# Perhalogenated Polyboron and Silicon–Boron Analogues of Borane

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The compound $B_8F_{12}$, prepared by disproportionation of $F_2BBFBF_2$, has been characterised. It is believed to be a structural analogue of diborane. It has been treated with electron-pair donors to give complexes $(BF_2)_3BL$ (L = CO, $PF_3$, $PCl_3$, $PH_3$, $AsH_3$, and $SMe_2$). Related complexes have been made from $SiCl_2$ or $SiF_2$ and diboron tetrahalides in the presence of CO or $PF_3$, and the compounds $(SiCl_3)_2(BCl_2)BCO$ and $(SiCl_3)_2(BF_2)BPF_3$ have been characterised.

It is well known that borane forms complexes with CO, $PF_3$, and other weak electron-pair donors. Many substituted boranes in which boron is joined to carbon, nitrogen, oxygen, or halogens, do not form stable complexes with these donors. However, in the compounds $(BF_2)_3BCO$ and $(BF_2)_3BPF_3$ described by Timms,[1] the $(BF_2)_3B$ moiety behaves like borane.

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[1] P. L. Timms, *J. Amer. Chem. Soc.*, 1967, **89**, 1629.

We have sought to extend this system of borane analogues in two ways. First, by studying the compound $B_8F_{12}$ [1,2] and its use in the formation of new complexes of $(BF_2)_3B$. Secondly, by attempting to prepare complexes of related molecules in which the $BF_2$ groups are displaced by $BCl_2$ or perhalogenosilicon groups.

## RESULTS AND DISCUSSION

*The Properties of* $B_8F_{12}$.—Condensation of BF with $B_2F_4$ at −196° yielded $B_3F_5$.[1] At −30°, liquid $B_3F_5$ disproportionated slowly according to equation (1).

$$4B_3F_5 \longrightarrow 2B_2F_4 + B_8F_{12} \qquad (1)$$

The rate of disproportionation increased rapidly with temperature and was quite violent at 0°; then boron trifluoride and yellow polymers were formed in addition to the above products.

The compound $B_8F_{12}$ was separated from unchanged $B_3F_5$ and $B_2F_4$ by low-temperature fractional distillation. Evidence for its molecular formula was obtained from its mass spectrum, vapour-density measurements, and chemical analysis by quantitative decomposition to boron and boron trifluoride at 850°.

The mass spectrum is shown in Table 1. The ion of lowest appearance potential was $B_7F_9^+$, but the presence of an ion $B_7F_{10}^+$ of higher appearance potential showed that the molecular formula could not be $B_7F_9$ or $B_7F_{10}$. Loss of $BF_3$ on electron impact is a ready process in boron–fluorine chemistry,[1,2] and the ion of lowest appearance potential is often (parent − $BF_3$)$^+$. Thus, the spectrum in Table 1 is quite consistent with a formula $B_8F_{12}$.

TABLE 1

Mass spectrum of $B_8F_{12}$

| | | Relative abundance [a] | |
|---|---|---|---|
| *m/e* | Formula | 50 ev | 15 ev |
| 60 | $B_2F_2^+$ | 36 | |
| 71 | $B_3F_2^+$ | 25 | |
| 79 | $B_2F_3^+$ | 32 | |
| 90 | $B_3F_3^+$ | 17 | |
| 101 | $B_4F_3^+$ | 100 | |
| 112 | $B_5F_3^+$ | 16 | |
| 120 | $B_4F_4^+$ | 55 | 23 |
| 131 | $B_5F_4^+$ | 5 | |
| 139 | $B_4F_5^+$ | 2 | |
| 150 | $B_5F_5^+$ | 5 | |
| 161 | $B_6F_5^+$ | 27 | |
| 169 | $B_5F_6^+$ | 20 | |
| 180 | $B_6F_6^+$ | 30 | 100 |
| 199 | $B_6F_7^+$ | 14 | |
| 229 | $B_7F_8^+$ | 2 | |
| 248 | $B_7F_9^+$ | 13 | 32 |
| 267 | $B_7F_{10}^+$ | 1 | |

[a] Corrected to 100% $^{11}B$.

