PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS

VII. FURTHER STUDIES ON TRIS(PENTAFLUOROPHENYL)BORON[*]

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INTRODUCTION

Previously we synthesised adducts of tris(pentafluorophenyl)boron with several donor molecules[2] and also estimated that the electro-negativity of the pentafluoro-phenyl group, C_6F_5, lies between that of the halogens, chlorine and bromine[3], therefore it is of interest to compare the acceptor strength of tris(pentafluorophenyl)boron with that of the boron trihalides. This was initially attempted using exchange reactions of the type $BX_3 \cdot D \rightarrow BY_3$ but later, following the work of Miller and Onyszchuk[4], we used the proton nuclear magnetic resonance (NMR) spectra of several adducts to estimate relative acceptor strengths of the boron compounds.

DISCUSSION

A qualitative indication of the relative strength of the boron–nitrogen bond in compounds of the type $BX_3 \cdot D$, where D is a nitrogen-containing donor molecule, can often be obtained by a study of displacement reactions, provided that the compounds studied are closely related and have similar lattice energies. In this manner, for example, the following series of acceptor power towards trimethylamine has been obtained[5]: $BBr_3 > BCl_3 > BF_3 > \frac{1}{2}B_2H_6$. In the many experiments we carried out involving adducts of tris(pentafluorophenyl)boron the only simple exchange reaction we obtained was that between trimethylamine-tris(pentafluorophenyl)boron and ammonia which, after some weeks at room temperature, gave a mixture of trimethyl-amine, ammonia and pentafluorobenzene, C_6F_5H. In almost all cases pentafluoro-benzene was the major (or only) component of the volatile products if a source of "hydrogen" was present in the reaction mixture. The preferential cleavage of penta-fluorophenyl groups from the boron atom rendered this method of obtaining relative acceptor strengths ineffective when applied to tris(pentafluorophenyl)boron and its adducts.

Considering the instability of $Al-C_6F_5$ compounds and perfluoroalkyl–boron derivatives, tris(pentafluorophenyl)boron is remarkably stable thermally; after several days at 270° in a vacuum no boron trifluoride can be detected in the volatiles whilst the starting material can be recovered in high yield. Conversely the adducts of tris(pentafluorophenyl)boron with ammonia or trimethylamine decompose at 70°

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[*] For Part VI see ref. 1.

giving 30 % and 65 % respectively of the available C_6F_5 groups as pentafluorobenzene in a similar reaction time. No reaction of tris(pentafluorophenyl)boron with pure oxygen can be detected during 10 days at room temperature or for short periods at 135°.

Several communications have been published giving details of the fluorine NMR spectra of a wide range of pentafluorophenyl compounds[6]. The chemical shifts of the *ortho, meta* and *para* fluorines depend on a number of factors such as the charge density (π-electrons) on the fluorine atom or its neighbouring carbon atom, on paramagnetic contributions, and on an "*ortho* effect". Our measurements on pentafluorophenyl–boron derivatives in which the boron atom is in a tetrahedral environment are consistent with published explanations; we find *ortho* shifts in the range of 130 to 136 ppm, para shifts of 157 to 164 ppm and meta shifts of 163 to 168 ppm (upfield) from CCl_3F (Table 3). In tris(pentafluorophenyl)boron the resonances occur at 128.7, 144.3 and 160.6 ppm and similar values (128.7, 146.0, 161.1) were reported by Bourn, Gillies and Randall[6] for the compound $C_6F_5BCl_2$. Although we measured the spectrum of tris(pentafluorophenyl)boron in pentane (to avoid complex formation) and the other spectra were recorded in ether, acetone or chloroform, we think the magnitude of the shifts involved rules out solution effects, *cf.* the chemical shifts for the tetrakis(pentafluorophenyl)borate anion in acetone and in ether lies within a range of less than one ppm. Thus the *ortho* and *meta* resonances in $B(C_6F_5)_3$ are shifted downfield by a few ppm whilst the *para* resonance is shifted downfield by some 20 ppm relative to the tetrahedral compounds. It is thought[7] that these results indicate an interaction of the π-aromatic systems of the phenyl rings in tris(pentafluoro)boron with the vacant boron p_z orbital, since this would tend to deshield the *para* fluorine to a greater extent than either the *ortho* or *meta* fluorine atoms and lead to a large chemical shift downfield. Such π-bonding would stabilise the tris(pentafluorophenyl)boron molecule toward pyrolytic and oxidative decomposition.

