PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS

I. TRIS(PENTAFLUOROPHENYL)BORON

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Many attempts were made to isolate compounds having fluorocarbon groups attached to boron before success was achieved. During the course of several investigations* it became apparent that tricoordinate boron compounds containing R_f–B linkages (R_f being a perfluoroalkyl group) are unstable with respect to fluorine migration from the organic side-chain to the boron atom to give boron trifluoride. In spite of this problem some fluorocarbon derivatives of boron have been described. This has been accomplished by reducing the electrophilic nature of the boron atom either by making boron tetracoordinate as in the $[CF_3BF_3]^-$ anion[3] or by linking to tricoordinate boron groups able to π-bond strongly with the boron p-orbital.

The perfluorovinylboron compounds[4] are the only known stable fluorocarbon derivatives of tricoordinate boron. However, it seemed probable that pentafluorophenylboron derivatives in which the boron atom is tricoordinate should also be capable of existence since the π-electrons of phenyl groups can lend π-character to boron–carbon bonds[5]. Moreover, in view of the isolation of salts of the anion $[CF_3BF_3]^-$ there seemed to be no reason why $[(C_6F_5)_4B]^-$ and related anions should not exist. These considerations led us to attempt the preparation of tris(pentafluorophenyl) boron and adducts derived from this Lewis acid.

EXPERIMENTAL**

All the manipulations were carried out under dry oxygen-free nitrogen or with the aid of a vacuum system. Pentafluorophenyllithium was prepared as a fine suspension at −78° by the addition of butyllithium (in hexane solution) to a vigorously stirred pentane solution of pentafluorophenyl bromide. Analyses were performed by ALFRED BERNHARDT, Max Planck Institute, Mühlheim, Ruhr, Germany.

Tris(pentafluorophenyl)boron

Pentafluorophenyllithium (formed from 18 g, 70 mmole, of pentafluorophenyl bromide and butyllithium, 70 mmole in 600 ml of dry pentane at −78°) was placed in a 1000-ml 3-necked flask equipped with a nitrogen inlet, dropping funnel, stirrer

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* The preparation and properties of fluorocarbon derivatives of the elements have recently been thoroughly reviewed[1,2].

** For a preliminary communication see reference 6.

and two feet of nylon tubing (1 mm diameter)—the latter entered one of the necks of the flask via a serum cap and acted as the nitrogen outlet during the initial stages of the reaction. Cooled pentane (50 ml) containing 2.3 g of boron trichloride, 20 mmole, was quickly run into the stirred pentafluorophenyllithium from the dropping funnel and the mixture stirred for 5–10 min before the temperature of the vessel was allowed to rise slowly towards ambient temperature. At about —20° lithium chloride began to separate out. After stirring for 10 min at room temperature the precipitate was allowed to settle (one hour) and the supernatant pentane solution of tris(pentafluorophenyl)boron was syphoned out of the reaction vessel by means of the nylon tube. Evaporation of the pentane solvent (20°) under vacuum left a white solid product; yields in this and similar preparations range from 30–50 %. An analytical sample, melting point 126–128°, was obtained by two sublimations at 80° under high vacuum. (Found: F, 55.7; mol.wt. osmometrically in benzene, 498. $C_{18}BF_{15}$ calcd.: F, 55.7 %; mol.wt., 512.) The product was further characterised by the preparation of several adducts (see below).

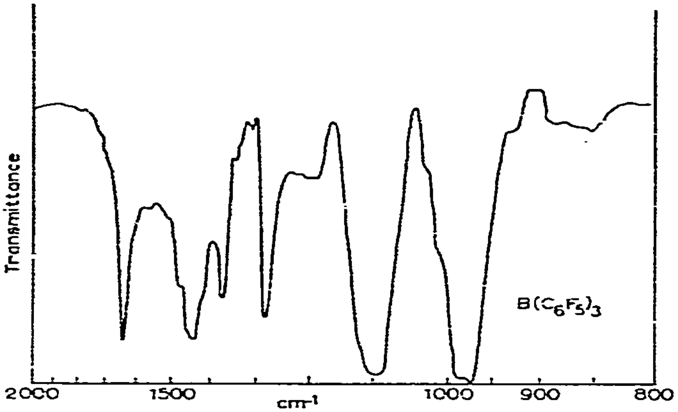

Fig. 1. The infrared spectrum of tris(pentafluorophenyl)boron in chloroform.

Ammonia-tris(pentafluorophenyl)boron, $H_3NB(C_6F_5)_3$

Dry ammonia gas was bubbled at room temperature through the pentane solution syphoned from the preparative vessel. This led to the precipitation of the ammonia addition compound $H_3NB(C_6F_5)_3$. This adduct was purified by recrystallisation from dry chloroform under nitrogen, or by sublimation at 170° in high vacuum. Yields of this and other adducts (see below) were about 30–40 % based on the pentafluorophenyl bromide initially taken. (Found: C, 41.1; H, 0.7; F, 53.7; N, 2.9; mol.wt., 536. $C_{18}H_3BF_{15}N$ calcd.: C, 40.9; H, 0.6; F, 53.7; N, 2.65 %; mol.wt., 529.) The adduct, m.p. 178–180°, is soluble in most organic solvents.