The i.r. spectrum of gaseous $B_8F_{12}$ was complex and dominated by strong absorptions in the B–F stretch region from 1100—1450 cm$^{-1}$. Rapid decomposition in the gas phase made it difficult to obtain high quality spectra.

The $^{19}F$ n.m.r. spectrum of neat liquid $B_8F_{12}$ over the temperature range −80° to 0° showed only a single resonance at +44·1 p.p.m. relative to $CCl_3F$. The resonance was *ca.* 100 Hz wide at half-height. The rate of decomposition of $B_8F_{12}$ was too great for spectra to be taken at temperatures above 0°. At temperatures below −80° the intensity of the signal decreased with some broadening of the peak, probably due to the increased viscosity of the liquid.

The $^{11}B$ n.m.r. spectrum of neat $B_8F_{12}$ at −50° showed only a very broad, symmetrical peak (800 Hz wide) centred at −25 p.p.m. relative to $BF_3,OEt_2$. No change in the spectrum was observed when the temperature was raised to −15°. Liquid $B_3F_5$ at −50° was found to give a similarly broad resonance also centred at −25 p.p.m.

The purest samples of $B_8F_{12}$ showed no e.s.r. spectrum at −50°, but samples which had decomposed slightly contained traces of free radicals which gave a complex spectrum.

The liquid was found to be quite volatile considering its molecular weight, with a vapour pressure of *ca.* 23 Torr at 0°, but it was unstable at this temperature and above, thus making accurate measurements of its vapour pressure difficult. The compound became glassy on cooling below −90° but could not be obtained crystalline. The viscosity of the liquid decreased with increasing temperature and at −20° $B_8F_{12}$ was a fairly mobile liquid. In the solid phase the compound was faintly yellow, but the liquid was bright yellow and the vapour intensely yellow-brown. The visible spectrum of the gas showed a broad absorption maximum at 345 nm and then an intense absorption starting around 320 nm and extending far into the u.v. region.

The compound reacted explosively with air or water. No inert solvent was found except liquid $B_2F_4$ or $B_3F_5$ with which it was completely miscible. It reacted with hydrogen at −80° to form involatile solids, $BF_3$ and $HBF_2$.

$B_8F_{12}$ *and Lewis bases; the Complexes* $(BF_2)_3BL$.—Treatment of $B_8F_{12}$ with powerful electron-pair donors such as diethyl ether, trimethylamine, or acetonitrile, caused decomposition even at −70°. The only products isolated were the $BF_3$ complexes of these bases.

However, on treatment with compounds of the type sometimes classified as 'soft' bases,[3] $B_8F_{12}$ formed complexes. Thus, when CO was passed over liquid $B_8F_{12}$ at −70°, the white solid $(BF_2)_3BCO$ [1] was formed in 90% yield according to the equation,

$$B_8F_{12} + 2CO \longrightarrow 2(BF_2)_3BCO$$

In a similar reaction, gaseous $PF_3$ formed $(BF_2)_3BPF_3$ in high yield.

Slightly volatile, white solids were obtained by treating $B_8F_{12}$ at a temperature of −70 to −20° with $PCl_3$, $PH_3$, $AsH_3$, and $SMe_2$. Yellow involatile solids were also formed together with small amounts of $BF_3$. The mass spectrum of each of the white compounds showed a very close resemblance to that of $(BF_2)_3BCO$ and

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[2] R. W. Kirk, Ph.D. Thesis, Univ. of California, Berkeley, 1969.

[3] R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **89**, 3533.

$(BF_2)_3BPF_3$. The ion group of lowest appearance potential in each case was $B_3F_3L^+$ and the ion group of highest *m*/*e*, $B_4F_5L^+$. The arsine compound was only obtained in amounts sufficient for mass spectrometry, but for the others chemical analysis and $^{19}F$ n.m.r. measurements confirmed that they were of the structural type $(BF_2)_3BL$. The sequence of $^{19}F$ chemical shifts for these compounds shown in Table 2 seems to reflect the electron-donor power of the ligands.

