of disodium maleonitriledithiolate. To this solution was added a methanol solution of 1.52 g (0.0050 mol) of tetra-*n*-butylammonium nitrate. The precipitated product was filtered and recrystallized from ethanol.

$[(C_2H_5)_4N]Ga(mnt)_2$.—Anhydrous gallium trichloride (3.74 g, 0.020 mol) was sublimed into 50 ml of dry pyridine. To the resulting solution was added 7.82 g (0.040 mol) of disodium maleonitriledithiolate and 3.48 g (0.020 mol) of tetraethylammonium chloride dissolved in methanol. The mixture was allowed to stand in the refrigerator for 2 days. The precipitated product was filtered and recrystallized from isopropyl alcohol.

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Perhaloalkyl Hypochlorites. V. Perfluoroalkyl Borate Esters from Reactions with Boron Trichloride[1]

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Fluoroalkyl borate esters have been prepared from reactions of fluorinated alcohols and boron trichloride[2-4] and from the reactions of sodium borohydride with hexafluoroacetone[5]

$$3CF_3CH_2OH + BCl_3 \longrightarrow (CF_3CH_2O)_3B + 3HCl \quad (1)$$

$$3(CF_3)_2CO \xrightarrow[2.\ H^-]{1.\ BH_4^-} [(CF_3)_2CHO]_3B \quad (2)$$

Perhaloalkyl borate esters result when boron halides other than boron fluorides are added to hexafluoroacetone[6] or hexafluorocyclobutanone[7]

$$3(CF_3)_2CO + BCl_3 \longrightarrow [(CF_3)_2CClO]_3B \quad (3)$$

$$3(CF_2)_3CO + BCl_3 \longrightarrow [(CF_2)_3CClO]_3B \quad (4)$$

Several investigators have observed that the haloalkyl borate esters have greater Lewis acidities than their alkyl counterparts,[2,4,6] a consequence attributed to inductive effects which decrease interaction of the electron pairs on oxygen with the empty p_z orbital on boron.

There have been no reports of *per*fluoroalkyl borate esters (these should be the most acidic alkyl borates according to inductive arguments), and the usual methods of synthesis are not available; *i.e.*, primary and secondary perfluoro alcohols are generally inaccessible, and boron–fluorine bonds do not add across the carbon–oxygen double bond of perfluorinated carbonyl compounds.[6,7]

In our studies of perhaloalkyl hypochlorites, we have discovered a novel reaction with boron trichloride in which chlorine is oxidatively displaced from boron yielding the first perfluoroalkyl borate esters.

Experimental Section

Standard vacuum line procedures with a Monel–Kel-F or glass vacuum system were used throughout. The reaction vessels were Type 304SS cylinders of either 30- or 225-cm^3 capacity.

Reagents.—Carbonyl fluoride was prepared by the reaction of phosgene and NaF at 150° in a 500-cm^3 stainless steel cylinder and was purified by vacuum-line fractionation. Hexafluoroacetone was obtained from Allied Chemical Corp. (Specialty Chemical Division), and nonafluoro-*tert*-butyl alcohol was prepared by antimony pentafluoride fluorination of $CCl_3C(CF_3)_2OH$.[8,9] Chlorine monofluoride was obtained from the Ozark-Mahoning Co., and BCl_3, $(CH_3)_3N$, and NH_3 were obtained from the Matheson Co. and carefully purified before use. Trifluoromethyl, heptafluoroisopropyl, and nonafluoro-*tert*-butyl hypochlorites were prepared by chlorofluorination of F_2CO, $(CF_3)_2CO$, and *tert*-C_4F_9OH, respectively, by previously described methods.[10,11]

