Thermal Elimination of Hydrogen Chloride from Adducts of Aromatic Amines with Boron Trichloride with Reference to Borazole Formation

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The adducts of 2,3,5,6-tetrachloroaniline, 2,4,6-tribromoaniline, pentafluoroaniline, 2-bromoaniline, and N-methylaniline with boron trichloride have been prepared and the elimination of hydrogen chloride from them in boiling benzene and in more basic solvents has been examined. Some kinetic measurements have been made. The first product of reaction in benzene, which is anilinodichloroborane for each amine except pentafluoroaniline, has been isolated and characterised. In no case was borazole isolated from reaction in boiling benzene. The compound 2-nitro-4-trifluoromethylanilinodichloroborane has also been characterised. The reaction of aromatic amines with BCla in general, and the possible mechanisms of formation of borazoles by elimination of hydrogen chloride from them are discussed.

MANY reactions are possible between amines and boron halides in equimolar amounts.¹⁻¹¹ Some of these for aromatic amines are shown in Scheme 1. The most important is possibly the production of borazoles,^{1,7} which is usually brought about by reaction of a tertiary amine base (e.g., triethylamine) on the adduct of a primary aromatic amine with boron trichloride. Observations on amine-boron halide interactions extend over a wide range of amine behaviour. Arylamines (mostly primary) with a variation of 10¹¹ in basicity $(pK_a \text{ range } -6.4 \text{ to } +5.1)$ have been examined and variations in stereochemistry have been mainly accomplished by use of ortho-substitution. There seem to be three categories of primary aromatic amine with regard to their reactions with boron halides; these are o-nitroamines, amines with ortho-substituents other than nitro, and amines with no ortho-substituent. Each of these follows one of the sequences in Scheme 1.



Most aromatic amines form adducts with BCl₃ (step a) which are stable solids at room temperature.5,7,10 We have found this even for the least basic amine studied (2,3,5,6-tetrachloroaniline, p $K_a = -0.86$) provided it had no nitro-substituent ortho to the amino-group. Such o-nitroamines are a special category which form no adduct (even for the most basic, $pK_a + 0.77^{8,9}$) but

give reaction b. We can define two categories of aromatic amine among those which do form adducts and these again seem to depend on *ortho*-substituents. It has been shown that aminodichloroboranes (step c) can be isolated only when the amine has an ortho-substituent.7 When the amine has no ortho-substituent, borazole and tetrachloroborates have been detected in the reaction but no aminodichloroborane.^{7,10} We have extended some of these observations and have attempted with only moderate success to study the mechanisms of some of the steps involved.

EXPERIMENTAL

Preparation of Adducts.-With the exception of the pentafluoroaniline and N-methylaniline adducts, these were made as before from equimolar quantities of amine and boron trichloride in sodium-dried light petroleum or dichloromethane.⁵ The adduct of N-methylaniline is very soluble in dichloromethane, but removal of a large amount of solvent and addition of light petroleum produces a gum which eventually crystallises. The adduct of pentafluoroaniline is unstable at room temperature (solid or solution) and for later experiments it was made by mixing equimolar amounts of amine and boron trichloride in situ. The adducts were characterised by their analysis, and their infrared and n.m.r. spectra (see Tables 1 and 2).

Dehydrochlorination of Adducts in Kinetic Reactions and Measurements of the Rate of Evolution of HC1.—Apparatus. The method devised in ref. 7 was used with a few modifications. Figure 1 describes the apparatus. A flow of dry nitrogen was passed over boiling solvent. A weighed sample of adduct in a small quantity of benzene was admitted through an inlet; after ca. 1 min the solute had dissolved and the solvent was again boiling. The nitrogen flow rate was fast enough to eliminate hold-up of HCl in the dead-space and to avoid any back-diffusion of water into the reaction vessel. Control experiments on the solubility of HCl in boiling benzene under experimental conditions showed this to be negligible. Further control experiments where a non-volatile but highly reactive halide (PhBCl₂) was present in boiling benzene showed

⁶ J. R. Blackborow and J. C. Lockhart, J. Chem. Soc. (A), 1968, 3015.
⁷ R. K. Bartlett, H. S. Turner, R. J. Warne, M. A. Young, and I. J. Lawrenson, J. Chem. Soc. (A), 1966, 449.
⁸ J. C. Lockhart, J. Chem. Soc. (A), 1966, 809.
¹⁰ W. Gerrard and E. F. Mooney, J. Chem. Soc., 1960, 4028.
¹¹ H. Knoth, Progr. Boron Chem., 1970, 3, 211.

