795. *Chemistry Related to Borazole. Part I. The Boron Trichloride and Boron Trifluoride Complexes of Primary Aromatic Amines.*

By W. Gerrard and E. F. Mooney.

Infrared spectroscopic and chemical evidence suggests that the complexes of primary aromatic amines with boron trichloride and trifluoride are best described as the hydrohalides of the arylaminoboron dihalides, $(Ar\cdot NH\cdot BX_2),HX$, with a possible " π-type " complex structure. Hydrolysis of the complexes, and their reactions with amines and Grignard reagents, are described.

The 1 : 1 complexes of boron trichloride with aniline,[1] *p*-toluidine,[2] and *p*-anisidine [3] have been described, but owing to the renewed interest in borazole and its derivatives these complexes have been re-investigated as intermediates in the preparation of the derivatives of *B*-trichloroborazole. The 1 : 1 complexes of *p*-bromoaniline and *p*-chloroaniline have now been prepared by the addition of the amine (1·0 mol.) in methylene dichloride to boron trichloride, in slight excess, in the same solvent at −80° (Table 6, p. 4034). In addition to the insoluble 1 : 1 complex the impure arylaminoboron dichloride $Ar\cdot NH\cdot BCl_2$ was obtained from the filtrate, the impurity being the corresponding *N*-triaryl-*B*-trichloroborazole $(ArNBCl)_3$. *m*-Toluidine and *p*-anisidine showed anomalous behaviour; for addition of the former to boron trichloride afforded the insoluble *m*-tolylammonium tetrachloroborate $[m\text{-}CH_3\cdot C_6H_4\cdot NH_3]^+[BCl_4]^-$ and the 1 : 1 complex was obtained from the filtrate; the pure complex of *p*-anisidine could not be obtained from methylene dichloride because of the ready occurrence of reaction (1). Kinney and Mahoney [3] could not get the pure complex from benzene.

$$p\text{-}MeO\cdot C_6H_4\cdot NH_2,BCl_3 \longrightarrow p\text{-}MeO\cdot C_6H_4\cdot NH\cdot BCl_2 + HCl \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

The boron trifluoride complexes of aniline [4–6] and *p*-toluidine [6] have not been fully characterised. The 1 : 1 complexes of aniline, *p*-toluidine, and *m*-toluidine (Table 7, p. 4035)

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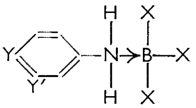
[1] Jones and Kinney, *J. Amer. Chem. Soc.*, 1939, **61**, 1378.
[2] Kinney and Kolbezen, *J. Amer. Chem. Soc.*, 1942, **64**, 1584.
[3] Kinney and Mahoney, *J. Org. Chem.*, 1943, **8**, 526.
[4] Landolph, *Ber.*, 1879, **12**, 1578; *Compt. rend.*, 1879, **89**, 173.
[5] Rideal, *Ber.*, 1889, **22**, 992.
[6] Sugden and Waloff, *J.*, 1932, 1492.

have now been prepared by addition of the amine to the boron trifluoride–ether complex in ether solution.

Infrared spectra of the boron trihalide complexes showed interesting features; significant is the presence of only one NH stretching band near 3200 cm.$^{-1}$. Arylaminoboron dichlorides also show a single NH band in the same position. If the structure were of the classical co-ordination type (I) at least two NH bands would be expected, arising from the symmetrical and asymmetrical stretching modes of the NH bonds. The parent aromatic amines show these two bands, together with an additional one due to the bonded NH group.[7] The NH bands found in the 3300 cm.$^{-1}$ region of the spectra of aromatic primary amines, the complexes, and the arylaminoboron dichlorides are shown in Table 1. The NH deformation bands of the complexes and the arylaminoboron dichlorides are found in the region of 1560 cm.$^{-1}$; the NH deformation band of a primary aromatic amine is normally observed in the 1650—1590 cm.$^{-1}$ region.[8] The bands associated with the NH deformation modes in these compounds are shown in Table 2. These results are not consistent with the presence of an NH_2 group in the complex.



(I)

(X = Cl or F, Y or Y′ = H, Me, MeO, Cl, or Br)

Another feature is the similarity between the infrared spectra of the amine–boron trichloride complexes and of the arylaminoboron dichlorides in the 850 cm.$^{-1}$ region (Fig. 1).

TABLE 1. *The position of* NH *stretching bands of primary aromatic amines, boron trichloride and boron trifluoride complexes, and the arylaminoboron dichlorides.*

Ar	$Ar{\cdot}NH_2$ (cm.$^{-1}$)	Assignment	$Ar{\cdot}NH_2,BCl_3$ (cm.$^{-1}$)	$Ar{\cdot}NH{\cdot}BCl_2$ (cm.$^{-1}$)	$Ar{\cdot}NH_2,BF_3$ (cm.$^{-1}$)
Ph	3425 *	sym. NH	3145	3135	3236
	3333	asym. NH			
	3195	bonded NH			
p-C_6H_4Me	3425	sym. NH	3135	3145	3205
	3333	asym. NH			
	3195	bonded NH			
m-C_6H_4Me	3448	sym. NH	3175		3226
	3356	asym. NH	3185 ‡		
	3215	bonded NH			
p-C_6H_4Br	3460 †	sym. NH	3120	3145	
	3390	asym. NH			
	3175	bonded NH			
p-C_6H_4Cl	3472	sym. NH	3135		
	3390	asym. NH			
	3205	bonded NH			

* Spectrum of liquid film. † Spectrum of chloroform solution. ‡ Spectrum of methylene dichloride solution.