TABLE 2

N.m.r. chemical shifts of borane carbonyl analogues and related compounds

| | $^{11}B$ N.m.r. (p.p.m. from $BF_3,OEt_2$) | | $^{19}F$ N.m.r. (p.p.m. from $CCl_3F$) |
|---|---|---|---|
| Compound | 3 co-ord. | 4 co-ord. | $BF_2$ groups |
| $SiCl_3BCl_2$ | −63 | | |
| $(SiCl_3)_2(BCl_2)BCO$ | −70 | +20 | |
| $B_2F_4$ | −23 | | +55·7 |
| $B_8F_{12}$ | −25 | | +44·1 |
| $SiF_3BF_2$ | −28 | | +40·9 |
| $(Si_2F_5)(SiF_3)(BF_2)BPF_3$ | −30 | +52 | +33·5 |
| $(SiCl_3)_2(BF_2)BPF_3$ | −30 | +36 | +35·2 |
| $(BF_2)_3BPF_3$ | −32 | +49 | +37·4 |
| $(BF_2)_3BCO$ | n.m. | n.m. | +38·4 |
| $(BF_2)_3BPCl_3$ | n.m. | n.m. | +40·3 |
| $(BF_2)_3BPH_3$ | n.m. | n.m. | +43·5 |
| $(BF_2)_3BSMe_2$ | n.m. | n.m. | +46·8 |

n.m. = Not measured.

The compounds were also formed by co-condensing BF and the ligand vapours at −196° although it was then difficult to pump the products away from an involatile residue when the cold surface was warmed to room temperature.

The complexes were stable solids at room temperature in the absence of air or moisture. It was observed that when any of the complexes was treated with another of the electron-pair donors at 25° there was no replacement of one donor by another. The original complex was recovered in each case.

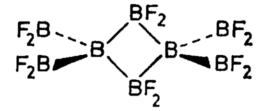
A complex was believed to be formed between $B_8F_{12}$ and $SF_4$. The slightly volatile solid proved to be spontaneously explosive and was not studied further. The reaction of $B_8F_{12}$ and $P(PF_2)_3$[4] gave only a small yield of $(BF_2)_3BPF_3$ together with involatile solids.

*The Structure of* $B_8F_{12}$.—The formation of the complexes $(BF_2)_3BL$ from $B_8F_{12}$ and 'soft' bases even at very low temperatures, suggests that $B_8F_{12}$ might be $B_2(BF_2)_6$. The presence of $BF_2$ groups in the compound is strongly supported by the $^{19}F$ n.m.r. spectrum. The observed chemical shift are close to that found for the complexes $(BF_2)_3BL$ and for the silicon–boron fluorides.[5]

The $^{11}B$ n.m.r. spectrum indicates that the boron atoms in $B_8F_{12}$ behave as three-co-ordinate atoms as opposed to the four-co-ordinate atoms in $(BF_2)_3BL$ for which high-field shifts are observed. However, the results with $B_3F_5$ show that there need not be detectable differences in chemical shift between three-co-ordinate boron atoms in different chemical environments. Thus, the $^{11}B$ spectrum of $B_8F_{12}$ does not rule out the presence of more than one kind of boron atom in the structure.

Both vapour-density measurements and mass spectrometry seem to preclude appreciable dissociation of $B_8F_{12}$ in the gas phase. The absence of free $(BF_2)_3B$ is indicated from the mass spectrum by the low abundance of $B_4F_6^+$ or $B_4F_5^+$, and by the early disappearance of $B_3F_3^+$ as the electron voltage was reduced.

On the basis of this data we suggest $B_8F_{12}$ is a structural analogue of $B_2H_6$ with bridging $-BF_2-$ groups as in (I) below. This structure can account for the ready formation of $(BF_2)_3BL$ when the compound is treated with electron-pair donors. The $^{19}F$ n.m.r. spectrum can be explained if exchange process, fast even at −80°, makes all the $-BF_2$ groups appear equivalent on an n.m.r. time scale (*cf*. $Al_2Me_6$). The observed $^{11}B$ n.m.r. spectrum may be the result of coincidence between the chemical shifts of the two skeletal boron atoms and those in the $BF_2$ groups (*cf*. $B_3F_5$ above).



(I)

The viscosity of the liquid at low temperatures may be caused by intermolecular B–F ··· B bridging. We see no simple explanation of the intense colour of the compound, particularly as Kirk and Timms[2,6] have observed more complex boron fluorides, containing 12—14 boron atoms, to be colourless.