¹ W. Gerrard, 'The Organic Chemistry of Boron,' Academic Press, London, 1961.

² K. Niedenzu and J. W. Dawson, 'Boron Nitrogen Com-pounds,' Springer-Verlag, Berlin, 1965.

³ N. N. Greenwood, K. A. Hooton, and J. Walker, J. Chem. Soc. (A), 1966, 21. ⁴ N. N. Greenwood and K. A. Hooton, J. Chem. Soc. (A),

^{1966, 751.} 5

J. R. Blackborow and J. C. Lockhart, J. Chem. Soc. (A), 1969, 816.

TABLE 1 Characterisation of adducts R¹NHR²,BCl₃ of aromatic amines

		Analysis										
	Empirical		:	Found (9	%)		×		Calc. (%	ົ		vN-H stretching/
Aromatic amine Tetrachloroaniline Tribromoaniline 2-Bromoaniline	$\begin{array}{c} \text{Empirical} \\ \text{formula} \\ \text{ie} C_8H_3BCl_7N^{b} \\ C_8H_4BBr_3Cl_3N^{b} \\ C_6H_6BBrCl_3N^{b} \end{array}$	б	Н	N	$B \\ 3 \cdot 1 \\ 2 \cdot 5 \\ 3 \cdot 7$	Cl a 30·3 23·25 35·45	ć—	н	N	B 3·1 2·4 3·75	Cl a 30.6 23.1 36.8	cm ⁻¹ 3100b 3120b 3203,
N-Methylaniline	C7H9BCl3N	37·4	4 ·2	6 ∙ 4 5	4 ·9	46·1	37.5	4 ∙05	6 ∙25	4 ∙8	47.4	3165
		Easily-nyarolysed chloride.				• New compound.						

TABLE 2

Chemical shift	s of boron-nitrogen compo	unds referred to in the	e text	
Compound	¹ H (90 MHz)	¹¹ B (28·84 MHz)	¹⁹ F (84	77 MHz)
PhNHMe, BCl ₃	-7.6(Ph) - 3.3(Me) * d	- 8.5 ª	· · ·	·
PhNMe·BCl ₂	$-7.1(Ph) - 3.2(Me)^{d}$			
Cl ₄ C ₆ H·NH ₂ ,BCl ₃	-7.78			
Br ₃ C ₆ H ₂ ·NH ₂ ,BCl ₃	-7.84	-13.85		
Br ₃ C ₆ H ₂ ·NH·BCl ₂	-7.56			
4-ČF ₃ –2-NO ₂ ·C ₆ H ₃ ·NHBCl ₂	$ \begin{array}{r} -8.69 \text{ (NH)} \\ -8.02, -7.85, -7.7 \\ -7.4 - 7.26 \end{array} $	-15.45	- 64.4	(CFCl ₃)
C.F. NH·BCl	5.91 "	- 34·4 d		
[(C,F,)NH],BCl	- 5.69 %		27.7 .	ء 11€
(Ċ ₆ Ĕ ₅ ŇH) ₃ Ē	-5.37 6		27.7 •	ء 15.95
	1.01			

Solvents " neat, " MeCN, " benzene, " CH₂Cl₂.

* Accidental sextet from coupling to NH hydrogen (J 3.0 Hz) and ^{11}B (J 3.0 Hz).