The spectrum of ammonia-tris(pentafluorophenyl)boron (Fig. 1) shows fine structure due to spin–spin coupling between the several fluorine atoms but we could
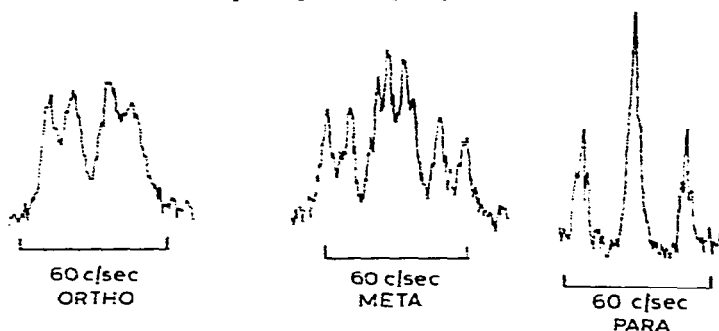

60 c/sec
ORTHO

60 c/sec
META

60 c/sec
PARA

Fig. 1. Fluorine NMR spectrum of $B(C_6H_5)_3 \cdot NH_3$.

not analyse it fully owing to the limited solubility of the adduct which resulted in a low signal-to-noise ratio; no coupling due to the boron nucleus can be seen. The NMR spectrum of lithium tetrakis(pentafluorophenyl)borate provides some evidence for boron–fluorine coupling over four and perhaps five bonds. If this ion is tetrahedral then the field gradient at the boron nucleus should be zero and ^{11}B–^{19}F spin–spin

coupling will occur. The spectrum of this ion (Fig. 2) shows a very broad *ortho* peak, a broadened *meta* resonance and a *para* triplet (which might be slightly broadened) the broadening in all cases probably being due to boron–fluorine coupling.
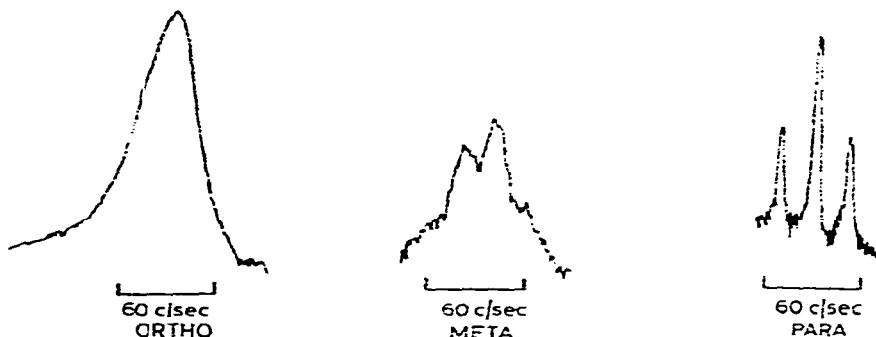

| 60 c/sec | 60 c/sec | 60 c/sec |
| ORTHO | META | PARA |

Fig. 2. Fluorine NMR spectrum of LiB(C₆F₅)₄.

Most of the compounds whose proton NMR spectra are reported in this work have been characterised previously (including molecular weight determinations). The possibility of rearrangement or preferential formation of ionic complexes such as [Bpy$_2$I$_2$]$^-$–I$^-$ shows the necessity of such characterisation. Observations on the spectra of some of our solutions (particularly those of the triethylamine complexes) over a period of time showed that impurity lines developed (usually just upfield of the pure adduct) whilst simultaneously a white precipitate formed in the solution. We repeated the work of Onyszchuk and Miller[1] in order to reduce as much as possible instrument and solvent variations when comparing adducts of tris(pentafluorophenyl)boron with known X$_3$B·D compounds; as we found slight discrepancies in their spectra we feel it worthwhile to describe our spectra in some detail.

