2-O_2$	178.1	0.9
Fe-C <sub>3</sub>	1.749	0.010	FeC <sub>3</sub> -O <sub>3</sub>	178.3	0.9
Fe-C <sub>5</sub>	2.114	0.009	$O_4 - C_4 - C_5$	115.5	0.8
Fe-C <sub>6</sub>	2.067	0.010	$O_4 - C_4 - C_{10}$	121.3	0.9
Fe-C7	2.042	0.010	$C_{3}-C_{4}-C_{10}$	123.0	0.9
Fe-C <sub>8</sub>	2.149	0.010	$C_4 - C_6 - C_6$	127.4	0.8
$O_1 - C_1$	1.160	0.012	$C_{5}-C_{6}-C_{7}$	120.4	0.9
$O_2 - C_2$	1.134	0.012	$C_{6}-C_{7}-C_{8}$	121.4	0.9
O <sub>3</sub> -C <sub>3</sub>	1.170	0.013	$C_{7}-C_{8}-C_{9}$	122.2	0.9
O4-C4	1.248	0.012	$C_8 - C_9 - C_{10}$	126.9	0.9
$C_4 - C_5$	1.492	0.013	$C_4 - C_{10} - C_9$	123.8	0.9
$C_4 - C_{10}$	1.447	0.014			
$C_{3}-C_{6}$	1.442	0.013			
$C_6-C_7$	1.396	0.013			
C7-C8	1.435	0.014			
$C_8 - C_9$	1.463	0.014			
$C_{9}-C_{10}$	1.343	0.014			

After several cycles of least-squares refinement, the R factor is 0.116 for the 1465 observed reflections and 0.065 for the stronger half of these reflections. The final atomic positions and temperature factor along with their estimated standard deviations are listed in Table I.

The view of the molecule given in Fig. 1 clearly shows that the iron atom is bonded to the  $\pi$ -system of

just four of the carbon atoms. The tropone molecule is nonplanar, but can be referred to two planes that intersect at a dihedral angle of about  $47^{\circ}$ . The  $C_4-O_4$  group is displaced from the mean plane of  $C_5-C_8-C_9-C_{10}$  so that  $O_4$  is actually 0.76 Å. out of this plane. This may arise from the packing arrangement, which finds the  $C_4-O_4$  group cradled by a nearby  $Fe(CO)_3$  group.

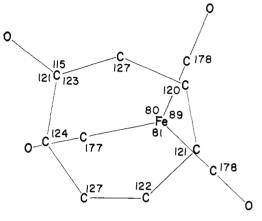


Fig. 3.—Bond angles in  $(C_6H_6CO)Fe(CO)_3$ .

The important bond distances and angles (Table II, Fig. 2 and 3) are all in good agreement with those of Smith and Dahl. It is noteworthy that the shorter distance of 1.396 Å. for  $C_6-C_7$  is likely to be significant in that this shortening is also observed by Smith and Dahl. Likewise, the same effect is observed in the butadiene unit of the cyclooctatetraene complexes of iron tricarbonyl.<sup>7</sup>

Acknowledgment.—The author wishes to thank the authors of the several computer programs for making their efforts generally available, Dr. Walter Hübel of Union Carbide European Research Associates for supplying the samples, and Dr. V. Schomaker for many helpful discussions.

(7) B. Dickens and W. N. Lipscomb, J. Chem. Phys., 37, 2084 (1962).

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# Bisamine Complexes of Boronium Ions. The Reaction of Amine Boranes with Iodine<sup>1</sup>

## By JAMES E. DOUGLASS

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The reaction of amine boranes with iodine in the presence of excess amine is found to be a convenient, general method for the synthesis of bisamine complexes of boronium ions,  $R_2B(amine)_2^+$ .