All values in p.p.m. relative to the standards tetramethylsilane (¹H), Et_2OBF_3 (¹¹B), and C_6F_6 (¹⁹F), except where given otherwise in parentheses.

that hydrolysis due to leaks or back-diffusion of water was also negligible under experimental conditions. The escape of solvent is less than 5% during the reaction time. The dead-space above the reaction in which HCl can remain



FIGURE 1 Apparatus for thermal dehydrochlorination of R¹R²NH,BCl₃ in boiling benzene

during the reaction was reduced to a minimum (30 ml). After the reaction the vessel was sealed and allowed to cool. The products were then extracted in a dry-box. The concentration of reactant was in the range $(5-20) \times 10^{-3}$ mol l⁻¹. Results are shown in Table 3 and Figure 2. Second-order rate constants reproducible within a factor of two were obtained in the N-methylaniline system.

Preparation of Aminodichloroboranes.—Analyses and characterisation are given in Tables 2—4.

R¹NR²BCl₂

- (I) $R^1 = 2,3,5,6$ -tetrachlorophenyl, $R^2 = H$
- (II) $R^1 = 2,4,6$ -tribromophenyl, $R^2 = H$
- (III) $R^1 = 2$ -bromophenyl, $R^2 = H$
- (IV) $R^1 = Ph$, $R^2 = Me$
- (V) $R^1 = 4$ -trifluoromethyl-2-nitrophenyl, $R^2 = H$
- (VI) $R^1 = 2,3,4,5,6$ -pentafluorophenyl, $R^2 = H$



FIGURE 2 Plot of HCl evolved from R¹R²NH,BCl₃ in boiling benzene against time: A, 2,4,6-tribromoaniline-boron trichloride; B, 2-bromoaniline-boron trichloride; and C, Nmethylaniline-boron trichloride

Dehydrochlorination of adducts of aromatic amines and boron trichloride in boiling benzene Adduct concn. 10⁻²M

	Moles HCl		Reaction half-life/
Adduct	evolved	Product	min
2,3,5,6-Tetrachloro- aniline	1.00	RNHBCl ₂	ca. 2
2,4,6-Tribromoaniline	1.00	RNHBCl ₂	ca. 2
2-Bromoaniline	1.15	RNHBCl ₂	ca. 2.5
N-Methylaniline	1.00	$RNMeBCl_2$	ca. 4
2		-	rate ª =
			k[adduct] ²

Products characterised by: elementary analysis, mass spectrum, n.m.r. (¹H and/or ¹¹B), and i.r. " $k=0.23\pm0.1$ 1 mol^-1 s^-1.

(a) Tetrachloro-, tribromo-, 2-bromo-, and N-methylanilines. These were prepared by dehydrochlorination of the adducts under conditions described in the previous section (see Table 3). Tetrachloroanilino- and tribromo-

TABLE 4

Characterisation of anilinochloroboranes (R¹NR²·BCl₂)

	Anal	NT TT			
Four	nd (%)	Calc	. (%)	stretching b/	
\mathbf{B}	Cl a	в	Cl ª	cm ⁻¹	
3.31	$22 \cdot 0$	3.45	22.70	3362	
2.7	16.9	2.68	17.3	3301,	
				3363,	
				3398	
4.22	27·0 *	4.28	28.1	3368	
5.47	37.15 *	5.76	37.8		
3.91	24.7	3.85	$24 \cdot 8$		
				3390	
	Four B 3·31 2·7 4·22 5·47 3·91	Anal Found (%) B Cl a 3.31 22.0 2.7 16.9 4.22 27.0* 5.47 37.15* 3.91 24.7	Analysis Found (%) Calc B Cl ^a B 3·31 22·0 3·45 2·7 16·9 2·68 4·22 27·0* 4·28 5·47 37·15* 5·76 3·91 24·7 3·85	Analysis Found (%) Calc. (%) B Cl ^a B Cl ^a 3.31 22·0 3·45 22·70 2·7 16·9 2·68 17·3 4·22 27·0* 4·28 28·1 5·47 37·15* 5·76 37·8 3·91 24·7 3·85 24·8	