Chemical shifts of the methyl protons in trimethylamine complexes of various boron compounds were found to decrease in the order BI$_3$ > BBr$_3$ > BCl$_3$ > B(C₆F₅)$_3$ ~ BF$_3$ ~ BH$_3$ > BMe$_3$ using dichloromethane as the solvent. Miller and

TABLE 1

NUCLEAR MAGNETIC RESONANCE DATA FOR TRIMETHYLAMINE ADDUCTS

Compound	δ (chemical shift)	Remarks
BMe$_3$·NMe$_3$	−141.5	$Q = 2$, BMe$_3$: δ = +22.5. $Q = 6$
BH$_3$·NMe$_3$	−155	$Q = 4$, BH$_3$: δ = −99. $J(^{11}$B–H$_B) = 97$
BF$_3$·NMe$_3$	−156	$J(^{11}$B–Hc$) \sim 1.4$. $J($F–Hc$) \sim 0.7$
B(C₆F₅)$_3$·NMe$_3$	−156	$Q = 0.5$
BCl$_3$·NMe$_3$	−182	$J(^{11}$B–Hc$) = 2.7$
BBr$_3$·NMe$_3$	−189	$J(^{11}$B–Hc$) = 3.1$
BI$_3$·NMe$_3$	−201	$J(^{11}$B–Hc$) = 3.5$

All figures are in cycles per second; resonances to the low field of the internal standard (TMS) are assigned negative. Q is the peak width at half height for single lines.

Onyszchuk[1] observed an order of BBr$_3$ > BCl$_3$ > BH$_3$ > BF$_3$ in chloroform, whilst Coyle and Stone[8] using dichloromethane as solvent and reference found that the res-

onance for BF_3NMe_3 occurred at lower field than that of BH_3NMe_3, the difference between the shifts of these adducts is very small and may be due to solvent effects only. The chemical shifts of the methyl and methylene protons, and also the internal chemical shift of the triethylamine adducts decrease in magnitude in the order $BI_3 > BBr_3 > BCl_3 > B(C_6F_5)_3 \sim BF_3$ with dichloromethane as solvent.

Withdrawal of electron density from the donor moiety would be expected to result in proton deshielding, the effect decreasing with increasing distance between the boron and nitrogen atom; that such an effect is observed in the proton spectra of the trimethylamine and triethylamine adducts suggests that the order of electron withdrawing power (*i.e.* acceptor strength) of the boron compounds is $BI_3 > BBr_3 > BCl_3 > B(C_6F_5)_3 \sim BF_3 \sim BH_3 > BMe_3$. The position of tris(pentafluorophenyl)-boron in this series is probably a further manifestation of considerable π-bonding between the phenyl ring and the vacant p_z orbital.

The proton NMR spectrum of trimethylamine-trimethylboron showed a broadened line due to the methyls attached to boron and a slightly broadened line due to the methyl groups bonded to nitrogen. Trimethylamine-borane shows a slightly broadened single line due to the methyl groups and a quartet of broadened lines due to the borane group, the coupling constant (J 97 cps) agrees with the value[9] determined by ^{11}B NMR (J 97 cps). Previous workers[1,8] have observed a slightly broadened single line for the proton spectrum of trimethylamine-boron trifluoride. Our spectrum shows fine-splitting, understandable in terms of boron ($J \sim 1.4$ cps) and fluorine ($J \sim 0.7$
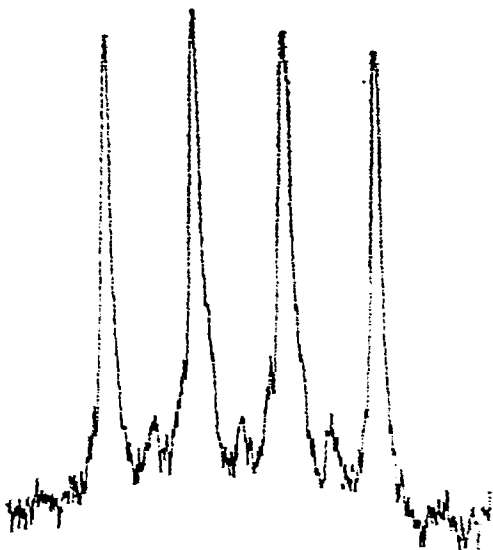