Nonafluoro-*tert*-butyl Borate.—The reaction cylinder was charged with $(CF_3)_3COCl$ (10.8 mmol) and BCl_3 (3.4 mmol) at −196°. The materials were allowed to warm to room temperature and shaken for 20 hr. The product mixture was then fractionated through −23, −80, and −196° traps. The −196° fraction contained 9.8 mmol of essentially pure Cl_2. The −80° fraction contained a small amount of $(CF_3)_3COH$ (impurity in starting hypochlorite), and the −23° fraction contained transparent, soft crystals of (*tert*-$C_4H_9O)_3B$. The solid melts at 35° and has a vapor pressure of about 1 mm at 25°. The gas-phase infrared spectrum of the solid was obtained in a heated cell (60°) and is tabulated below. The fluorine-19 nmr spectrum was a singlet at +68.1 ppm with respect to CCl_3F while the boron-11 nmr spectrum consisted of a singlet at −13.4 ppm with respect to $BF_3O(C_2H_5)_2$. Although the molecular ion was not observed in the mass spectrum at *m/e* 716 or 715, (*tert*-$C_4F_9O)_2$(*tert*-$C_4F_8O)^{11}B^+$ and (*tert*-$C_4F_9O)_2$(*tert*-$C_4F_8O)^{10}B^+$ at *m/e* 697 and 696 and other expected ions at *m/e* 628–627 ($^{11}BC_{11}F_{23}O_3^+$, $^{10}BC_{11}F_{23}O_3^+$), 609–608 ($^{11}BC_{11}F_{22}O_3^+$, $^{10}BC_{11}F_{22}O_3^+$), and 481–480 ($^{11}BC_8F_{18}O_2^+$, $^{10}BC_8F_{18}O_2^+$) were present in the 4:1 intensity required of ions containing one boron atom. Ir spectrum (cm^{-1}): 1422 (mw), 1396 (s), 1288 (vs), 1202 (w), 1150 (m), 1124 (m), 988 (s), 952 (mw), 730 (m), 534 (w).

Heptafluoroisopropyl Borate.—The reaction cylinder was charged with *i*-C_3F_7OCl (16.0 mmol) and BCl_3 (4.9 mmol) at −196°. The materials were allowed to warm to −20° and stand for 40 hr. Fractionation through traps held at −45 and −196° effected separation of reaction products. The −196° fraction contained 16.7 mmol of Cl_2 contaminated with traces of $(CF_3)_2CO$, BF_3, $CF_3C(O)F$, and CF_3Cl (the latter two materials are known decomposition products of *i*-C_3F_7OCl). The −45° fraction contained clear, colorless, liquid (*i*-$C_3F_7O)_3B$ which had a vapor pressure of about 10 mm at 25°. The infrared spectrum, obtained in the gas phase, showed no $(CF_3)_2CO$ or BF_3; the spectrum is tabulated below. The fluorine-19 nmr spectrum consisted of a doublet at +82.3 ppm (J_{FF} = 2.8 Hz) and a complex signal at +137.4 ppm relative to CCl_3F. Integration of the signals gave a ratio of 6:1 as expected for *i*-C_3F_7O–. The product composition was further verified in several experiments by allowing samples to decompose at 25° over a period of several hours or at −20° over a period of several weeks to the expected amounts of $(CF_3)_2CO$ and BF_3 in a 3:1 ratio according to the equation

$$(i\text{-}C_3F_7O)_3B \longrightarrow BF_3 + 3(CF_3)_2CO \quad (5)$$

Ir spectrum (cm^{-1}): 1439 (ms), 1408 (s), 1315 (vs), 1255 (vs), 1198 (m), 1177 (s), 1122 (s), 1002 (vs), 788 (w), 736 (ms), 720 (m).

Trifluoromethyl Borate.—A reaction cylinder was charged

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with CF_3OCl (5.3 mmol) and BCl_3 (1.7 mmol) at −196°. The contents were then allowed to warm to −20° and stand for 20 hr. The reaction mixture was then fractionated on the vacuum line through traps held at −111 and −196°. The material passing −111° to the −196° trap (6 mmol) consisted mainly of Cl_2 with traces of F_2CO and BF_3, indicating that the reaction proceeded in accordance with the equation

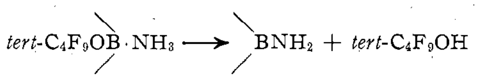
$$3CF_3OCl + BCl_3 \longrightarrow (CF_3O)_3B + 3Cl_2 \qquad (6)$$

The material in the −111° trap was investigated by gas-phase infrared spectroscopy. Because the borate decomposes to BF_3 and F_2CO above −20°, it was necessary to record spectra quickly. The spectra showed F_2CO and BF_3 in addition to bands attributed to $(CF_3O)_3B$ at 1350, 1282, 1225, 1176, and 1110 cm^{-1}. After 1 hr in the infrared cell, the product bands had disappeared completely, and F_2CO and BF_3 absorptions were intensified as the only remaining bands.