^a Easily hydrolysed Cl; (pH meter titrations) or ^{*} gravimetric. ^b As solid mulls in Nujol or liquid film. ^e New compound.

anilino-dichloroboranes (I) and (II) were precipitated as solids from benzene solution by addition of light petroleum. 2-Bromoanilinodichloroborane (III) was obtained after evaporation of the benzene, by distillation at very low pressure. It was never obtained completely pure and discoloured rapidly. N-Methylanilinodichloroborane (IV) was obtained, though discoloured, by evaporation of the benzene.²

(b) 2-Nitro-4-trifluoromethylaniline. 2-Nitro-4-trifluoromethylaniline (1.055 g; 0.005 mol) in acetonitrile (35 ml) was added at -80 °C to a solution of boron trichloride in acetonitrile (0.005-mol in 15 ml). Light petroleum (35 ml; b.p. 40-60°) was added and the red precipitate of (V) filtered off and dried *in vacuo*. Its n.m.r. spectra are described in Table 2.

(c) Pentafluoroaniline. Pentafluoroaniline (Imperial Smelting Co.; not purified further) (0.027 mol) was dissolved in dry dichloromethane (50 ml) and added with stirring to a solution of boron trichloride (0.030 mol) in dichloromethane at -80 °C. After one week at room temperature the solvent was removed *in vacuo* to yield a solid and a liquid phase. Portions of this mixture were filtered. The colourless filtrate was pentafluoroanilinodichloroborane (VI): its ¹¹B and ¹H n.m.r. spectra were single lines

in dichloromethane or in the neat liquid (see Table 2). The solid from the reaction mixture was shown to be bis-(pentafluoroanilino)chloroborane (cf. earlier work ¹² on the boron tribromide-pentafluoroaniline system).

Preparation of Bis(amino)chloroboranes.---(a) Pentafluoroaniline. The solid in the reaction mixture (preceding section) was dissolved in benzene and precipitated on addition of light petroleum (b.p. 40-60°) as a white powder or large colourless crystals, depending on the amount of solvent added, which analysed as bis(pentafluoroanilino)chloroborane (Found: C, 34.0; H, 0.59; N, 5.3; B, 2.3; Cl, 8.6. $C_{12}H_2BClF_{10}N_2$ requires C, 35.0; H, 0.5; N, 6.8; B, 2.6; Cl, 8.6%); ¹H n.m.r. signal (NH) at 4.31. Parent ion in mass spectrum (70 eV) m/e 410. Evaporation of the mother liquor from this preparation left a residue with a mass spectrum (70 eV) showing a major peak at m/e 410, and small peaks at m/e 557 [attributed to tris-(pentafluoroanilino)borane] and m/e 681 [attributed to NN'N"-tris(pentafluorophenyl)-BB'B"-trichloroborazole) with the correct isotopic ratios. A parent ion m/e 557 was also obtained from the product of the reaction of bis(pentafluoroanilino)chloroborane (0.0032 mol) and pentafluoroaniline (0.0032 mol) in benzene after 5 h at reflux. This product, a white microcrystalline powder, did not give consistent analyses even on samples from the same batch. The compound is probably trispentafluoroanilinoborane.

(b) Tetrachloraniline. The mother liquor from the preparation of tetrachloroanilinodichloroborane was evaporated to dryness and the white residue sublimed at 170 °C. The sublimate was aminodichloroborane (correct isotopic parent ions at 70 eV in its mass spectrum (317–308). The residue was bis(tetrachloroanilino)chloroborane (Found: B, 2·35; easily hydrolysed Cl, 7·44. $C_{12}H_4BCl_9N_2$ requires B, 2·18; easily hydrolysed Cl, 7·03%).

