

Perfluoroalkyl Borate Esters

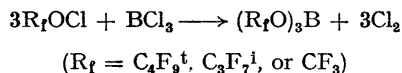
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Summary The first perfluoroalkyl borate esters have been obtained by the action of perfluoroalkyl hypochlorites on boron trichloride.

ALTHOUGH partially fluorinated alkyl borates may be obtained by reactions of fluorinated alcohols with boron trichloride¹ or by additions of boron halides (except BF₃) to fluoro-ketones,² the perfluoro-analogues may not be obtained in this manner; in the one case the simple aliphatic perfluoro-alcohols are unknown, and in the second case addition of B-F to the carbonyl function does not occur.

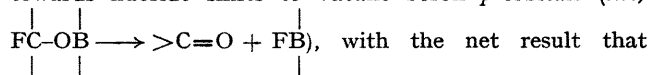
In our studies with perfluoroalkyl hypochlorites, we have discovered a novel reaction with boron trichloride in which displacement of chlorine from BCl₃ yields perfluoroalkyl borate esters.



In the case of (C₄F₉^t)₃B, a typical reaction sequence involved introduction of C₄F₉^tOCl³ and BCl₃ in a 3:1 mole ratio into a stainless-steel reactor at -196°. The reactor then was allowed to warm to ambient temperature, was agitated for several hours, and fractionated through low-temperature traps. This procedure led to the separation and recovery of pure chlorine and colourless, crystalline (C₄F₉^tO)₃B (vapour pressure 1 mm at 25°, m.p. 35°) according to the stoichiometry of the above equation. The ¹⁹F

n.m.r. spectrum shows a single sharp resonance at $\phi + 68.1$ p.p.m. and the ¹¹B spectrum exhibits a singlet at -13.4 p.p.m. relative to BF₃OEt₂. A mass spectrum showed the fragments expected for a unimolecular entity, although no parent ion was observed. The i.r. spectrum (60°) of the gas showed absorptions characteristic of B-O, C-F, and C-O bonds at 1422(mw), 1396(s), 1288(vs), 1202(w), 1150(m), 1124(m), 988(s), 952(mw), 730(m), and 534(w) cm⁻¹.

The (C₃F₇ⁱO)₃B and (CF₃O)₃B esters were prepared in similar fashion from BCl₃ and C₃F₇ⁱOCl⁴ or CF₃OCl,⁴ respectively. The increasing amounts of α -fluorine in their structures, as might be expected, renders them less stable towards fluoride shifts to vacant boron *p*-orbitals (*i.e.*,



decomposition leads eventually to BF₃ and carbonyl compounds. In the case of (C₃F₇ⁱO)₃B, decomposition to (CF₃)₂CO and BF₃ occurs slowly at 25° whereas (CF₃O)₃B decomposes to F₂CO and BF₃ above -20°. Thus, preparations must be carried out at temperatures not exceeding -20° in these two cases. The *t*-butyl ester, (C₄F₉O)₃B, with no α -fluorine available for this decomposition mode, is stable indefinitely at room temperature.

The perfluoroalkyl borates are readily hydrolysed and appear to be relatively strong boron Lewis acids from preliminary experiments with various amine bases.

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² E. W. Abel, D. J. Walker, and J. N. Wingfield, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 139; G. W. Parshall, *Inorg. Chem.*, 1965, **4**, 52.

³ D. E. Young, L. R. Anderson, D. E. Gould, and W. B. Fox, *J. Amer. Chem. Soc.*, 1970, **92**, 2313.

⁴ D. E. Gould, L. R. Anderson, D. E. Young, and W. B. Fox, *J. Amer. Chem. Soc.*, 1969, **91**, 1310.