TABLE 2. *The* NH *deformation bands of the primary aromatic amines, boron trichloride and boron trifluoride complexes, and the arylaminoboron dichlorides.*

Ar	$Ar{\cdot}NH_2$ (cm.$^{-1}$)	$Ar{\cdot}NH_2,BCl_3$ (cm.$^{-1}$)	$Ar{\cdot}NH{\cdot}BCl_2$ (cm.$^{-1}$)	$Ar{\cdot}NH_2,BF_3$ (cm.$^{-1}$)
Ph	1618	1560	1560	1587
p-C_6H_4Me	1613	1560	1560	1562
m-C_6H_4Me	1621	1558		1562
p-C_6H_4Br	1613	1560	1560	
p-C_6H_4Cl	1613	1555		

Infrared spectra of complexes of nitrogen compounds and boron trichloride show, in the 850 cm.$^{-1}$ region, a strong absorption envelope which has been associated with the partial tetrahedral configuration of the boron atom in such complexes. Such characteristic absorption has been observed in the boron trichloride complexes of nitriles (II),[9] secondary

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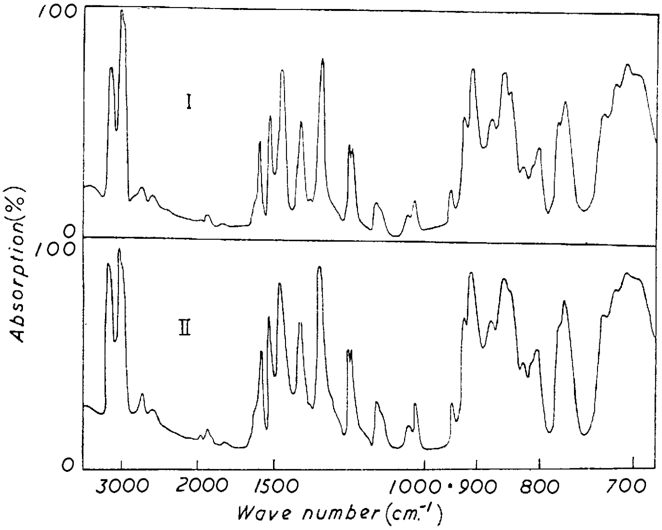
[7] Jones and Sandorfy, " Technique of Organic Chemistry," Vol. IX, 1956, p. 516.

[8] Thompson, *J.*, 1948, 328.

[9] Gerrard, Lappert, Pyszora, and Wallis, *J.*, 1960, 2182.

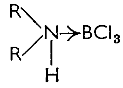
aliphatic amines (III),[10] diphenylamine, and triethylamine.[11] However, the corresponding primary aromatic amine complexes do not show this characteristic 850 cm.$^{-1}$ absorption envelope, but show a strong band which is associated with the $NBCl_2$ group. The B–Cl mode in such compounds as $ArBCl_2$ has been assigned [12] at 885 cm.$^{-1}$, but with the increased electron-donating power of the nitrogen atom it would be expected that the B–Cl mode in compounds of the type $Ar{\cdot}NH{\cdot}BCl_2$ would occur at lower frequencies, and in general, bands between 850 and 830 cm.$^{-1}$ have been assigned to the B–Cl mode in these compounds. In addition, there is a weaker band in the 1180 cm.$^{-1}$ region which we suggest is also associated with a B–Cl mode. These bands are shown in Table 3.

FIG. 1. *Infrared spectra of reaction products of* p-*toluidine and boron trichloride.*



(I) p-*Toluidine–boron trichloride.* (II) p-*Tolylaminoboron dichloride.*

(II) $R{-}C{\equiv}N{\rightarrow}BCl_3$

 (III)

$R_2N(H){\rightarrow}BCl_3$

TABLE 3. *Bands (cm.$^{-1}$) associated with the* B–Cl *mode in the spectra of arylamine–boron trichloride and arylaminoboron dichlorides.*

Ar	Ph	p-C_6H_4Me	m-C_6H_4Me	p-C_6H_4Br	p-C_6H_4Cl
$Ar{\cdot}NH_2,BCl_3$	1188, 828	1188, 847	1212, 838	1188, 849	1198, 856
$Ar{\cdot}NH{\cdot}BCl_2$	1188, 828	1190, 849	—	1189, 851	—

Although the analysis of the 1 : 1 boron trichloride complexes (see Table 6, p. 4034) is consistent with structure (I), infrared data fit better a complex of arylaminoboron dichloride with hydrogen chloride. An ionic structure (IV) has been suggested [13] for the dimethylamine- and diethylamine-boron trichloride complexes; evidence [14,15] has also been put forward to support the normal co-ordination structure (V). The ionic structure of the aromatic amine complexes is represented by structure (VI), but this structure is not consistent with infrared spectra. Although ionic complexes of secondary amines (IV)

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[10] Gerrard, Hudson, and Mooney, unpublished work.

[11] Gerrard, Lappert, and Pearce, unpublished work.