Preparation of Borazole from 2-Bromoaniline-Boron Trichloride.—2-Bromoaniline-boron trichloride (5 g; 0.016 mol) was treated with benzene (100 ml) for one day at ambient temperature and then refluxed under nitrogen for 30 min. Evaporation to 30 ml yielded (A) white crystals of the starting adduct, which were filtered off. The filtrate was further evaporated and treated with light petroleum (b.p. 80-100°) to give further white crystals (B) with no i.r. absorption in the N-H stretching region. The mother-liquor gave a brown oil which after distillation analysed as 2-bromoanilinodichloroborane. The white crystals (B) were refluxed in benzene and precipitated with light petroleum (b.p. 80-100°) to give the borazole BB'B"-trichloro-NN'N"-tris-(2-bromophenyl)borazole (Found: C, 33.0; H, 2.1; Br, 36.8; Cl, 16.3; N, 6.5. $C_{18}H_{12}B_{3}Br_{3}$ -Cl₃N₃ requires C, 33.8; H, 1.9; Br, 37.0; Cl, 16.4; N, 6.5%). The mass spectrum showed a group of 16 lines corresponding to the parent ion around m/e 648, corresponding to the expected isotopic pattern. The borazole does not give boric acid on aqueous hydrolysis: treatment with peroxide is necessary. Presumably the intermediate BB'B"-trihydroxyborazole is stable. Such a fragment (with appropriate isotopic pattern) was observed in the mass spectrum of a sample exposed to moisture.

Basicity of Amines.—For correlation purposes, the basicities of amines were required. Values of pK_a measured in this work by the customary spectrophotometric titration ^{8,13,14} are collected in Table 5 and were referenced to

¹⁴ M. J. Jorgenson and D. R. Hartter, J. Amer. Chem. Soc., 1963, 85, 878.

V. S. V. Nayar and R. D. Peacock, Nature, 1965, 207, 630.
 K. N. Bascombe and R. P. Bell, J. Chem. Soc., 1959, 1096.

Jorgensen's ¹⁴ or Bell's data ¹³ (dilute acids) as necessary except that the chloro- and bromo-amines used were extremely insoluble in water (a precipitate of tribromoaniline was observed even at 10⁻³M concn. in 3% ethanol).

TABLE 5

pK_a Values for the reaction RNH_3^+							
$RNH_2 + H^+$ in aq. H_2SO_4							
Aniline	M.p./°C	(Lit.)	pK_{a}				
4-CF ₃ -2-NO ₂	106	106—107 •	-2.62 ± 0.04				
$2,3,5,6-(Cl)_4$	108	(107—108) ^b	-0.86 ± 0.16				
$2,4,6-(Br)_3$	120	(120) °	-0.39 ± 0.15				
2,3,4,5,6-(F) ₅	Wax	(01 - 00) 1	$+0.16\pm0.2$				
2-0F ₃ -4-NO ₂	91.9-92	(91·9—93) a	0.0 ± 0.04				

^a M. R. Pettit and J. C. Tatlow, J. Chem. Soc., 1954, 3852. A. T. Peters, F. M. Rowe, and D. M. Stead, J. Chem. Soc., 1943, 233. ^e F. G. Mann and B. C. Saunders, 'Practical Organic Chemistry,' Longmans, Green and Co., London, 3rd edn., 1952. ^a R. Filler and H. Novar, J. Org. Chem., 1961, 06, 2707. **26**, 2707.

Ionisation ratios for these amines were obtained for acid solutions containing 26% ethanol (v/v). The pK_a were estimated by stepwise comparison with 2-nitro-4-trifluoromethylaniline in the same solvents. These two polyhalogenoamines and the pentafluoroaniline exhibit no broad band in the visible region of the type observed in nitroaniline spectra. Cation and free base instead have closely overlapping u.v. spectra and the ionisation ratios for these amines are considered less accurate (Table 5).

In seeking to measure the basicity of the amines towards BCl₃ as reference acid, we considered Satchell's spectrophotometric titration in non-aqueous solvents.¹⁵ However the reactions discussed elsewhere in this paper are expected to interfere and the method was not applied. Satchell and Satchell's pK values in ethers for the amine-boron trifluoride adduct dissociation 15 correlate reasonably well with aqueous pK values, except where the amine has bulky substituents close to the basic site. We thus make the assumption that the pK_a values in Table 5 give a rough guide to the relative basicities of the amines towards BCl₃ as reference acid.