Reactions with Ammonia and Trimethylamine.—In the case of $(\textit{tert}\text{-}C_4F_9O)_3B$, reactions with NH_3 and $N(CH_3)_3$ were carried out in 5-mm glass nmr tubes containing external standards of $BF_3O(C_2H_5)_2$ in glass capillaries. The tubes were attached to Kontes high-vacuum valves. Approximately 0.5–1.0 mmol of the borate was condensed in the tube and CCl_3F was added as solvent. Excess NH_3 or $N(CH_3)_3$ was then added to the tube. With NH_3 a solid complex insoluble in CCl_3F formed immediately as the components in the tube melted. After the materials had been allowed to warm to room temperature and stand for 1 hr, the CCl_3F and excess NH_3 were pumped from the tube. The white solid was found to have no dissociation pressure due to NH_3 or borate and could be sublimed slowly at room temperature without change in composition. The boron-11 nmr spectrum of a sample dissolved in glyme consisted of a singlet with a chemical shift of +1.2 ppm, an upfield shift of 14.6 ppm from the borate. In another sample of the adduct to which excess NH_3 was added, no change in the chemical shift value was observed. The fluorine-19 nmr spectrum consisted of a singlet at +74.8 ppm.

Since it was found that hydrolysis of $(\textit{tert}\text{-}C_4F_9O)_3B$ occurs readily with the formation of $(CF_3)_3COH$ and $B(OH)_3$, it was necessary to show that we were observing adduct formation and not ammonolysis in the ammonia reactions. A sample of the borate was allowed to react in CCl_3F with a molar deficiency of NH_3 at temperatures not exceeding −23°. After 2 hr, the materials were allowed to warm to room temperature and stand overnight. Investigation of materials which were volatile at −8° showed no $(CF_3)_3COH$, the most volatile ammonolysis product. When the solid adduct was strongly heated with a heat gun, however, it melted with apparent evolution of a gas. After cooling to room temperature, the volatile thermal reaction product was found to be perfluoro-*tert*-butyl alcohol. These observations indicate that acid–base complex formation is the primary reaction at moderate temperatures and ammonolysis occurs when the complex is heated.

$$(\textit{tert}\text{-}C_4F_9O)_3B + NH_3 \longrightarrow (\textit{tert}\text{-}C_4F_9O)_3B\cdot NH_3 \qquad (7)$$



$$\textit{tert}\text{-}C_4F_9OB\cdot NH_3 \longrightarrow BNH_2 + \textit{tert}\text{-}C_4F_9OH \qquad (8)$$

With $N(CH_3)_3$ no solid complex formed with $(\textit{tert}\text{-}C_4F_9O)_3B$ from −80 to +25°. Boron-11 nmr showed only free borate, and the amine could be completely recovered from the system by routine vacuum line fractionation.

In the case of $(\textit{i}\text{-}C_3F_7O)_3B$, a reaction was carried out in a weighed glass reaction tube. The borate (0.3202 g, 0.566 mmol) was dissolved in CCl_3F, and excess $N(CH_3)_3$ was added to the solution at −196°. Upon warming, a white solid formed which was insoluble in CCl_3F. The volatile materials were then removed at 0°, and the reaction tube was weighed again. It was found that 0.0329 g of $N(CH_3)_2$ (0.558 mmol) had reacted with the borate confirming formation of the 1:1 adduct $(\textit{i}\text{-}C_3F_7O)_3B\cdot N(CH_3)_3$. No dissociation pressure of amine or borate developed above the solid at 25°.