*Silicon–Boron Compounds*.—The observation that $B_3F_5$ disproportionated to $B_2F_4$ and $B_8F_{12}$ gave the idea that other compounds of type $RBXBX_2$ might disproportionate in a similar way. The groups, R, considered to have electronic properties most similar to the $BF_2$ group were $BCl_2$, $SiF_3$, $SiCl_3$, and their perhalogenosilicon homologues. It was hoped that analogues of $B_8F_{12}$ and complexes of type $R_2(BX_2)BL$ or $R(BX_2)_2BL$ could be made.

Silicon dichloride gas was condensed with $B_2Cl_4$ vapour at −196° and the condensate was warmed to room temperature with continuous vacuum pumping. A very complex mixture of volatile products was obtained which steadily decomposed; $SiCl_3BCl_2$ was the only product which was isolated and characterised. However, when the experiment was repeated and the condensate allowed to warm from −196° in the presence of 400 Torr pressure of CO, a colourless slightly volatile compound was formed.

The i.r. spectrum of a film of this product at −196° showed it to be a carbonyl complex with a strong absorption at 2176 cm$^{-1}$ [*cf*. $(BF_2)_3BCO$ 2162 cm$^{-1}$ gas phase]. The mass spectrum showed no ions of higher *m*/*e* than a group at 269—280 ($Si_2BCl_5CO^+$), although the prominent ion group at *m*/*e* 258—268 ($SiB_2Cl_6^+$) proved that the compound contained at least two boron

[4] D. Solan and P. L. Timms, *Chem. Comm.*, 1968, 1540.

[5] P. L. Timms, T. C. Ehlert, J. L. Margrave, F. E. Brinckmann, T. C. Farrar, and T. D. Coyle, *J. Amer. Chem. Soc.*, 1965, **87**, 3819.

[6] R. W. Kirk and P. L. Timms, unpublished observations.

atoms. Chemical analysis was consistent with the formula $Si_2B_2Cl_8CO$. The $^{11}B$ n.m.r. spectrum showed two resonances of almost equal areas, at 20 p.p.m. and −70 p.p.m. relative to $BF_3,OEt_2$. The broad resonance at −70 p.p.m. was in a typical position for boron in $-BCl_2$ groups, *e.g.* $SiCl_3BCl_2$ −63 p.p.m.[7] The difference of 90 p.p.m. between the two resonances suggested the high field peak was due to a four-co-ordinate boron atom. The presence of two $SiCl_3$ groups in the molecule was indicated by a very strong polarised line at 355 $cm^{-1}$ which dominated its Raman spectrum.

On this evidence the structure of the compound appears to be $(SiCl_3)_2(BCl_2)BCO$. The compound melts at −5° and is fairly stable at 25° in the absence of air or water.

Silicon dichloride is presumed to have inserted into a B−Cl bond of $B_2Cl_4$ to give $SiCl_3BClBCl_2$, an unstable compound which disproportionated in the presence of CO at some temperature above −196° to give $B_2Cl_4$ and $(SiCl_3)_2(BCl_2)BCO$. In the absence of CO, the disproportionation gave no stable analogue of $B_8F_{12}$ but only complex products.

When $SiCl_2$ was condensed with $B_2Cl_4$ at −196° and the products were allowed to warm to room temperature in the presence of $PF_3$, two products were obtained. The known compound $B_2Cl_4,2PCl_3$ and a small amount of a less volatile material. The mass spectrum of the latter showed a group of ions at *m/e* 378—389 $(Si_2B_2PF_5Cl_5^+)$, a very prominent ion group at 329—338 $(Si_2BPF_3Cl_5^+)$, and another prominent group at 245—250 $(SiB_2PF_5Cl_2^+)$. By comparison with the mass spectrum of $(BF_2)_3BPF_3$, this fragmentation suggested a molecular formula $Si_2B_2PF_5Cl_6$ with loss of Cl, $BF_2Cl$, or $SiCl_4$ to form the major ion groups observed. The $^{19}F$ n.m.r. spectrum of the compound dissolved in $CCl_3F$ showed a broad resonance at +35·2 p.p.m. believed due to a $BF_2$ group (Table 2), and a widely spaced doublet of triplets centred at +50·9 p.p.m. assigned to a co-ordinated $PF_3$ molecule ($J_{P-F}$ 1339 Hz and $J_{F-B-P-F}$ 4·8 Hz). The $^{19}F(^{11}B)$ and $^{19}F(^{31}P)$ INDOR n.m.r. spectra showed respectively, a pair of broad resonances of equal intensity at 36 and −30 p.p.m. relative to $BF_3,OEt_2$, and a well resolved quartet of quartets ($J_{B-P} = 122$ Hz) centred at −84·0 p.p.m. relative to 85% $H_3PO_4$. This suggested the structure $(SiCl_3)_2(BF_2)BPF_3$. Presumably, $PF_3$ acted both as a ligand and as a fluorinating agent converting $BCl_2$ to $BF_2$ groups.