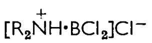
[12] Bellamy, Gerrard, Lappert, and Williams, *J.*, 1958, 2412.

[13] Brown and Ostoff, *J. Amer. Chem. Soc.*, 1952, **74**, 2342.

[14] Goubeau, Rantz, and Becher, *Z. anorg. Chem.*, 1933, **213**, 77.

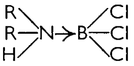
[15] Gerrard, Lappert, and Pearce, *J.*, 1957, 381.

which have been isolated [10] show bands which are normally assigned to NH^+ modes, bands due to the NH_2^+ modes (which have been fully characterised [16,17]) have not been observed in the aromatic amine complexes. Consequently, the structure of these might best be represented as " π-type " hydrogen halide complexes of the arylaminoboron dihalides (VII).

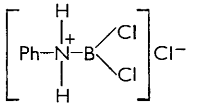


$[R_2\overset{+}{N}H{\cdot}BCl_2]Cl^-$

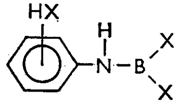
(IV; R = Me or Et)



(V)



(VI)



(VII; X = Cl or F)

The interaction of boron trichloride with benzylamine, cyclohexylamine, and diphenylamine was also investigated in view of this interesting formation of isolable π-complexes. As previously reported,[18] benzylamine and cyclohexylamine gave the substituted ammonium tetrachloroborates (VIII) and the aminoboron dichloride (IX) in equimolecular

$$2R{\cdot}NH_2 + 2BCl_3 \longrightarrow \underset{\text{(VIII)}}{[R{\cdot}NH_3]^+[BCl_4]^-} + \underset{\text{(IX)}}{R{\cdot}NH{\cdot}BCl_2}$$

(R = cyclohexyl or benzyl)

quantities. We confirmed that reaction of diphenylamine and boron trichloride leads to the tetrachloroborate,[10] but some of the 1 : 1 complex was also isolated. The NH stretching and deformation frequencies of the aminoboron dichlorides of benzylamine and cyclohexylamine and the 1 : 1 complex of diphenylamine are consistent with those found in the aromatic amine complexes (Table 4). In addition, the 1 : 1 complex of diphenylamine–boron trichloride shows the characteristic strong absorption of the partially tetrahedral $N{-}BCl_3$ group in the 800 cm.$^{-1}$ region; this complex is of the classical co-ordination structure (X) (Table 4).

TABLE 4. NH *Stretching and deformation frequencies* (*cm.*$^{-1}$) *of the aminoboron dichlorides of benzylamine and cyclohexylamine and the* 1 : 1 *complex of diphenylamine–boron trichloride.*

Compound	$Ph{\cdot}CH_2{\cdot}NH{\cdot}BCl_2$	$C_6H_{11}{\cdot}NH{\cdot}BCl_2$	Ph_2NH,BCl_3 (X)
NH stretch	3145	3155	3145
NH deformn.	1560	1550	1592

Contrary to earlier observations,[1] the aniline–boron trichloride complex did not disproportionate when heated; only hydrogen chloride was evolved in boiling benzene or on pyrolysis. Thermal decomposition of the 1 : 1 complexes and the substituted ammonium tetrachloroborates in boiling benzene is a convenient method of preparing the corresponding *N*-triaryl-*B*-trichloroborazole (2). The complexes of aniline, *p*-toluidine,

$$Ar{\cdot}NH_2,BCl_3 \longrightarrow \tfrac{1}{3}(ArNBCl)_3 + 2HCl \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$[R{\cdot}NH_3]^+[BCl_4]^- \longrightarrow \tfrac{1}{3}(RNBCl)_3 + 3HCl$$

and *p*-bromoaniline show similar decomposition curves (Fig. 2); the initial stage involves a heterogeneous system, the complex being insoluble in benzene; the second stage shows essentially first-order kinetics (Fig. 3). The system involves a consecutive decomposition of the complex *via* the arylaminoboron dichloride to the *N*-aryl-*B*-chloroborazyne which trimerises to the *N*-triaryl-*B*-trichloroborazole. Pyrolysis of the complex follows a similar pattern, but it is difficult to obtain pure products, there being further decomposition

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[16] Stone, Cymerman-Craig, and Thompson, *J.*, 1958, 52.
[17] Heacock and Marion, *Canad. J. Chem.*, 1956, **34**, 1782.
[18] Gerrard and Mooney, *Chem. and Ind.*, 1958, 1259.

beyond the chloroborazole stage; when the *N*-triaryl-*B*-trichloroborazoles are heated hydrogen chloride is eliminated.[19]

$$Ar{\cdot}NH_2,BCl_3 \xrightarrow{-HCl} Ar{\cdot}NH{\cdot}BCl_2 \xrightarrow{-HCl} (ArNBCl)_3$$

The reaction of pyridine and alkylamine–boron trichloride complexes normally results in base interchange (3).[20] With the aromatic amine–boron trichloride complexes only