Results and Discussion

Boron trichloride has been found to react with perfluoroalkyl hypochlorites, R_fOCl, with the formation of perfluoroalkyl borate esters

$$3R_fOCl + BCl_3 \longrightarrow (R_fO)_3B + 3Cl_2 \qquad (9)$$

where $R_f = CF_3$, $\textit{i}\text{-}C_3F_7$, or $\textit{tert}\text{-}C_4F_9$. The utility of the fluoroalkyl hypochlorites for introducing the R_fO grouping into compounds by insertion of certain molecules into the O–Cl bond has been demonstrated in detail.[1,11–13] The preparation of perfluoroalkyl borates demonstrates a second reaction mode, that of "oxidative displacement." These oxidative displacement reactions might be envisioned as involving the combination of "chloronium" (supplied by R_fOCl) and chloride (supplied by the covalent chloride) to form molecular chlorine. Others have shown examples of halonium–halide reactions in which halogen or interhalogen is a product[14–16] and in which the electrophilicity of positive halogen is demonstrated.

The thermal stability of the products is apparently a function of the number of fluorine atoms attached to the α carbon. Thus, $(CF_3O)_3B$ decomposes much more rapidly at 25° than $(\textit{i}\text{-}C_3F_7O)_3B$, while $(\textit{tert}\text{-}C_4F_9O)_3B$ is indefinitely stable since there can be no α-fluoride shift to the acceptor boron atom.

$$(CF_3O)_3B \xrightarrow[25°]{\text{fast}} 3F_2CO + BF_3 \qquad (10)$$

$$(\textit{i}\text{-}C_3F_7O)_3B \xrightarrow[25°]{\text{slow}} 3(CF_3)_2CO + BF_3 \qquad (11)$$

$$(\textit{tert}\text{-}C_4F_9O)_3B \xrightarrow[25°]{} \text{no decomposition} \qquad (12)$$

Although alkyl borates are known to be relatively weak Lewis acids, our observations that the perfluoroalkyl examples which we examined are relatively strong are expected. The electronegativity of the R_f group diminishes the back-bonding (π bonding) of electron pairs on oxygen to the acceptor orbital on trigonal boron. Therefore, $(\textit{i}\text{-}C_3F_7O)_3B$ forms a strong complex with trimethylamine

$$(\textit{i}\text{-}C_3F_7O)_3B + N(CH_3)_3 \longrightarrow (\textit{i}\text{-}C_3F_7O)_3B\cdot N(CH_3)_3 \qquad (13)$$

In contrast, alkyl borates other than methyl borate apparently complex with $N(CH_3)_3$ only very weakly if at all.[17]

Furthermore, complex formation effectively blocks α-fluoride shift and the resulting indirect formation of B–F bonds since the boron atom no longer behaves as an acceptor site. Thus, $(\textit{i}\text{-}C_3F_7O)_3B\cdot N(CH_3)_3$ is very stable thermally compared to $(\textit{i}\text{-}C_3F_7O)_3B$.

On the surface it appears that $(\textit{tert}\text{-}C_4F_9O)_3B$ should also behave as a strong Lewis acid; indeed ammonia forms a strong complex with the borate. With bulky $(CF_3)_3C$ groups, however, steric factors apparently cause reversal of the Lewis acidity with respect to bulkier nitrogen bases. Thus, although the more sterically sensitive $N(CH_3)_3$ molecule reacts with $(\textit{i}\text{-}C_3F_7O)_3B$, it does not combine with $(\textit{tert}\text{-}C_4F_9O)_3B$ even at low temperatures. Since $N(CH_3)_3$ is generally considered a stronger donor than NH_3 with respect to relatively unhindered boron Lewis acids, it is reasonable to assume that steric effects are being observed in reactions of $(\textit{tert}\text{-}C_4F_9O)_3B$ with amine bases. The borate, therefore, is a selective Lewis acid which can

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react with small base molecules in preference to larger ones which are electronically stronger donors.