Condensation of $SiF_2$ with $B_2F_4$ and $PF_3$ at −196° gave small yields of a mixture of slightly volatile products which were not separated completely on low-temperature distillation. The mass spectrum of the mixture showed prominent groups of ions at *m/e* 363—368 $(Si_3B_2PF_{12}^+)$, 297—302 $(Si_2B_2PF_{10}^+)$, 264—267 $(Si_4F_8^+)$, 249—252 $(Si_2BPF_8^+)$, 231—235 $(SiB_2PF_8^+)$, 217—220 $(Si_3F_7^+)$, 212—216 $(SiB_2F_7^+)$, and 198—200 $(Si_3F_6^+)$. The $^{11}B$ n.m.r. spectrum of a solution of the mixture showed two resonances of equal area, one very broad at −30 p.p.m. and the other less broad at +52 p.p.m. relative to $BF_3,OEt_2$. The positions of these resonances were close to those observed for the three- and four-co-ordinate boron atoms respectively in $(BF_2)_3BPF_3$ (Table 2). The $^{19}F$ n.m.r. spectrum of a solution in $CCl_3F$ showed a broad resonance at +33·5 p.p.m. assigned to a $BF_2$ group, a widely spaced doublet centred at 48·4 p.p.m. assigned to a co-ordinated $PF_3$ molecule ($J_{P-F} = 1320$ Hz), and a complex series of resonances in the range +110 to +139 p.p.m. These high-field resonances were in the region expected for $SiF_3$ and $SiF_2$ groups.[5]

The mass spectral and n.m.r. data are consistent with the mixture containing perfluorosilanes $Si_4F_{10}$ and $Si_5F_{12}$, and analogues of $(BF_2)_3BPF_3$ such as $(Si_2F_5)(SiF_3)(BF_2)BPF_3$ and $(SiF_3)_2(BF_2)BPF_3$, although the exact nature of the perfluorosilicon substituents is unknown. Reactions of $SiF_2$ commonly give products containing one, two, or more silicon atoms,[8] and reaction with $B_2F_4$ at −196° may have formed $SiF_3BFBF_2$ and $Si_2F_5BFBF_2$ in low yield. Kirk and Timms have reported highly unstable and reactive products from this reaction.[9] In the presence of $PF_3$, disproportionation probably gave the observed mixture of analogues of $(BF_2)_3BPF_3$.

## EXPERIMENTAL

The species BF,[1,2] $SiCl_2$,[10,11] and $SiF_2$ [8] were prepared from the tri- or tetra-halides and the metalloids at high temperatures and low pressure as described elsewhere. The apparatus used enabled the species to be condensed on the liquid-nitrogen cooled surface of the vacuum chamber together with the vapours of other compounds.

Diboron tetrachloride was made by the reaction of copper vapour with $BCl_3$ at −196°,[12] and $B_2F_4$ by condensation of BF and $BF_3$ [1] or by fluorination of $B_2Cl_4$ with $SbF_3$.

Volatile products were pumped out of the vacuum chamber when it was warmed from −196° to room temperature. They were handled in glass vacuum lines equipped with greaseless O-ring stopcocks. Mixtures of sufficient volatility were fractionated using a low-temperature vacuum-distillation column.[13]

Three mass spectrometers were used during the investigations, a Bendix 1400 time-of-flight instrument, a Granville-Phillips quadrupole, and a modified AEI MS10c2. With each instrument, it was found necessary to use an all-glass inlet system to avoid decomposition of the molecules studied, especially $B_8F_{12}$.