Fig. 3. Proton NMR spectrum of $BCl_3 \cdot NMe_3$.

cps) coupling to the protons*. The proton NMR spectra of the trimethylamine adducts of boron trichloride (Fig. 3), boron tribromide and boron triiodide all exhibited quartets with peaks of almost equal intensity and coupling constants of 2.7, 3.1 and 3.5 cps respectively. Lines of a lower intensity were also present; if the quartet is assigned to

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* Whilst this paper was in the manuscript stage a paper appeared in the literature[13] describing a similar spectrum to ours for F_3BNMe_3.

[11]B–H coupling then the low intensity lines lie exactly in the places calculated for the septet arising from the [10]B isotope (20 % abundance, spin 3); the possibility of nitrogen coupling (cf. ref. 4) is thus eliminated. Miller and Onyszchuk[4] observed a quartet for trimethylamine-boron trichloride and reported a further splitting of each line into doublets ($J = 0.7$ cps) but this effect could be due to an imperfect adjustment of the spectrometer since our spectral lines were less than 0.4 cps wide. The spectrum of trimethylamine-tris(pentafluorophenyl)boron showed a slightly broadened single line.

The adducts with triethylamine all gave first order spectra, with no sign of boron coupling to the methyl groups. The methylene groups in the boron trifluoride complex were slightly broadened probably by the boron and fluorine coupling. The methylene region of triethylamine-boron trichloride has a complex structure which can be explained by methyl-proton-to-methylene-proton ($J = 7.4$ cps) and [11]B-to-methylene-proton ($J = 2.6$ cps) couplings. Broad, stunted triplets were observed for the adducts with boron tribromide and boron triiodide; the rapidity with which solutions of these compounds precipitated a white solid (which impaired the resolution) made a detailed study impossible. The spectra are not inconsistent with methyl and boron couplings leading to overlapping lines, approximate values for the boron coupling constants are given in Table 2. Boron coupling in triethylamine-tris(pentafluorophenyl)boron was not observed.

TABLE 2

NUCLEAR MAGNETIC RESONANCE DATA FOR TRIETHYLAMINE COMPLEXES

Compound	Chemical shift CH$_3$	Chemical shift CH$_2$	Remarks
BF$_3$NEt$_3$	−71	−175	$J(CH_3$–$CH_2) = 7.3$
B(C$_6$F$_5$)$_3$·NEt$_3$	−75	−184	$J(CH_3$–$CH_2) = 7$
BBr$_3$·NEt$_3$	−86	−212	$J(CH_3$–$CH_2) = 7.5$
			$J(^{11}B$–$CH_2) = 2.7$
BI$_3$·NEt$_3$	−91	−224	$J(CH_3$–$CH_2) = 7.5$
			$J(^{11}B$–$CH_2) = 3$

Several authors[4,10] have correlated chemical shifts with properties of the donor–acceptor bond (e.g. thermodynamic properties, dipole moments, and infrared spectral shifts; such correlations are often linear. We find that the magnitude of the proton chemical shift in adducts of boron halides with trimethylamine increases linearly with the magnitude of the boron–proton coupling constant. On current theory the coupling constant $J(^{11}B$–H) depends on the amount of s character at the boron and hydrogen atoms (in the linkage between them) hence it follows that $J(^{11}B$–H) is a measure of the amount of s character in the region of space between boron and nitrogen. Other factors may be involved, for example, it has been reported that for atoms containing non-bonded electrons an interaction of low lying triplet states with the bonding molecular orbital joining the coupled atoms, can lead to a contribution to the coupling constant. The magnitude of the coupling constant increases on replacing fluorine in turn by chlorine, bromine and iodine (each of decreasing electronegativity). This apparently violates Bent's rule[11] that "the atomic s character concentrates in orbitals directed toward electropositive substituents"; he points out however several examples

where anomalous results have been found when halogens are involved and suggests participation of halogen d orbitals.