It is now well established that very stable tetravalent boron cations of the type  $R_2BL_2^+$  can be formed in a number of ways and may conveniently be considered as ligand- (L) stabilized boronium ions. The recent reports of Miller and Muetterties<sup>2</sup> and of Nöth and co-workers<sup>3</sup> clearly delineate the possibilities of formation of unsubstituted cations (H<sub>2</sub>BL<sub>2</sub><sup>+</sup>). Davidson

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 N. E. Miller and E. L. Muetterties, J. Am. Chem. Soc., 86, 1033 (1964).

and French<sup>4</sup> and Mikhailov and co-workers,<sup>5</sup> in particular, have described a number of amine-stabilized organoboronium ions of the type  $R_2B(amine)_2^+$ , where R is either alkyl, cycloalkyl, or aryl. Numer-

(4) J. M. Davidson and C. M. French, J. Chem. Soc., 3364 (1962).

(5) B. M. Mikhailov and T. K. Kosminskaya, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1703 (1963); B. M. Mikhailov, V. D. Sheludyakov, and T. A. Shchegoleva, *ibid.*, 1698 (1962); B. M. Mikhailov and N. S. Fedotov, *ibid.*, 1590 (1960); 1482 (1959); B. M. Mihkailov, N. S. Fedotov, T. A. Shchegoleva, and V. D. Sheludyakov, Dokl. Akad. Nauk SSSR, 145, 340 (1962).

<sup>(3)</sup> H. Nöth, H. Beyer, and H.-J. Vetter, Ber., 97, 110 (1964).

## Table I

RBH(amine)2+ SALTS

<b>C</b>			Analyses, %							
Com- pound	M.p., °C.ª	Formula	Calcd.	Found	Calcd.	H Found	Caled.	N———— Found	Calcd.	Found
IVa	199-202	$C_{16}H_{16}BIN_2$	51.4	51.6	4.28	4.26	7.49	7.29	2.89	2.96
IVb	206 - 209	$C_{16}H_{22}BIN_2$	50.6	48.5	5.80	5.76	7.37	7.27	2.84	2.90
IVe	190 - 195	C <sub>6</sub> H <sub>20</sub> BIN <sub>2</sub>	27.9	28.1	7.81	8.00	10.9	10.6	4.19	4.26
IVd	154 - 158	$C_{18}H_{16}BIN_2$	54.3	54.0	4.05	4.17	7.04	6.98	2.72	2.76
Va	182 - 184	C <sub>16</sub> H <sub>16</sub> BClN <sub>2</sub> O <sub>4</sub>	55.5	55.7	4.65	4.86	8.08	7.79	3.12	3.09
VЪ	220 - 222	C <sub>16</sub> H <sub>22</sub> BClN <sub>2</sub> O <sub>4</sub>	54.5	54.3	6.29	6.25	7.95	7.88	3.07	3.11
Ve	167 - 170	C <sub>6</sub> H <sub>20</sub> BClN <sub>2</sub> O <sub>4</sub>	31.3	31.3	8.75	8.42	12.2	11.5	4.69	4.68
Vd	125 - 127	$C_{18}H_{16}BClN_2O_4$	58.3	57.9	4.35	4.23	7.56	7.60	2.92	2.97

<sup>a</sup> All of the iodides (IVa-d) melt with decomposition.

ous other reports of the preparation of boron cations can be found.  $^{\rm 6}$ 

With but few exceptions, the compounds cited above have been synthesized by one of two methods: (1) the displacement of halogen by base in haloboranes (eq. 1) or (2) the reaction of amine boranes with onium salts at elevated temperatures (eq. 2).

$$R_2BX \cdot L + L \longrightarrow R_2BL_2^+X^-$$
(1)

$$H_3B \cdot L + LH^+X^- \longrightarrow H_2BL_2^+X^- + H_2 \qquad (2)$$

The present work was suggested by the finding<sup>7</sup> in this laboratory that iodine reacts with pyridine phenylborane (I) in the presence of excess pyridine according to eq. 3. Compound II may formally be con-

$$C_{6}H_{5}BH_{2} \cdot C_{5}H_{5}N + I_{2} + 2C_{5}H_{5}N \longrightarrow$$

$$I$$

$$C_{6}H_{5}BH(C_{5}H_{5}N)_{2}+I^{-} + C_{5}H_{5}NH^{+}I^{-} \quad (3)$$

$$II$$

sidered to be the bispyridine adduct of phenylboronium iodide. We now wish to report that this type of reaction affords a convenient, general method for the preparation of bisamine complexes of boronium ions.