Varian A56/60 or HA100 instruments were used for all the n.m.r. measurements; $^{11}B$ spectra were run at 30·4 MHz using an external reference of $BF_3,OEt_2$.

Infrared spectra were run on Perkin-Elmer 257, 411, or 457 instruments using a 7-cm gas cell with KBr windows or a

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[7] D. L. Smith and P. L. Timms, unpublished observations.

[8] J. L. Margrave and P. W. Wilson, *Accounts Chem. Res.*, 1971, **4**, 145.

[9] R. W. Kirk and P. L. Timms, *J. Amer. Chem. Soc.*, 1969, **91**, 6315.

[10] P. L. Timms, *Inorg. Chem.*, 1968, **7**, 387.

[11] P. L. Timms, *Advan. Inorg. Rad. Chem.*, 1972, **14**, in the press.

[12] P. L. Timms, *Chem. Comm.*, 1968, 1525; *J.C.S. Dalton*, 1972, 830.

[13] See description in D. F. Shriver, 'Manipulation of Air Sensitive Compounds,' McGraw-Hill, New York, 1969.

liquid $N_2$ cooled NaCl window on which the vapour of a compound could be frozen *in vacuo*.

Specific analytical methods were devised for some of the compounds as described below, others were sent to commercial analysts.

*Preparation and Characterisation of Compounds.*—$B_8F_{12}$. Triboron pentafluoride was prepared as previously described from BF and $B_2F_4$.[1] Liquid $B_3F_5$ (*ca.* 8 mmol) was kept under helium or nitrogen at −30° for 1 h. The yellow liquid was then distilled on a low-temperature column. A little $BF_3$, *ca.* 3 mmol of $B_2F_4$, 1 mmol of $B_3F_5$, 1·5 mmol of $B_8F_{12}$, and a small amount of colourless higher boron fluorides were obtained. A yellow solid remained at the bottom of the column.

For the vapour-density determinations, pressures of up to 20 Torr of $B_8F_{12}$ vapour were measured by a mercury manometer in a 30 ml constant-volume system at room temperature. The vapour was immediately condensed and sealed for weighing in quill tubing (Found: 316 ± 5. Calc. 314·6).

The B : F ratio was found by pumping an unweighed sample of $B_8F_{12}$ vapour (*ca.* 0·1 mmol) through a weighed alumina tube heated to 850° and collecting the off-gases in liquid nitrogen. The compound was dissociated into $BF_3$ which was collected, and boron which was deposited on the walls of the hot tube. The $BF_3$ was measured manometrically and the boron by reweighing the alumina tube. The B : F ratio was found to be 1 : 1·51 ± 0·015.

Rapid decomposition of $B_8F_{12}$ in the vapour state at room temperature made it necessary to take the gas-phase i.r. spectrum in 200 $cm^{-1}$ stages with a fresh sample each time. Bands were observed at 1412s, 1380s, 1225s, 1206sh, 1160sh, 1128m, 835w, and 735w.

The visible spectrum of $B_8F_{12}$ was measured with a Cary 14 spectrometer in a 10-cm gas cell at *ca.* 1 Torr pressure.

$(BF_2)_3BL$. The complexes $(BF_2)_3BCO$ and $(BF_2)_3BPF_3$ were made most efficiently by passing CO over $B_8F_{12}$ at −70° and condensing BF and $PF_3$ together at −196°, respectively. Other adducts were made by condensing 2 mmol of $B_8F_{12}$ into a tube at −196° and then condensing a slight excess of the ligand above it. The tube was warmed slowly until reaction was seen to commence, usually above −70°. The tube was finally warmed to −20° and then the products were pumped out.