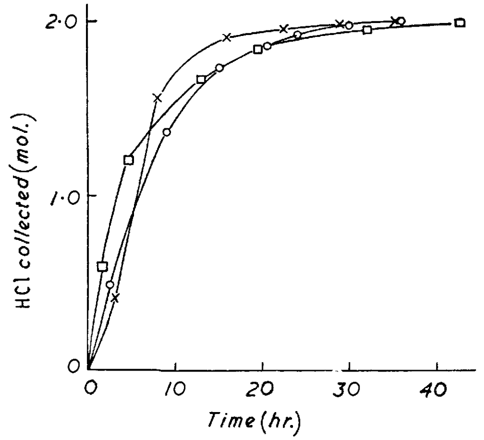
$$R_2NH,BCl_3 + C_5H_5N \longrightarrow C_5H_5N,BCl_3 + R_2NH \quad \text{. . . . . (3)}$$

$$Ar{\cdot}NH_2,BCl_3 + 2C_5H_5N \longrightarrow C_5H_5N,HCl + Ar{\cdot}NH{\cdot}BCl_2,C_5H_5N \quad \text{. . . . . (4)}$$

$$[R{\cdot}NH_3]^+[BCl_4]^- + C_5H_5N \longrightarrow C_5H_5N,BCl_3 + R{\cdot}NH_3{}^+Cl^- \quad \text{. . . . . . . (5)}$$

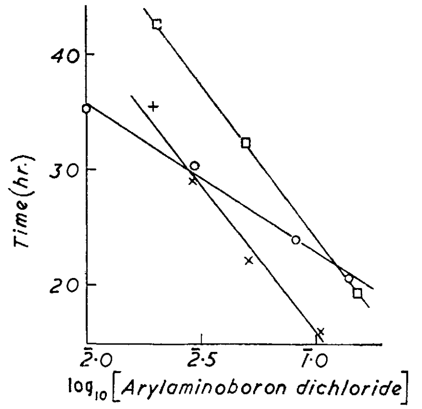
pyridinium hydrochloride is isolated by sublimation, together with a material which approximates to the arylaminoboron dichloride–pyridine complex (reaction 4), pointing to the structure (VII). The substituted ammonium tetrachloroborates and pyridine give pyridine–boron trichloride and the substituted ammonium chloride (reaction 5).

FIG. 2.



○ *Aniline–boron trichloride.* × p-*Toluidine–boron trichloride.* □ p-*Bromoaniline–boron trichloride.*

FIG. 3.



○, ×, □ *As for Fig.* 2.

The primary aromatic amine–boron trichloride complexes are violently hydrolysed with water and alcohols; in contrast, the boron trifluoride complexes dissolved in water without apparent reaction. Ultraviolet spectra of the aqueous solutions of the boron trifluoride complexes (Fig. 4) show the presence of the substituted arylammonium ion, accounted for by the formation of the arylammonium hydroxytrifluoroborate (XI) (reaction 6). The 2 : 1 complex of water and boron trifluoride has been shown, by *X*-ray diffraction[21] and electrolysis,[22] to be the hydroxonium hydroxytrifluoroborate $[H_3O]^+[HO{\cdot}BF_3]^-$; the corresponding arylammonium salt of this acid is that proposed in structure (XI). Other evidence has been reported.[23]

$$Ar{\cdot}NH_2,BF_3 + H_2O \longrightarrow \underset{\text{(XI)}}{[Ar{\cdot}NH_3]^+[HO{\cdot}BF_3]^-} \quad \text{. . . . . (6)}$$

$$C_6H_5{\cdot}NH_2,BF_3 + C_4H_8O \longrightarrow C_6H_5{\cdot}NH_2 + C_4H_8O,BF_3 \quad \text{. . . . . (7)}$$

The aniline–boron trifluoride complex is soluble in tetrahydrofuran, giving a yellow solution, which suggests possible base-exchange (7); on removal of the solvent under reduced pressure the aniline–boron trifluoride complex was recovered. The infrared

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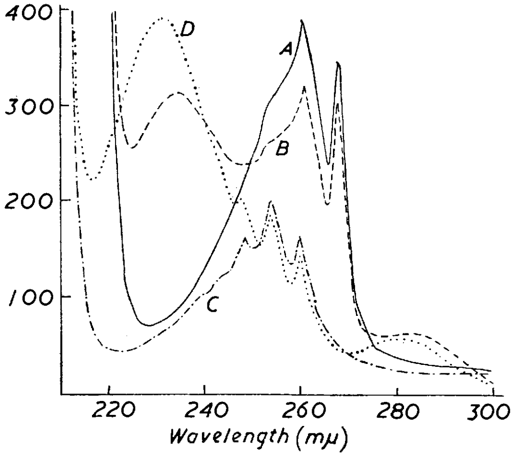
[19] Gerrard and Mooney, unpublished work.
[20] Brown, *J. Amer. Chem. Soc.*, 1952, **74**, 1219.
[21] Klinkenberg and Ketelaar, *Rev. Trav. chim.*, 1935, **54**, 959.
[22] Greenwood and Martin, *J.*, 1951, 1915.
[23] Ryss and Idels, *Zhur. neorg. Khim.*, 1959, **4**, 1990.