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The Methylpentaaquochromium(III) Ion

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Kochi[1] assumed the existence of a methylpentaaquochromium(III) ion in order to account for the formation of methane by the reaction between *tert*-butyl peroxide and chromium(II). The main product of this reaction is *tert*-butyl alcohol formed by

$$\textit{tert}\text{-}C_4H_9OOH + Cr^{2+} \longrightarrow \textit{tert}\text{-}C_4H_9O\cdot + Cr^{3+} + OH^- \tag{1}$$

$$\textit{tert}\text{-}C_4H_9O\cdot + Cr^{2+} + H_2O \longrightarrow \textit{tert}\text{-}C_4H_9OH + Cr^{3+} + OH^- \tag{2}$$

The detection of acetone and methane gas among the reaction products (in nearly equivalent amounts and a maximum yield of 16%) was explained by the competing reaction path

$$C_4H_9O\cdot + Cr^{2+} \longrightarrow \text{acetone} + Cr(H_2O)_5CH_3^{2+} \tag{3}$$

$$Cr(H_2O)_5CH_3^{2+} + H_2O \longrightarrow Cr(H_2O)_6^{3+} + CH_4 + OH^- \tag{4}$$

The fact that no methylo complex was found led to the conclusion that it is a transient, unstable ion, in contrast to its stable halogen-substituted derivatives.[2]

After the work described in the present paper was concluded, Schmidt, Swinehart, and Taube[3] reported the discovery of the methylpentaaquochromium(III) and gave the rate law of its aquation: $-d \ln [CrL^{2+}]/dt = k_2[H^+]$; $10^3k_2 = 5.2 \pm 0.2\ M^{-1}\ sec^{-1}$ at 298°K.

Our results confirm these findings and contain data of the absorption spectrum and the Cr : CH_4 ratio of this complex, which was observed during a reinvestigation of the reaction between *tert*-C_4H_9OOH and Cr(II) in this laboratory. The methylpentaaquochromium(III) ion was found to be a relatively stable complex with a half-life of several hours at 0°. Its low yield prevents visual detection because its red color is masked by the gray-blue color of the hexaaquo ion which is present in large excess in the solution.

Ion-exchange chromatography enabled us to separate the methylo complex from the reaction mixture by the following procedure. A 20-ml amount of 0.65 *M* $CrClO_4$ in 0.65 *M* $HClO_4$ was added under nitrogen to 170 ml of an ice-cooled stirred solution containing 6.5 m*M* *tert*-C_4H_9OOH and 7.5 m*M* $HClO_4$. The color change from sky blue Cr(II) to gray-blue Cr(III) follows without delay. Air was introduced in order to oxidize the excess of Cr(II) and the solution was passed through an ice-cooled Dowex 50-X2 cation-exchange column. A narrow purple band was observed, just ahead of the blue hexaaquo band and was eluted by the reaction mixture together with some hexaaquo ion. The resulting mixed solution was absorbed on a second ice-cooled Dowex 50-X2 column and the brown-red methyl complex band was eluted with 0.35 *M* $HClO_4$. This ion-exchange behavior is typical for a 2+ ion. Hexaaquochromium(III) was eluted with $HClO_4$ (4 *M*), and some green chromium(III) dimer[4] was left on the column.

The red fraction was collected into a 50-cm^3 gas bulb submerged in a salt–ice bath and the bulb was sealed. The sample thus collected was allowed to decompose at room temperature overnight. After 0.5 hr of exposure to room temperature the purple color turned to gray-blue and the sample was replete with bubbles.

The evolved gas was identified as methane by gas chromatography on an activated charcoal column heated to 80° using helium as the carrier gas. The quantity of methane in the bulb was measured by injection of a fraction of the gas from the gas bulb and measurement of the peak area. Calibration was done by injection of the same fraction of known quantities of methane introduced into the same glass bulb containing the decomposed sample solution in order to duplicate solubility losses. A calibration curve with six different known quantities of methane was prepared for each sample of complex analyzed. The chromium content of the solution was determined spectrophotometrically as CrO_4^{2-} at 372 mμ.[5] The ratio of chromium to CH_4 was 1.01 ± 0.05 (average of eight samples).

The absorption spectrum of the complex was measured at ~2° with a Cary 14 spectrophotometer in the visible and near-uv region. Peaks were observed at 258 mμ (ε 2160), 392 mμ (ε 196), and 550 mμ (ε 9.6). The spectrum is similar to those of the halogen-substituted complexes reported by Johnson, *et al.*[2]

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