

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

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

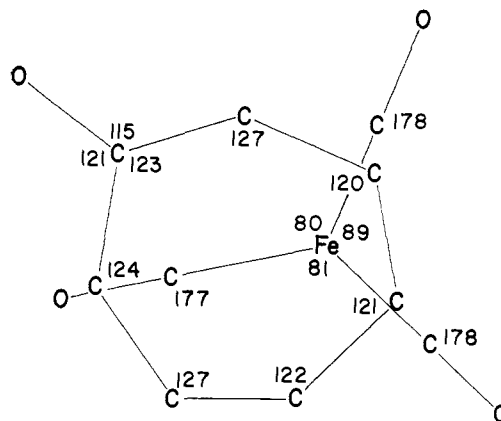
BOND DISTANCES AND ANGLES

Bond	Distance, Å.	σ	Angle	Degrees	σ
Fe-C ₁	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 ₃	1.749	0.010	Fe-C ₃ -O ₃	178.3	0.9
Fe-C ₅	2.114	0.009	O ₄ -C ₄ -C ₅	115.5	0.8
Fe-C ₆	2.067	0.010	O ₄ -C ₄ -C ₁₀	121.3	0.9
Fe-C ₇	2.042	0.010	C ₅ -C ₄ -C ₁₀	123.0	0.9
Fe-C ₈	2.149	0.010	C ₄ -C ₅ -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 ₃ -C ₃	1.170	0.013	C ₇ -C ₈ -C ₉	122.2	0.9
O ₄ -C ₄	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 ₅ -C ₆	1.442	0.013			
C ₆ -C ₇	1.396	0.013			
C ₇ -C ₈	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 π -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° . The C₄-O₄ group is displaced from the mean plane of C₅-C₈-C₉-C₁₀ so that O₄ is actually 0.76 Å. out of this plane. This may arise from the packing arrangement, which finds the C₄-O₄ 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 C₆-C₇ 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.⁷

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 Iodine¹

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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, $R_2B(\text{amine})_2^+$.

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 Muettterties² and of Nöth and co-workers³ clearly delineate the possibilities of formation of unsubstituted cations ($H_2BL_2^+$). Davidson

and French⁴ and Mikhailov and co-workers,⁵ in particular, have described a number of amine-stabilized organoboronium ions of the type $R_2B(\text{amine})_2^+$, where R is either alkyl, cycloalkyl, or aryl. Numer-

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

(1) Supported in part by a grant from the National Science Foundation.
(2) N. E. Miller and E. L. Muettterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964).

(3) H. Nöth, H. Beyer, and H.-J. Vetter, *Ber.*, **97**, 110 (1964).

(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. Mikhailov, N. S. Fedotov, T. A. Shchegoleva, and V. D. Sheludyakov, *Dokl. Akad. Nauk SSSR*, **145**, 340 (1962).

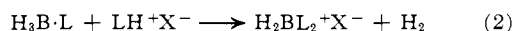
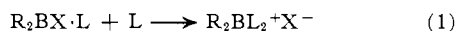
TABLE I
 RBH(amine)₂⁺ SALTS

Compound	M.p., °C. ^a	Formula	Analyses, %							
			C		H		N		B	
			Calcd.	Found	Calcd.	Found	Calcd.	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
IVc	190-195	C ₆ H ₂₀ BIN ₂	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 ₁₆ H ₁₆ BClN ₂ O ₄	55.5	55.7	4.65	4.86	8.08	7.79	3.12	3.09
Vb	220-222	C ₁₆ H ₂₂ BClN ₂ O ₄	54.5	54.3	6.29	6.25	7.95	7.88	3.07	3.11
Vc	167-170	C ₆ H ₂₀ BClN ₂ O ₄	31.3	31.3	8.75	8.42	12.2	11.5	4.69	4.68
Vd	125-127	C ₁₈ H ₁₆ BClN ₂ O ₄	58.3	57.9	4.35	4.23	7.56	7.60	2.92	2.97

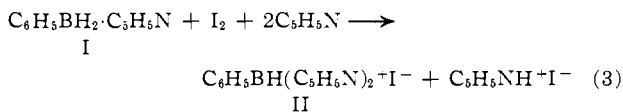
^a All of the iodides (IVa-d) melt with decomposition.

ous other reports of the preparation of boron cations can be found.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).



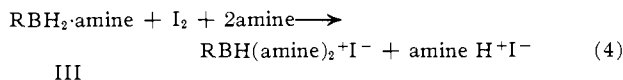
The present work was suggested by the finding⁷ in this laboratory that iodine reacts with pyridine phenylborane (I) in the presence of excess pyridine according to eq. 3. Compound II may formally be con-



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).



- IVa, R = C₆H₅; amine = C₅H₅N
 b, R = cyclo-C₆H₁₁; amine = C₅H₅N
 c, R = H; amine = (CH₃)₃N
 d, R = H; amine = C₉H₇N

(6) 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. McAhran, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., 1964, p. 25L.

(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, cm. ⁻¹	Compound	Assignment
2430-2600 (singlet)	IVa,b; Va,b	B-H stretching ^a
2400-2600 (doublet)	IVa,d; Vc,d	BH ₂ stretching ^a
1450-1465	IVa-d; Va-d	N-B-N stretching ^b
1140-1170	IVc,d; Vc,d	BH ₂ deformation ^{a,c}
1090-1120	IVa-d	Possibly $\geq \overset{+}{N}-\overset{-}{B} \leftarrow \overset{+}{N} \leftarrow \overset{-}{B} \leftarrow \overset{+}{N}$ ^{a,d}

^a L. J. Bellamy, *et al.*, *J. Chem. Soc.*, 2412 (1958). ^b 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)]. ^c W. J. Lehman, C. O. Wilson, Jr., and I. Shapiro, *J. Chem. Phys.*, **32**, 1088 (1960). ^d In compounds Va-d, any absorption near 1100 cm.⁻¹ due to this grouping is obscured by the strong perchlorate band.

In addition, the B¹¹ n.m.r. spectrum of the bistrimethylamine salt (IVc) was obtained.⁸ A 1:2:1 triplet centered at -4 ± 1 c.p.s. relative to (C₂H₅)₂OBF₃ ($J = 102 \pm 15$ c.p.s.) clearly demonstrates the existence of the BH₂ grouping in this molecule.^{1,9}

The chemical behavior of those boron cations is quite unusual as noted by Miller and Muetterties.² 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.¹⁰ 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.

(8) Kindly furnished by Dr. Thomas P. Onak, Los Angeles State College.

(9) T. P. Onak and I. Shapiro, *J. Chem. Phys.*, **32**, 952 (1960).

(10) However, Miller and Muetterties² have found that these hydrogens can be displaced under sufficiently stringent conditions.