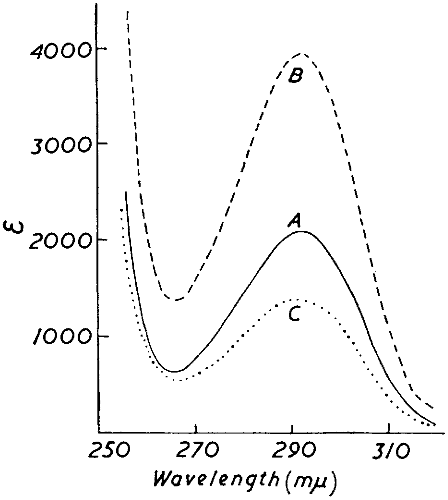
spectrum of the tetrahydrofuran solution, however, showed that no base-exchange had occurred; only one NH band (3390 cm.$^{-1}$) was observed. A solution of aniline in tetrahydrofuran showed the presence of the usual three bands, symmetrical NH stretching (3475 cm.$^{-1}$), asymmetrical NH stretching (3390 cm.$^{-1}$), and bonded NH (3245 cm.$^{-1}$); the presence of free aniline in the solution of the complex would be readily detected.

FIG. 4. *Ultraviolet spectra of aniline–boron trifluoride and* m-*toluidine–boron trifluoride in aqueous solution.*

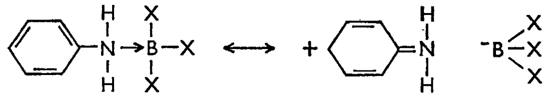


(*A*) m-*Tolylammonium chloride in* 0·1N-*hydrochloric acid.* (*B*) m-*Toluidine–boron trifluoride in water.* (*C*) *Anilinium chloride in* 0·1N-*hydrochloric acid.* (*D*) *Aniline–boron trifluoride in water.*

FIG. 5. *Ultraviolet spectra of* (*A*) *aniline,* (*B*) *aniline–boron trifluoride, and* (*C*) *aniline–boron trichloride in tetrahydrofuran solution.*



The ultraviolet spectra of the aniline–boron trichloride and –boron trifluoride complexes in tetrahydrofuran are shown in Fig. 5. If the structure of the complexes were of the classical co-ordination type (I), the expected canonical forms of type (XII) with a *p*-quinonoid structure would cause the movement of $\lambda_{max.}$ to longer wavelength; there is

(I)


(XII)

no observed movement of $\lambda_{max.}$ (Table 5). The reduction in the ratio $\varepsilon_{max.}/\varepsilon_{min.}$, which is in the order of increasing Lewis acid strength of HX, HCl > HF, could be explained by the "π-type" complex bonding of HX to the aromatic nucleus (VII), resulting in the localisation of the π-electron system.

Reaction of the boron trifluoride–ether complex and arylmagnesium halides is known to afford the triarylborons;[24] if the aniline–boron trifluoride complex were of structure (I), reaction with phenylmagnesium bromide would be expected to yield aniline–triphenylboron (XIII), a compound previously prepared[25] from aniline and triphenylboron. However, anilinodiphenylboron (XIV) was produced, consistent with the "π-complex"

TABLE 5. *Ultraviolet spectra of aniline, aniline–boron trifluoride and aniline–boron trichloride in tetrahydrofuran solution.*

	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε	$\varepsilon_{max.}/\varepsilon_{min.}$
Aniline	292	2070	265	650	3·19
Aniline,BF_3	292	3900	265·5	1360	2·87
Aniline,BCl_3	291	1390	266	540	2·57

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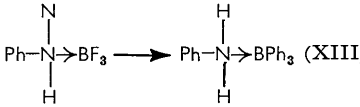
[24] Krause *et al.*, *Ber.*, 1922, **55**, 1261; 1926, **59**, 777; 1930, **63**, 934; 1931, **64**, 2112; Wittig and Hertwig, *Chem. Ber.*, 1955, **88**, 962.

[25] Krause, *Ber.*, 1924, **57**, 813.

structure (VII; X = F). The isolation of anilinodiphenylboron is not, however, compelling evidence of " π-complex " structure (VII), because after reaction of the Grignard

(I)  (XIII)

$$\mathrm{Ph{-}\overset{\displaystyle N}{\underset{\displaystyle H}{N}}{\rightarrow}BF_3 \longrightarrow Ph{-}\overset{\displaystyle H}{\underset{\displaystyle H}{N}}{\rightarrow}BPh_3}$$

reagent with the active hydrogen, intermolecular or intramolecular elimination of the magnesium dihalide could occur from structure (I); however, intermolecular elimination would be expected to yield preferentially the hexaphenylborazole. *m*-Toluidine–boron trifluoride and n-butylmagnesium bromide gave *m*-tolylaminodi-n-butylboron, but the reaction of aniline–boron trifluoride and trichloride with n-butylmagnesium bromide appears to be more complicated.

EXPERIMENTAL

Preparation of 1 : 1 *Complexes of Boron Trichloride with Aniline,* p-*Toluidine,* p-*Bromoaniline, and* p-*Chloroaniline.*—The amine (1·0 mol.) in methylene dichloride was added dropwise to boron trichloride (1·02—1·05 mol.), at −80°, in the same solvent. The insoluble complex was filtered off at room temperature (Table 6), and the filtrate evaporated to dryness under reduced pressure to afford the impure arylaminoboron dichloride [the impurity was the corresponding *N*-triaryl-*B*-trichloroborazole $(\mathrm{ClBNAr})_3$, indicated by the appearance of a band in the region of 1410 cm.$^{-1}$]. Attempts to recrystallise the arylaminoboron dichlorides were unsuccessful.