### **Results and Discussion**

Iodine was found to react with a selected group of amine boranes (III) in the presence of excess amine to give the iodide salts of bisamine boronium ions (IV).

$$RBH_{2} \cdot amine + I_{2} + 2amine \longrightarrow$$

$$RBH(amine)_{2} + I^{-} + amine H^{+}I^{-} \qquad (4)$$
III
$$IVa, R = C_{6}H_{5}; amine = C_{5}H_{5}N$$

$$b, R = cyclo-C_{6}H_{11}; amine = C_{5}H_{5}N$$

$$c, R = H; amine = (CH_{3})_{3}N$$

$$d, R = H; amine = C_{9}H_{7}N$$

(7) J. E. Douglass, J. Am. Chem. Soc., 84, 121 (1962).

The metathesis of the iodides (IVa-d) with silver perchlorate yields the corresponding perchlorates (Va-d). As these latter compounds burn with near explosive violence, prudence dictates that they be prepared in only very small amounts.

The identities of compounds IVa-d and Va-d were established by their elemental analyses (Table I) and by their infrared spectra (Table II).

### TABLE II

### INFRARED SPECTRA

Band, cm1	Compound	Assignment
2430-2600 (singlet)	IVa,b; Va,b	B–H stretching <sup>a</sup>
2400-2600 (doublet)	IVa,d; Vc,d	BH <sub>2</sub> stretching <sup>a</sup>
1450 - 1465	IVa-d; Va-d	N–B–N stretching <sup>b</sup>
1140-1170	IVe,d; Ve,d	BH <sub>2</sub> deformation <sup>a,c</sup>
1090-1120	IVa-d	Possibly $\geq N - B < a, d$

<sup>a</sup> L. J. Bellamy, et al., J. Chem. Soc., 2412 (1958). <sup>b</sup> Comparable to bands found in bisaminoboranes [K. Niedenzu, H. Beyer, and J. W. Dawson, Inorg. Chem., 1, 738 (1962)] and in borazines [H. C. Newsom, et al., J. Am. Chem. Soc., 83, 4134 (1961)]. <sup>c</sup> W. J. Lehman, C. O. Wilson, Jr., and I. Shapiro, J. Chem. Phys., 32, 1088 (1960). <sup>d</sup> In compounds Va-d, any absorption near 1100 cm.<sup>-1</sup> due to this grouping is obscured by the strong perchlorate band.

In addition, the B<sup>11</sup> n.m.r. spectrum of the bistrimethylamine salt (IVc) was obtained.<sup>8</sup> A 1:2:1 triplet centered at  $-4 \pm 1$  c.p.s. relative to  $(C_2H_5)_2$ -OBF<sub>3</sub> ( $J = 102 \pm 15$  c.p.s.) clearly demonstrates the existence of the BH<sub>2</sub> grouping in this molecule.<sup>1,9</sup>

The chemical behavior of those boron cations is quite unusual as noted by Miller and Muetterties.<sup>2</sup> Two properties, in particular, stand out: (1) the hydrogens bonded to boron are essentially nonhydridic, and (2) the amine moieties are more strongly coordinated to boron than in simple amine boranes. The stability of the boron-hydrogen bonds is made evident by their resistance to both hydrolysis and oxidation; *e.g.*, these bonds are not attacked in aqueous acid and they are not susceptible to reaction with iodine.<sup>10</sup> The enhanced strength of the boron-nitrogen bonds is demonstrated by the fact that the amine portions cannot be titrated with perchloric acid in nonaqueous solvent as they can be in simple amine boranes.