DISCUSSION

Published data 7,10 on the rate of evolution of HCl in thermal dehydrochlorination of adducts of primary aromatic amines and boron trichloride indicate that amines with pK_a ca. 4 undergo evolution of two moles of HCl per mole of adduct, but that the rate processes are not simply two concurrent first- or second-order reactions. In this work we have studied BCl₃ adducts of weak aromatic amines with ortho-substituents $(pK_a 2.3 \text{ to } -0.9)$ and the secondary amine N-methylaniline $(pK_a + 5)$ which (with the exception of 2-bromoaniline) gave only one mole of HCl per mole of adduct (see Table 3) and gave as the other product RNHBCl₂ (RNMeBCl₂). Aminodichloroboranes (RNHBCl₂) have been considered as potential intermediates in the formation of borazoles from amine-BCl₃ adducts (sequence a followed by d in Scheme 1). The clean evolution of one mole of HCl enabled us to examine the rate of formation of these potential intermediates and their subsequent reactivity.

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From published data on dehydrohalogenation of adducts of primary amines with no ortho-substituent, it can be deduced that adducts of weaker bases react more quickly.^{5,7,10} The half-lives for evolution of the first mole of HCl (two moles are evolved altogether) were in the order $4-BrC_6H_4\cdot NH_2 > PhNH_2 > 4-MeC_6$ - H_4 ·NH₂ for a heterogeneous reaction in boiling benzene. Gerrard and Mooney suggest these reactions are of the first order over the last 10% of total HCl evolution.¹⁰ For the homogeneous reaction of the aniline adduct in boiling toluene it is claimed that the order is initially first, rising steadily to second at the end of the evolution of the second mole of HCl,⁷ supporting a first-order process (for evolution of the first mole, giving RNHBCl₂) and a concurrent second-order process for the second mole (giving borazole). Methylamine gives a fractional order ca. $\frac{2}{3}$ in initial adduct concentration.¹⁶ These are all at high (ca. molar) concentration. The kinetics reported in this work were measured at ca. 10⁻²M and cover the evolution of the first mole of HCl to form $R^1NR^2BCl_2$ (except for 2-bromoaniline adduct which gives 1.15 mole of HCl; Figure 2). The amount of HCl evolved for our adducts in boiling benzene (homogeneous) is plotted against time in Figure 2. Unfortunately we could not make a complete rate comparison since the reactions of pentafluoro-, tribromo-, and tetrachloro-anilines were too fast; but it is clear from Table 3 and Figure 2 that the amines which are weakest in terms of pK_a , or have the heaviest ortho-substitution (trends which run parallel) do react more quickly. We do not know if the reactions we are comparing do in fact have the same order. The initial rate in the 2-bromoaniline adduct is probably of the second order. For the N-methylaniline adduct, rate is of the second order in adduct concentration over 70% of the reaction. A direct bimolecular reaction between two adduct molecules is improbable, especially if the effect of decreasing amine basicity is considered. To explain this it is necessary to postulate pre-equilibria involving adduct, followed by some rate-determining reaction (cf. ref. 5).

We tested 2-bromoanilinodichloroborane (III) as a possible intermediate *en route* to the borazole, which has been independently synthesised. The adduct 2-bromoaniline-boron trichloride gives 1.15 moles HCl in thermal elimination. No borazole was found in the resulting mixture, but whatever side-products are formed in addition to the aminodichloroborane, they do not react further under these conditions to produce more HCl. In contrast, this adduct in a sealed system in benzene (from which HCl cannot escape) does yield after a few days at room temperature quantities of trichlorotris-(2-bromophenylborazole). The adduct and free HCl were also present. The anilinodichloroborane (III) was isolated from a thermal dehydrochlorination experiment and treated for 12 h in boiling benzene under the conditions of the kinetic experiments (see

¹⁵ D. P. N. Satchell and R. S. Satchell, J. Chem. Soc. (B), 1967, 36.
 ¹⁶ H. S. Turner and R. J. Warne, J. Chem. Soc., 1965, 6421.