TABLE 6. 1 : 1 *Aromatic amine–boron trichloride complexes and arylaminoboron dichlorides.*

$\mathrm{Ar{\cdot}NH_2,BCl_3}$

			Found (%)			Required (%)		
Ar	Yield (%)	M. p. (decomp.)	N	e.h.Cl *	B	N	e.h.Cl	B
Ph	58	140°	6·7	50·4	5·2	6·7	50·6	5·2
p-C_6H_4Me	62	145—150	6·2	46·8	4·9	6·2	47·4	4·8
p-C_6H_4Br	78	300	4·7	37·0	3·8	4·8	36·8	3·8
p-C_6H_4Cl	80		5·6	42·6 †	4·5	5·7	43·5	4·4

$\mathrm{Ar{\cdot}NH{\cdot}BCl_2}$

	Found (%)			Calc. (%)		
Ar	N	e.h.Cl	B	N	e.h.Cl	B
Ph	7·4	41·9	6·4	8·1	40·8	6·2
p-C_6H_4Me	7·6	34·7	6·0	7·5	37·7	5·8
p-C_6H_4Br	5·6	24·7	5·1	5·5	28·0	4·3
p-C_6H_4Cl	6·3	30·1	5·4	6·7	34·0	5·2

* Easily hydrolysed chlorine. † Total chlorine: Found, 58·3. $C_6H_6BCl_4N$ requires Cl, 58·5%.

Reaction of p-*Anisidine with Boron Trichloride.*—*p*-Anisidine (52·46 g., 1·0 mol.) in methylene dichloride (200 ml.) was added in 2 hr. to boron trichloride (52·49 g., 1·05 mol.) in the same solvent (100 ml.) at −80°. The first-formed violet complex dissolved on attaining room temperature. The solution was filtered (insoluble, 0·56 g., 0·5%) and the filtrate evaporated under reduced pressure, giving a mixture of *p*-anisidine–boron trichloride complex and *p*-methoxyphenylaminoboron dichloride (94·9 g.) (Found: N, 6·1; Cl, 39·0; B, 4·9. Calc. for $C_7H_9BCl_3NO$: N, 5·8; Cl, 44·3; B, 4·5. Calc. for $C_7H_8BCl_2NO$: N, 6·9; Cl, 34·7; B, 5·3%).

Hydrolysis of Reaction Products of p-*Anisidine and Boron Trichloride.*—The mixture of *p*-anisidine–boron trichloride and *p*-anisylaminoboron dichloride (3·18 g.) was hydrolysed with 10% sodium hydroxide solution (10 ml.); the solution was saturated with carbon dioxide and extracted with ether. The extracts were combined, dried ($MgSO_4$), filtered, and evaporated to afford *p*-anisidine (1·22 g., 78%), m. p. 53—54°; no *p*-aminophenol was isolated, consequently there was no ether fission on addition of boron trichloride to *p*-anisidine.

Reaction of m-*Toluidine with Boron Trichloride.*—*m*-Toluidine (21·11 g., 1·0 mol.) in methylene dichloride (50 ml.) was added (1 hr.) to boron trichloride (24·20 g., 1·05 mol.) in the same solvent (50 ml.) at −80°. After attaining room temperature, the white crystalline m-*tolylammonium tetrachloroborate* (8·23 g.) (Found: N, 5·7; Cl, 53·2; B, 4·1. $C_7H_{10}BCl_4N$ requires N, 5·4; Cl, 54·3; B, 4·1%) was filtered off, and, on cooling of the blue filtrate, a white crystalline m-*toluidine–boron trichloride* complex (20·81 g.) (Found: N, 6·1; Cl, 47·6; B, 4·7. $C_7H_9BCl_3N$ requires N, 6·2; Cl, 47·5; B, 4·8%), m. p. 130—140° (decomp.), was filtered off.

Reaction of Diphenylamine with Boron Trichloride.—Diphenylamine (14·75 g., 1·0 mol.) in methylene dichloride (50 ml.) was added in 1 hr. to boron trichloride (10·27 g., 1·02 mol.) in the same solvent (50 ml.) at −80°. On attaining room temperature the white insoluble diphenylammonium tetrachloroborate (5·14 g., 0·18 mol.) (Found: N, 4·5; Cl, 44·9; B, 3·7. Calc. for $C_{12}H_{12}BCl_4N$: N, 4·3; Cl, 44·2; B, 3·4%) was filtered off. The filtrate was concentrated under reduced pressure to yield the crystalline diphenylamine–boron trichloride complex (7·34 g., 0·30 mol.), which was filtered off and washed with benzene (Found: N, 5·0; Cl, 37·6; B, 3·7. Calc. for $C_{12}H_{11}BCl_3N$: N, 4·9; Cl, 37·2; B, 3·8%).

Preparation of Primary Aromatic Amine–Boron Trifluoride Complexes.—The primary aromatic amine (1·0 mol.) in ether was added dropwise to boron trifluoride–ether complex (1·1 mol.) in ether, to yield the insoluble 1 : 1 complex (Table 7).

TABLE 7. 1 : 1 *Complexes of primary aromatic amines and boron trifluoride,* $Ar{\cdot}NH_2,BF_3$.