<sup>(6)</sup> H. Nöth and S. Lukas, Ber., 95, 1506 (1962); N. Wiberg and J. W. Buchler, J. Am. Chem. Soc., 85, 244 (1963); E. L. Muetterties, J. Inorg. Nucl. Chem., 15, 182 (1960); C. E. Nordman and C. R. Peters, J. Am. Chem. Soc., 81, 3551 (1959); R. W. Parry, et al., ibid., 80, 4 (1958), and following papers; W. Gerrard, M. F. Lappert, and R. Shafferman, J. Chem. Soc., 3828 (1957); P. B. Brindley, W. Gerrard, and M. F. Lappert, ibid., 1540 (1956); J. Goubeau and A. Zappel, Z. anorg. allgem. Chem., 279, 38 (1955); S. G. Shore and G. E. McAchran, Abstracts, 147th National Meeting of the American Society, Philadelphia, Pa., 1964, p. 25L.

<sup>(8)</sup> Kindly furnished by Dr. Thomas P. Onak, Los Angeles State College.
(9) T. P. Onak and I. Shapiro, J. Chem. Phys., **32**, 952 (1960).

<sup>(10)</sup> However, Miller and Muetterties<sup>2</sup> have found that these hydrogens can be displaced under sufficiently stringent conditions.

The unexpectedly high solubility of the iodide salts in chloroform is also worthy of note. Furthermore, when precipitated from chloroform solution by addition of a solvent such as hexane, it is often difficult to free these salts completely of chloroform.<sup>11</sup> While chloroform is as suitable a solvent as any tried for this reaction, its use can be a mixed blessing; *i.e.*, it permits a clean-cut separation of product from amine hydriodide by-product, but it can itself become a difficultly separable constituent.

A plausible two-step sequence of reactions which accounts for the net reaction shown by eq. 4 is

 $RBH_2 \cdot amine + I_2 + amine \longrightarrow$   $RBHI \cdot amine + amine H^+I^- (5)$ 

$$RBHI \cdot amine + amine \longrightarrow RBH(amine)_2^+I^- \quad (6)$$

The first step (eq. 5) is essentially the oxidation of hydride ion to hydrogen ion with free amine functioning as a hydrogen ion acceptor.<sup>12</sup> The second step (eq. 6) involves the displacement on boron of iodine by amine, a reaction which mechanistically may be similar to the SN2 reaction of amines with alkyl halides to give ammonium salts. Compounds of the type BH<sub>2</sub>X · amine are known<sup>13</sup> and have been shown to react with amines according to eq. 4.<sup>3</sup> This reaction has recently been reported to be reversible at temperatures above  $120^{\circ}$ .<sup>14</sup>

### Experimental

Elemental analyses were performed by Drs. Weiler and Strauss, Oxford, England. Infrared spectra were determined in chloroform or as Nujol mulls using a Perkin-Elmer Model 21 spectrophotometer. Melting points were measured in sealed capillaries and are corrected.

Materials.—Pyridine phenylborane was prepared by a minor modification of the procedure described by Hawthorne.<sup>15</sup> Ethylene benzeneboronate, rather than diethyl benzeneboronate, was used, and was prepared by fractionally distilling a mixture of benzeneboronic acid (0.10 mole), ethylene glycol (0.11 mole), and toluene (100 ml.). Water and excess glycol were removed by distilling successively their toluene azeotropes (b.p. 84 and 110°, respectively). Following distillation of the remaining toluene, the ester was collected at  $52-53^{\circ}$  (0.5 mm.); yields were nearly quantitative. The lithium aluminum hydride reduction of the ester was performed as reported by Hawthorne; yields were 60-65%.

Pyridine cyclohexylborane was synthesized by the following scheme.