Linear correlations between chemical shifts or coupling constants and other properties associated with the boron-to-donor bond are not too surprising; linear correlations are observed also with properties of the boron trihalides. Thus the plot of $J(^{11}B-H)$ against boron–halogen bond energy, $\bar{E}(B-X)$, in BX_3 is linear whilst similar correlations with effective stretching constants and bond lengths exist. Some properties do not correlate however, particularly the ^{11}B chemical shifts for the boron trihalides.

TABLE 3

^{19}F NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME PENTAFLUOROPHENYL DERIVATIVES OF BORON ppm relative to CCl_3F.

Compound	Chemical shifts (ppm)			Remarks
	ortho	para	meta	
$B(C_6F_5)_3$	128.7	144.3	160.6	In pentane
$B(C_6F_5)_3 \cdot NEt_3$	131.2	163.5	167.1	In acetone
$LiB(C_6F_5)_4$	131.6	164.2	167.9	In ether
$B(C_6F_5)_3 \cdot NH_3$	134.2	157.3	163.9	In ether
$B(C_6F_5)_3 py$	130.7	157.1	163.5	In ether
$B(C_6F_5)_3 \cdot N_3Me_3$	135.6	159.4	164.4	In chloroform

We have also recorded the proton NMR spectrum of trimethylamine-diboron tetrachloride which consists of a single line centred at -179 cps relative to TMS (dichloromethane solution). This would indicate that the acceptor strength of diboron tetrachloride towards trimethylamine is but little different from that of boron trichloride although an added complication here is that the trimethylamine adduct is reported to be a tetramer[12] in solution making a direct comparison to monomeric trimethylamine-boron trichloride rather uncertain.

EXPERIMENTAL

The preparation and purification of tris(pentafluorophenyl)boron, lithium and tetraethylammonium tetrakis(pentafluorophenyl)borate and the adducts of tris-(pentafluorophenyl)boron with ammonia, trimethylamine, pyridine and triphenyl-phosphine have been described previously by us[2]. Triethylamine-tris(pentafluoro-phenyl)boron was prepared by mixing pentane solutions of triethylamine and tris-(pentafluorophenyl)boron at room temperature under dry nitrogen; the adduct was precipitated as a white solid which was twice recrystallised from an ether/chloroform mixture. (Found*: C, 46.9; H, 2.6; F, 46.7; N, 2.2. $C_{24}H_{15}BF_{15}N$ calcd.: C, 47.0; H, 2.45; F, 46.5; N, 2.3 %.)

Proton NMR spectra were recorded on a Varian model A60 using precalibrated charts; shifts are quoted to $\pm$ 1 cycle. Dichloromethane was the solvent for all the proton spectra, and was purified by washing several times with distilled water fol-

* Analyses performed by ALFRED BERNHARDT, Max Planck Institute, Mülheim, Ruhr, Germany.

lowed by drying with molecular sieve and fractional distillation. Fluorine NMR spectra
were recorded on a Perkin–Elmer model R10 spectrometer using precalibrated charts
and a decade shift; shifts are quoted to $\pm$ 0.2 ppm.

Reactions on the millimole scale were carried out using "pyrex" glass tubes of
about 50 cc volume fitted with breakseals of conventional pattern. The reaction tubes
were outgassed under vacuum by heating to near the collapsing point for about five
minutes. Each tube was fitted with a side arm through which weighed quantities of
solid in glass containers could be introduced; the side arms were then sealed, and the
tubes evacuated to 10^{-4} mm. Volatile material was condensed into the reaction bulbs
before sealing.