When 186.0 mg of ammonia-tris(pentafluorophenyl)boron (0.35 mmole) were heated for 30 h at 110° with 63.0 ml of dry hydrogen chloride gas (2.81 mmole), hydrogen chloride was consumed and 2.5 ml of pentafluorobenzene (0.11 mmole) were produced. The latter was identified by comparison of its infrared spectrum, and its retention time in a vapour phase chromatograph, with those of an authentic sample.

TABLE I

MAIN INFRARED PEAKS OF PENTAFLUOROPHENYL BORON DERIVATIVES

$B(C_6F_5)_3$[a]	$H_3NB(C_6F_5)_3$[a]	$(CH_3)_3NB(C_6F_5)_3$[a]	$C_5H_5NB(C_6F_5)_3$[a]	$(C_6H_5)_3PB(C_6F_5)_3$[a]	$LiB(C_6F_5)_4$[b]	$KB(C_6F_5)_4$[b]	$N(C_2H_5)_4B(C_6F_5)_4$[b]
1642 w	1642 m	1639 m	1639 m	1639 m	1642 m	1642 m	1642 m
			1626 m				
1578 w	1595 w	1597 w	1597 w	1582 w			
1475 msh	1508 m		1506 msh	1504 m	1513 s	1513 s	1513 s
1451 s	1451 s	1449 s	1451 s	1449 s			
1426 msh	1410 msh				1410 vw	1410 vw	1410 vw
				1389 wsh			
1374 s	1372 m	1359 w	1368 m	1372 m			
1316 s				1326 w			
					1299 vw	1277 msh	
1292 m	1284 m	1274 w	1282 m	1282 m	1272 m	1266 m	1272 m
1151 m			1160 w				
1139 m					1129 msh	1124 wsh	1129 vw
							1115 w
1110 m						1105 msh	1105 msh
							1093 m
1093 wsh	1099 s	1081 s	1093 s	1093 s	1087 s	1088 m	1087 s
1071 w	1087 msh			1078 w	1031 w	1055 w	1055 wsh
1012 s	1026 m	1042 msh				1032 m	1031 w
						994 msh	996 m
973 s	962 s	971 s	982 s	976 s	980 s	977 s	979 s
926 vw		932 w				931 vw	
		917 w			909 vw	915 w	908 w
	871 m		880 w	893 w		901 vw	
			867 m				
					775 m	775 m	775 m
					769 m	769 w	770 wsh
					756 m	757 m	759 m
					682 m	682 m	683 m
					659 m	659 m	669 wsh
							662 m

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[a] Chloroform solution. [b] Nujol mull.

Trimethylamine–tris(pentafluorophenyl)boron, $(CH_3)_3NB(C_6F_5)_3$

Trimethylamine in dry pentane was added to a solution of freshly prepared tris(pentafluorophenyl)boron in the same solvent at room temperature under dry nitrogen. The adduct was precipitated as a white solid which was purified by recrystallisation from ether under nitrogen, m.p. 164–166°. (Found: C, 42.9; H, 2.7; F, 49.1; mol.wt., 575. $C_{21}H_9BF_{15}N$ calcd.: C, 44.1; H, 1.6; F, 49.8 %; mol.wt., 571.)

Pyridine–tris(pentafluorophenyl)boron, $C_5H_5NB(C_6F_5)_3$

This adduct was precipitated as a white solid on mixing pentane solutions of pyridine and tris(pentafluorophenyl)boron at room temperature. An analytical sample was obtained by sublimation at 160° under high vacuum. (Found: C, 46.5; H, 0.8; N, 2.5; mol.wt., 599. $C_{23}H_5BF_{15}N$ calcd.: C, 46.7; H, 0.85; N, 2.4 %; mol.wt., 591.)

Triphenylphosphine–tris(pentafluorophenyl)boron, $(C_6H_5)_3PB(C_6F_5)_3$

Addition of triphenylphosphine (twice recrystallised from alcohol) in pentane to tris(pentafluorophenyl)boron in the same solvent gave a fine, white precipitate of the adduct. An analytical sample was obtained by recrystallisation from dry ether. (Found: C, 55.7; H, 1.9; F, 37.0. $C_{36}H_{15}BF_{15}P$ calcd.: C, 55.8; H, 1.9; F, 36.8 %.)

Lithium tetrakis(pentafluorophenyl)borate, $LiB(C_6F_5)_4$

Addition of 23 mmole of pentafluorophenyllithium (formed from 14 ml of butyllithium solution in hexane and 6 g of pentafluorophenyl bromide in 100 ml of ether) to a pentane solution of tris(pentafluorophenyl)boron (20 mmole) caused precipitation of 6.3 g of lithium tetrakis(pentafluorophenyl)borate (43 % yield). On analysis it was found that the compound always contained appreciable amounts of "hydrogen" due to ether and water coordinated to the lithium ion. Characterisation was accomplished by direct precipitation of the tetraethylammonium and potassium derivatives. The white air-stable $LiB(C_6F_5)_4$ is soluble without reaction in cold air-free distilled water.