Vapour pressures were measured in a constant-volume system using a mercury manometer. Slight decomposition prevented reliable measurements being made over a range of temperatures except with $(BF_2)_3BCO$ and $(BF_2)_3BPF_3$. Melting points were determined under a nitrogen atmosphere. Vapour pressures, melting point and analytical data are summarised below. $(BF_2)_3BCO$:[1] $\log p_{\mathrm{Torr}} = (-2078/T) + 8{\cdot}742$; $(BF_2)_3BPF_3$:[1] $\log p_{\mathrm{Torr}} = (-2008/T) + 8{\cdot}665$; $(BF_2)_3BPCl_3$: 10 Torr pressure at 59°, m.p. 134° (Found: B, 14·3; Cl, 35·8. Required B, 14·7; Cl, 36·1%); $(BF_2)_3BPH_3$: 10 Torr pressure at 53°, m.p. 112° (Found: B, 22·1; H, 1·65. Required, B, 22·6; H, 1·65%); $(BF_2)_3BS(CH_3)_2$: 10 Torr pressure at 43°, m.p. 107° (Found: B, 19·5; S, 14·9. Required B, 19·75; S, 14·6%).

*Silicon–Boron Compounds.*—$SiCl_2$ (*ca.* 30 mmol) was condensed at −196° during 1 h with $B_2Cl_4$ vapour (50 mmol). The reaction vessel was then filled with a pressure of *ca.* 300 Torr of dry CO and it was allowed to warm to room temperature. A colourless liquid collected at the bottom of the vessel. Before the CO was pumped out, the vessel was recooled in liquid nitrogen to condense vapours. The vessel was cautiously re-evacuated and allowed to warm to room temperature with continuous vacuum pumping. About 2 mmol of $(SiCl_3)_2(BCl_2)BCO$ was isolated, a yield of 13% based on the $SiCl_2$.

The preparation of $(SiCl_3)_2(BF_2)BPF_3$ was carried out under similar conditions, although the $PF_3$ (130 mmol) was first condensed at −196° and then allowed to evaporate as the condensate of $SiCl_2 + B_2Cl_4$ warmed up. The yield of $(SiCl_3)_2(BF_2)BPF_3$ was *ca.* 0·3 mmol, 3% based on the $SiCl_2$.

The perfluorinated complexes were made by condensing $SiF_2$ (10 mmol) with a mixture of $B_2F_4$ (10 mmol) and $PF_3$ (10 mmol) at −196° and then warming to room temperature. About 5 mmol of $B_2F_4$ were lost in each run, but only about 50 mg of a mixture of perfluorosilanes and the complexes were obtained. A solid pyrophoric residue was left on the walls of the reaction vessel.

$(SiCl_3)_2(BCl_2)BCO$ Was analysed by decomposing a weighed sample with 1M-$AgNO_3$. The silver chloride was filtered off and weighed; the filtrate was neutralised with NaOH so that the boron could be estimated by a mannitol titration (Found: B, 5·95; Cl, 72·5. Required B, 5·55; Cl, 72·8%).

The infrared spectrum of $(SiCl_3)_2(BCl_2)BCO$ deposited as a film on a KBr window at −196°, showed bands at 2176vs, 1015sh, 991s, 957m, 920s, 823m, 770w, 750s, 682m, 585vs, 525s, 505s, 455s, and 435vs $cm^{-1}$.

The Raman spectrum of the liquid taken on a Coderg PHO Laser Raman instrument over the regions 100—800 $cm^{-1}$ and 2000—2300 $cm^{-1}$, showed bands at 2165vs, 790m, 543w, 525m, 460m, 355vvs(pol), 288w, 255w, 220w(pol), 196m, 147m, and 115w.

## CONCLUSIONS

The results suggest that disproportionation of compounds of type $RBXBX_2$, where R is a perhalogenoboron or perhalogenosilicon group, may be a general reaction. In the presence of electron-pair donors the reaction appears to take the form

$$2RBXBX_2 \xrightarrow{L} R_2(BX_2)BL + B_2X_4$$

rather than the alternative in which $R(BX_2)_2BL$ and $RBX_2$ would be products.

The disproportionation creates Lewis acids of exceptional power capable of complexing more strongly than borane with electron pair donors.

The structure of $B_8F_{12}$, if it is correctly assigned, indicates that $BF_2$ groups and H atoms contribute in a very similar way to the electron distribution in boranes. It is possible that higher boron fluorides will also be structurally related to boron hydrides.

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