Ar	Yield (%)	M. p.	Found (%) C	Found (%) H	Found (%) N	Required (%) C	Required (%) H	Required (%) N
Ph	77	164—166°	44·8	4·7	8·7	44·7	4·4	8·7
p-C_6H_4Me	75		47·7	4·9	8·0	48·1	5·2	8·0
m-C_6H_4Me	63				8·0			8·0

Thermal Decomposition of 1 : 1 *Primary Aromatic Amine–Boron Trichloride Complexes.*—The aniline–boron trichloride (4·86 g., 1·0 mol.) was heated under reflux in benzene (100 ml.), and the hydrogen chloride evolved (1·68 g., 1·99 mol.) was collected on potassium hydroxide pellets (see Fig. 2); there was no evidence that boron trichloride was evolved during the decomposition. The benzene solution was reduced to 30 ml. and, on cooling, *B*-trichloro-*N*-triphenylborazole separated as white needles (2·22 g., 70%) (Found: N, 10·1; Cl, 25·7; B, 7·8. Calc. for $C_{18}H_{15}B_3Cl_3N_3$: N, 10·2; Cl, 25·8; B, 7·9%).

The *p*-toluidine–boron trichloride complex (8·51 g.) was heated similarly in benzene (100 ml.); hydrogen chloride (2·72 g., 1·98 mol.) was evolved. Concentration of the benzene solution to 30 ml. and cooling yielded solvated B-*trichloro*-N-*tri*-p-*tolylborazole* (3·51 g., 61%) (Found: N, 8·8; Cl, 21·5; B, 6·6. $C_{21}H_{21}B_3Cl_3N_3,0{\cdot}5C_6H_6$ requires N, 8·6; Cl, 21·6; B, 6·6%). The *p*-bromoaniline–boron trichloride complex (38·71 g.), heated in benzene (200 ml.), evolved hydrogen chloride (9·70 g., 1·98 mol.) and gave the insoluble solvated N-*tri*-p-*bromophenyl*-B-*trichloroborazole* (24·91 g., 86·3%) (Found: N, 5·8; Cl, 14·5; B, 4·4. $C_{18}H_{12}Br_3Cl_3B_3N_3,C_6H_6$ requires N, 5·8; Cl, 14·6; B, 4·5%).

The mixture (41·54 g.) of *p*-anisidine–boron trichloride and *p*-anisylaminoboron dichloride was heated under reflux in toluene (250 ml.), whereupon hydrogen chloride [7·94 g., 1·26 mol. based on reaction (2)] was evolved. Part of the toluene was evaporated, and hexane added, yielding impure material which on recrystallisation from benzene gave N-*tri*-p-*anisyl*-B-*trichloroborazole* (15·27 g., 46%) (Found: N, 7·7; B, 6·0. $C_{21}H_{21}B_3Cl_3N_3O_3,0{\cdot}5C_6H_6$ requires N, 7·8; B, 6·0%).

The aniline–boron trichloride complex (1·79 g.) was heated at 110° (6 hr.) without decomposition. At 135° (5 hr.) it became yellow and began to decompose with elimination of hydrogen chloride (0·05 g.). At 140° the material melted to a dark brown viscous liquid, and during 12 hr. hydrogen chloride (0·31 g.) was evolved. The total loss in weight (0·46 g.) corresponded to 1·5 mol. of hydrogen chloride [based on reaction (2)], and no condensate was obtained in a cold trap. Analysis of the black viscous residue was erratic.

The *p*-bromoaniline–boron trichloride complex (5·01 g.), heated at 140° (4·5 hr.), evolved only hydrogen chloride (0·13 g.). At 160° (4·5 hr.) more hydrogen chloride (0·90 g., total 82%) was evolved, and during the next 6·5 hr. 0·11 g. was evolved [total, 1·13 g., 90%]. No boron trichloride was evolved, and a mixture of *N*-tri-*p*-bromophenyl-*B*-trichloroborazole and *p*-bromophenylaminoboron dichloride (3·88 g., 103% calc. as chloroborazole) (Found: N, 6·3; Cl, 20·4; B, 4·2%). At 160—180°/0·5 mm. (2 hr.) this mixture (1·91 g.) gave hydrogen chloride (0·09 g.) which constituted a loss beyond the chloroborazole stage, indicated also by analysis (Found: N, 6·6; Cl, 13·7; B, 5·5%; N : Cl : B = 1·0 : 0·8 : 1·0).

Interaction of Aniline–Boron Trichloride with Pyridine.—Pyridine (1·87 g., 2·0 mol.) in benzene (20 ml.) was added dropwise to a suspension of aniline–boron trichloride (2·45 g., 1·0 mol.) in the same solvent (50 ml.) with constant shaking. The solvent was removed under reduced pressure to afford a white residue (3·99 g.). A portion (2·76 g.) of the residue was heated at 80°/0·01 mm. (2 hr.), yielding a white sublimate of pyridine hydrochloride (0·78 g., 0·91 mol.) (Found: Cl, 30·6. Calc. for C_5H_6ClN: Cl, 30·7%), and a white non-hygroscopic residue (1·99 g.) of the impure *phenylaminoboron dichloride–pyridine complex* (Found: N, 10·5; Cl, 31·0; B, 4·0. $C_{11}H_{11}BCl_2N_2$ requires N, 11·1; Cl, 28·0; B, 4·3%). Attempts to obtain the pure complex by recrystallisation were unsuccessful.