Dimethyl cyclohexaneboronate was prepared by the method given by Brown and co-workers<sup>16</sup> for the preparation of dimethyl cyclopentaneboronate. The product was collected at  $61-63^{\circ}$  (12 mm.); lit.<sup>17</sup> b.p.  $67-68^{\circ}$  (14 mm.). The ester was reduced with lithium aluminum hydride by the method mentioned above.<sup>14</sup> Pyridime cyclohexylborane is a viscous oil at room temperature which solidifies into a glass upon cooling. A sample stored for 2 days over concentrated sulfuric acid in a vacuum desiccator was sufficiently pure for analysis. *Anal.* Caled. for C<sub>11</sub>H<sub>18</sub>BN: C, 75.5; H, 10.4; N, 8.00. Found: C, 74.9; H, 10.7; N, 8.23.

Trimethylamine borane (obtained from Callery Chemical Co.) was recrystallized from benzene–Skellysolve B before use.

Quinoline borane was prepared according to the method of Mikheeva and Fednova.  $^{\rm 18}$ 

Reagent grade chloroform was further purified by passing it through a column of activated alumina immediately before use. All reactions were carried out under an atmosphere of dry oxygenfree nitrogen.

**RBH**(amine)<sub>2</sub>I (**IVa-d**).—A solution of 20 mmoles of iodine in 60 ml. of chloroform was added dropwise to a stirred solution of 20 mmoles of amine borane III and 40 mmoles of amine in 20 ml. of chloroform at room temperature. After the addition was complete (*ca*. 1 hr.), the mixture was stirred for an additional 30 min. The precipitate of amine hydriodide was filtered off, and the filtrate was then reduced to *ca*. one-half its original volume *in vacuo*. Addition of an equal volume of hexane to the remaining solution precipitated the bisamine salt. The crude products were recrystallized from chloroform-hexane to give white powders. Yields of pure products ranged from 55 to 70%.

**RBH**(amine)<sub>2</sub>**C** $IO_4$  (Va-d).—One mmole of iodide salt IV and 1 mmole of powdered anhydrous silver perchlorate were stirred together as a slurry in 25 ml. of chloroform at room temperature for 2 hr. After removing the silver iodide by filtration, the reaction mixture was reduced to *ca*. one-half its original volume *in vacuo* and then chilled overnight at 0° to yield the crystalline bisamine perchlorate. The salts were recrystallized from either acetonitrile or methanol to give white needles. Vields of pure products ranged from 45 to 65%.

(18) V. I. Mikheeva and E. M. Fednova, Zh. Neorgan. Khim., 1, 891 (1956); Chem. Abstr., 51, 3347e (1956).

<sup>(11) (</sup>a) The bispyridine product of the reaction of pyridine borane with iodine was prepared but could not be obtained sufficiently free of chloroform to give a satisfactory analysis; in fact, the analysis agrees fairly well with the formulation,  $H_2B(C_8H_8N)_2I$ -CHCla. (b) Miller and Muetterties<sup>2</sup> have also found that some of their salts possess chloroform of crystallization when obtained from chloroform solutions.

<sup>(12)</sup> It is conceivable that the actual oxidizing species is the complex ion,  $(amine)_{I}I^{+}$ , formed by the reaction,  $2amine + I_{I} \rightleftharpoons (amine)_{I}I^{+}I^{-}$ . Studies concerning the detailed mechanism of the reaction shown by eq. 4 are in progress.

<sup>(13)</sup> H. Nöth and H. Beyer, Ber., 93, 2251 (1960).

<sup>(14)</sup> N. E. Miller, B. L. Chamberland, and E. L. Muetterties, Inorg. Chem.,  $\pmb{3},\,1064\,\,(1964).$ 

<sup>(15)</sup> M. F. Hawthorne, J. Am. Chem. Soc., 80, 4291 (1958).

<sup>(16)</sup> H. C. Brown, A. Tsukamoto, and D. B. Bigley, *ibid.*, **82**, 4703 (1960).

<sup>(17)</sup> H. C. Brown and G. J. Klender, Inorg. Chem., 1, 204 (1962).