Tetraethylammonium tetrakis(pentafluorophenyl)borate, $(C_2H_5)_4NB(C_6F_5)_4$

Addition of a cold aqueous solution of lithium tetrakis(pentafluorophenyl)borate to a solution of tetraethylammonium chloride in air-free distilled water led to the immediate precipitation of tetraethylammonium tetrakis(pentafluorophenyl)borate, m.p. 244–246°. After drying under vacuum the sample was pure enough for analysis. (Found: C, 47.5; H, 2.6; F, 47.0; N, 1.8. $C_{32}H_{20}BF_{20}N$ calcd.: C, 47.5; H, 2.6; F, 47.0; N, 1.7 %.) The compound appears to be largely insoluble in all the common organic solvents except acetone.

Potassium tetrakis(pentafluorophenyl)borate, $KB(C_6F_5)_4$

The potassium salt was made in a similar way to the tetraethylammonium derivative except that concentrated solutions of potassium chloride (or nitrate) and lithium tetrakis(pentafluorophenyl)borate had to be used in order to overcome the fairly high solubility of $KB(C_6F_5)_4$. An analytically pure compound was obtained by two recrystallisations from ether. (Found: C, 40.0; H, 0.1; F, 52.6. $C_{24}BF_{20}K$ calcd.: C, 40.2; H, 0.0; F, 52.9 %.) Potassium and lithium tetrakis(pentafluorophenyl)borates show a marked solubility in polar solvents such as acetone and ether; the lithium salt is also slightly soluble in chloroform.

DISCUSSION

We prepared tris(pentafluorophenyl)boron in pentane since boron compounds normally complex readily with ethers and make isolation of the desired product more difficult. In pentane, as in ether, pentafluorophenyllithium is unstable at ambient temperatures, hence the addition of boron trichloride to this reagent was carried out at —78°. On allowing the stirred mixture to warm up slowly towards room temperature visual evidence of reaction was observed at about —20° when lithium chloride began to separate out.

$$BCl_3 + 3C_6F_5Li \longrightarrow B(C_6F_5)_3 + 3LiCl$$

Tris(pentafluorophenyl)boron, a white solid, is soluble in many organic solvents and is monomeric in benzene at 30°. It shows relatively high thermal stability since it can be recovered in high yield after being held at 150° for short periods of time and can be sublimed repeatedly at 80° under high vacuum with virtually no decomposition. A weighed sample open to the air slowly increases in weight suggesting that tris(pentafluorophenyl)boron is hygroscopic; with a large excess of water under vacuum conditions at room temperature some cleavage of pentafluorophenyl groups occurs to produce pentafluorobenzene, C_6F_5H. Such a reaction involving boron–carbon bond cleavage is not typical of normal organoboranes but has been noted to occur with the more analogous perfluorovinylboron derivatives[4].

Like many tricoordinate boron compounds tris(pentafluorophenyl)boron shows marked acceptor properties towards the donor molecules ammonia, trimethylamine, triphenylphosphine and pyridine. The adducts formed are all stable in air, soluble in common organic solvents and are monomeric at 30° in benzene. Attempts to remove ammonia from the adduct ammonia–tris(pentafluorophenyl)boron, $H_3NB(C_6F_5)_3$, with hydrogen chloride gas result in the cleavage of pentafluorophenyl groups as pentafluorobenzene. This reaction and also those of the adducts with other trivalent boron compounds will be the subject of a subsequent paper.

Addition of a pentane solution of tris(pentafluorophenyl)boron to an ether solution of pentafluorophenyllithium at —78° results in the precipitation of lithium tetrakis(pentafluorophenyl)borate, a thermally stable white solid. This salt is soluble in cold air-free distilled water for short periods of time but an aqueous solution in pyrex vessels at room temperature produces much silica over a period of hours. The potassium and tetraethylammonium tetrakis(pentafluorophenyl)borates can be precipitated in the pure state by mixing solutions of the lithium derivative with the respective chlorides in air-free cold distilled water. The potassium tetrakis(pentafluorophenyl)borate is considerably more soluble in water than is its phenyl analogue, $KB(C_6H_5)_4$, and cannot therefore be used in gravimetric analysis for the estimation of potassium ions.

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SUMMARY

The relatively stable white solid tris(pentafluorophenyl)boron has been prepared in high yield from boron trichloride and pentafluorophenyllithium using pentane as a solvent. It shows strong acceptor properties towards the Lewis bases: ammonia, trimethylamine, triphenylphosphine, and pyridine. With excess of pentafluorophenyllithium the salt lithium tetrakis(pentafluorophenyl)borate is formed; the water-soluble borate precipitates the tetraethylammonium and potassium derivatives from concentrated aqueous solutions.

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