Interaction of p-*Bromoaniline–Boron Trichloride with Pyridine.*—Pyridine (6·85 g., 2·0 mol.) in methylene dichloride (25 ml.) was added (1 hr.) to a suspension of the complex (12·52 g., 1·0 mol.) in the same solvent (25 ml.). Volatile matter (63·7 g.) was removed under reduced pressure and trapped at −80°; a residue (19·73 g.) was left. The cold-trap condensate gave methylene dichloride (63·1 g., 99·1%), b. p. 40—41°, n_D^{20} 1·4249, and no pyridine was isolated. A portion (6·19 g.) of the residue was heated in a sublimation-apparatus for 2 hr. at 80°/0·01 mm., yielding pyridine hydrochloride (0·54 g., 0·91 mol.) (Found: Cl, 30·5%), and a final residue (5·60 g.) of impure *p*-bromophenylaminoboron dichloride–pyridine complex (Found: N, 7·5; Cl, 24·2; B, 2·7. Calc. for $C_{11}H_{10}BBrCl_2N_2$: N, 8·8; Cl, 21·4; B, 3·3%). Infrared examination of the residue showed it to be essentially free from pyridine hydrochloride. The primary product (5·04 g.) was heated for 3 hr. at 120°/0·01 mm., and a sublimate of pyridine hydrochloride (1·72 g., 1·34 mol., increased only to 1·83 g., 1·43 mol., during next 3 hr.) was obtained. The increased yield of pyridine hydrochloride at the higher temperature was due to the decomposition of the *p*-bromophenylaminoboron dichloride–pyridine complex.

Reaction of Cyclohexylammonium Tetrachloroborate with Pyrdine.—Pyridine (1·84 g., 1·0 mol.) in chloroform (25 ml.) was added dropwise (20 min.) to the tetrachloroborate (5·87 g., 1·0 mol.) suspended in the same solvent (35 ml.). The white gelatinous material formed immediately changed overnight into crystalline cyclohexylammonium chloride (3·34 g., 1·0 mol.) which was filtered off (Found: N, 10·3; Cl, 26·2. Calc. for $C_6H_{14}ClN$: N, 10·3; Cl, 26·2%). The filtrate was evaporated under reduced pressure, to yield impure pyridine–boron trichloride (3·81 g., 3·62 g., after being washed with water and dried) (Found: Cl, 54·2; B, 5·4; C_5H_5N, 40·0. Calc. for $C_5H_5BCl_3N$: C, 54·3; B, 5·5; C_5H_5N, 40·3%).

Interaction of Aniline–Boron Trifluoride with Tetrahydrofuran.—The complex (4·68 g., 1·0 mol.) was dissolved in tetrahydrofuran (38·34 g., 17·78 mol.), affording a slightly yellow solution, which slowly darkened. Tetrahydrofuran (37·81 g., 17·55 mol.), b. p. 68°, n_D^{21} 1·4063, was removed at 15 mm., and trapped at −80°, leaving aniline–boron trifluoride (4·67 g., 0·99 mol.) (Found: N, 8·6. Calc. for $C_6H_7BF_3N$: N, 8·7%).

Interaction of Aromatic Amine–Boron Trifluoride Complexes with Grignard Reagents.—Bromobenzene (164 g., 5·05 mol.) in ether (250 ml.) was added slowly to a suspension of aniline–boron trifluoride (33·32 g., 1·00 mol.) and magnesium (25·50 g., 5·06 g. atom) in ether (250 ml.) containing a crystal of iodine. The solution was stirred and, when the reaction was complete, the products were hydrolysed by slow addition of saturated ammonium chloride solution (500 ml.) until two layers were obtained; continuous extraction with ether afforded brown needles of *anilinodiphenylboron* (17·0 g.) (Found: N, 5·5; B, 4·2. $C_{18}H_{16}BN$ requires N, 5·5; B, 4·2%). Addition of hexane to the ethereal filtrate afforded a further crop (10·3 g., total yield 51·3%) (Found: N, 5·5; B, 4·2%). Recrystallisation from hot benzene gave white needles, m. p. 236° (decomp.) (Found: N, 5·5; B, 4·2%; *M*, 259. $C_{18}H_{16}BN$ requires *M*, 257).

*Formation of Di-n-butyl-*m-*tolylaminoboron.*—n-Butyl bromide (49·79 g., 6·03 mol.) was added during 3 hr. to a suspension of *m*-toluidine–boron trifluoride (10·52 g., 1·0 mol.) and magnesium (8·52 g., 6·0 g.-atom) in ether (250 ml.) containing a crystal of iodine. The butane evolved (3·05 g., 0·87 mol.) and collected at −80° was identified by its vapour spectrum. Hydrolysis with a saturated ammonium chloride solution (200 ml.) until the mixture separated into two phases, and continuous extraction with ether afforded, after removal of ether at 15 mm., a mobile yellow liquid (18·18 g.). Distillation gave *di-n-butyl-*m-*tolylaminoboron* (12·69 g., 72·5%) (Found: N, 6·1; B, 4·7. $C_{15}H_{26}BN$ requires N, 6·1; B, 4·7%), b. p. 54—56°/0·05 mm., n_D^{25} 1·4755, d_4^{25} 0·8673.

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