(1) Pyrolysis of tris(pentafluorophenyl)boron

Tris(pentafluorophenyl)boron (0.376 g, 0.735 mmole) were heated for 168 h at
150°; on cooling to room temperature the white crystals reformed. The tube was
heated at 210° for 96 h and the volatile material removed; only 0.29 mmoles of penta-
fluorobenzene were present. The reaction bulb was resealed and heated at 270° for
168 h; 0.28 mmole of pentafluorobenzene were recovered. The residue consisted largely
of pale yellow soluble crystals, shown to be undecomposed starting material. The
pentafluorobenzene probably arose due to hydrolysis caused by water initially ab-
sorbed by tris(pentafluorophenyl)boron despite the use of a dry-box during manipula-
tions at atmospheric pressure.

(2) Tris(pentafluorophenyl)boron and oxygen

Tris(pentafluorophenyl)boron (0.541 g, 1.05 mmole) and oxygen (16.85 cc, 0.752
mmole) were sealed together; after 10 days at room temperature no obvious change was
apparent. The reaction tube was heated to 135° [above the melting point of tris-
(pentafluorophenyl) boron] for 1 hour after which time 16.60 cc (0.743 mmole) of
non-condensable gases were removed.

(3) Tris(pentafluorophenyl)boron and water

Tris(pentafluorophenyl)boron (0.181 g, 0.354 mmole) was sealed with 6.1 mmole
of distilled oxygen-free water, after 18 days at room temperature all the volatile
material was removed and condensed onto phosphorus pentoxide to remove water.
After a few minutes at room temperature the unreacted material was removed; less
than 0.01 mmole of pentafluorobenzene was obtained. Although no C_6F_5H was
evolved there had been some interaction with the water; we plan a further study of
this reaction.

(4) Exchange reactions

Displacement reactions of the type $BX_3 \cdot D \rightleftharpoons BY_3$ and $BX_3 \cdot D \rightleftharpoons D'$ where X,
Y, = C_6F_5, F, Cl, Br, H and Me and D, D' = NMe_3 or NH_2 gave complex mixtures
of involatile products which could not be separated and led to inconclusive results.
Some exchange occurred in the system X = C_6F_5, D = NMe_3 and D' = NH_3:

Trimethylamine-tris(pentafluorophenyl)boron (0.181 g, 0.32 mmole) and am-
monia (0.48 mmole) were left sealed together for 26 days at room temperature. The
volatile reaction products consisted of pentafluorobenzene and a mixture of ammonia
(86 %) and trimethylamine (14 %) (analysed by calibration of the infrared spectrum).

(5) *Pyrolysis of ammonia-tris(pentafluorophenyl)boron*

Ammonia-tris(pentafluorophenyl)boron (0.112 g, 0.211 mmole) after being heated in a vacuum at 70° for 21 days gave 0.09 mmole of pentafluorobenzene. After a further 4 days at 125° another 0.129 mmole of pentafluorobenzene was recovered; at least two involatile components remained in the tube: white crystals, m.p. 180–183°, of undecomposed starting material (Found: C, 40.9; H, 0.7; F, 54.4. $C_{18}H_3F_{15}BN$ calcd.: C, 40.9; H, 0.6; F, 53.7%.) and an amorphous yellow powder, m.p. > 300°.

(6) *Pyrolysis of trimethylamine-tris(pentafluorophenyl)boron*

Trimethylamine-tris(pentafluorophenyl)boron (0.203 g, 0.356 mmole) gave 0.452 mmole of pentafluorobenzene after 13 days at 70°; over a further period of 7 days at the same temperature another 0.290 mmole of pentafluorobenzene was evolved. No identifiable compounds could be separated from the involatile solid residue.

SUMMARY

Tris(pentafluorophenyl)boron (I) is found to be very stable thermally and does not react with pure oxygen. Displacement reactions between adducts of (I) and BX_3 compounds give inconclusive results; a correlation between the ^1H NMR chemical shift of several adducts and the acceptor strength of the parent boron compounds is assumed and leads to the acceptor strength series $BI_3 > BBr_3 > BCl_3 > B(C_6F_5)_3 \sim BF_3$. ^{19}F NMR data are also presented.

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