Experimental section). It was recovered unchanged with no loss of HCl. These studies emphasise the fact that removal of HCl is necessary to form RNHBCl₂, and that conversion of RNHBCl, into borazole requires catalysis (step e). N-Methylanilinodichloroborane (IV) was also unchanged by treatment for 12 h in boiling benzene.

Pentafluoroaniline-boron trichloride is anomalous in that its stability is lower than would be expected from the base strength of the amine; the weaker amines 4-nitro-2-trifluoromethyl-, 2,4,6-tribromo-, and 2.3.5.6-tetrachloro-aniline form more stable solid adducts with boron trichloride. The decomposition of the pentafluoroaniline adduct was studied at 33 °C by ¹H n.m.r. spectroscopy, in acetonitrile, a more basic solvent than benzene. Salting-out of the major product N-pentafluorophenylacetamidinium chloride 17 does not obscure the formation of the aminodichloroborane, and subsequently the bisaminochloroborane. The decomposition of an equimolar mixture of pentafluoroaniline and boron trichloride in benzene produces bisaminochloroborane and aminodichloroborane, traces of tris(amino)borane, and borazole.

The reactions of tetrachloro- and tribromo-aniline adducts were also monitored in acetonitrile or bis-(2-chloroethyl) ether by ¹H n.m.r. during a period of days at room temperature. Since the two aromatic residues have a singlet aromatic C-H signal, each of the several new signals in the mixture after reaction corresponds to one new aromatic H environment. An attempt was made to identify these signals by comparison of their chemical shifts with those of authentic amine RNH₂, the ion RNH₃⁺, RNH₂·BCl₃, RNHBCl₂, (RNH)₂-BCl, etc., but it was not possible to identify all of the species present. Salting-out of the acetamidinium chloride complicates the acetonitrile spectra. The aminodichloroborane from each starting compound could be obtained as the major product by sublimation of the residue from evaporation of solvent: each was identified by analyses and by means of the isotopic patterns produced by the halogen atoms in the mass spectra. Attempts to evaporate the solution automatically remove HCl from the system. It is possible that the reaction to give RNHBCl₂ is a consequence of the removal of HCl (as in our kinetic experiments) while in solution at ambient temperatures a variety of intermediates, too labile to be isolated, can exist. These might be polyaminoboranes, boron cations, etc.

Although in the past we have synthesised several substituted 2-nitroanilinodihalogenoboranes,^{6,8} we have so far not obtained definite structural information.^{6,8,9} The curious colour of these species indicates some special interaction, albeit of low energy, which involves the nitro-group, and the ortho-NHBCl₂ moiety.¹⁸ In this work we prepared the derivative with a 4-CF3 ring substituent. This had a much greater solubility and volatility than any previously prepared analogue and we have obtained mass spectra and ¹H, ¹⁹F, and ¹¹B n.m.r. for the compound (Scheme 2), all of which support our previous formulations.6,8,9

This coloured nitro-compound could conceivably be a free radical. As such we would expect its n.m.r. spectra to consist of extremely wide lines and to exhibit contact shifts, owing to coupling of nuclear spins with the unpaired electron spin. The ¹H and ¹⁹F n.m.r.



spectra are broadly similar to those for the free amine, except that the NH hydrogen gives a signal well downfield from its position in the free amine. The signals gave the correct areas and are also of normal width (ruling out the free radical possibility) and seem consistent with an electron-withdrawing substituent on N affecting the shifts. The most useful spectrum from a structural point of view is that for ¹¹B. This is given in Table 2. It is well outside the region of RNR'BCl, monomer shifts, but lies in the expected region for tetrahedral boron. Interaction of the nitro-group with the boron would seem to be a rational explanation for a monomer containing four co-ordinate boron.

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- ¹⁷ J. R. Blackborow, unpublished work.
 ¹⁸ J. C. Lockhart, *Chem. and Ind.*, 1961, 2006.