Bonding Studies of Compounds of Boron and the Group 3—5 Elements. Part XIV.[1] Redistribution Equilibria in Phenylboron Dihalide and Boron Trihalide Systems

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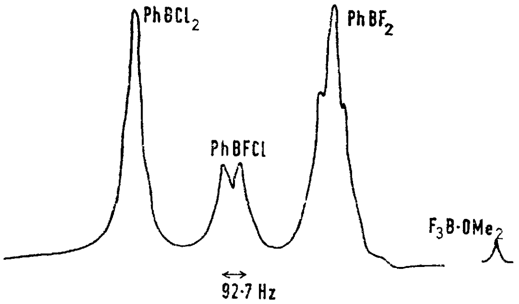
Redistribution reactions for two sets of trigonal boron systems, (*i*) $PhBX_2$–$PhBY_2$ and (*ii*) $PhBX_2$–BY_3, have been investigated, principally by ^{11}B n.m.r. spectroscopy for samples in sealed tubes. For (*i*) when X = F and Y = Cl or Br, equilibrium constants at 316·5 K have been obtained, and small $\Delta H^{\ominus}$ values and close to statistical $\Delta S^{\ominus}$ for the former have been derived from second-law plots. For (*ii*), $PhBF_2$ and BCl_3 or BBr_3 give quantitative transformation into $PhBCl_2$ or $PhBBr_2$ and BF_3 at 316·5 K. From these and literature data, standard heats of reactions are derived for various systems related to (*i*) and (*ii*).

We have previously made use of ^{11}B n.m.r. spectra for a quantitiative study of redistribution equilibria among boron trihalides.[2] We have now extended our studies to cover the systems $PhBX_2$–$PhBY_2$ and $PhBX_2$–BY_3 (X, Y = F, Cl, or Br). Brinckman and Stone [3] have shown by isotopic-labelling experiments that in the systems $RBCl_2$–BF_3 and R_2BCl–BF_3 (R = Me, Et, or vinyl) exchange only of halogen but not R takes place. The same authors obtained mass-spectroscopic evidence for the presence of mixed species of the type RBXY (X = F, Y = Cl or Br). Lockhart *et al.* have studied the $PhBCl_2$–$PhBBr_2$ equilibrium both by i.r.[4] and ^{11}B n.m.r. spectroscopy.[5] However, no quantitative data have been obtained by any of the techniques mentioned.

EXPERIMENTAL

The commercial boron trihalides were purified by standard vacuum-line procedures. $PhBF_2$,[6] $PhBCl_2$,[7] and $PhBBr_2$ [8] were prepared by literature methods. Methylcyclohexane was dried by heating with $Li[AlH_4]$ under reflux and then fractionally distilling using a Vigreux column. Standard solutions of phenylboron halides in methylcyclohexane were prepared in a nitrogen-filled dry-box. Measured volumes of these solutions were transferred to n.m.r. tubes from a graduated pipette, keeping the total volume to *ca.* 2 cm³. The tube was immediately attached to the vacuum line, evacuated after the solution was frozen, and sealed off. For study of exchange of BY_3 (Y = F, Cl, or Br) with a phenylboron halide, the latter in methylcyclohexane solution (*ca.* 2 cm³) was transferred to an n.m.r. tube as before. The tube was attached to the vacuum line and a known quantity of boron trifluoride, trichloride, or tribromide was added by use of a calibrated bulb, from which the trihalide was condensed into the tube, whereafter the tube was sealed off. For ^{19}F n.m.r. measurements, the use of methylcyclohexane solutions was not satisfactory in view of the broadness of the signals especially when studying the mixed species PhBFCl. Consequently $PhBF_2$ (0·25 cm³) and $PhBCl_2$ (0·25 cm³) were successively distilled into an n.m.r. tube which was sealed off after $CFCl_3$ (as standard) had also been condensed in. Even when neat liquids were mixed, the mixed species PhBFCl could barely be detected by ^{19}F n.m.r. spectroscopy.



32·1 MHz ^{11}B N.m.r. spectrum of a mixture of $PhBF_2$ and $PhBCl_2$ in methylcyclohexane at 303 K

Details of the ^{11}B n.m.r. measurements, using a Perkin-Elmer R10 spectrometer operating at 19·3 MHz, or a Varian HA 100 spectrometer operating at 32·1 MHz, and the evaluations of the equilibrium constants from the spectral traces have been described in Part IV.[2] By utilising a spectrum

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[1] Part XIII, M. F. Lappert, J. B. Pedley, O. Stelzer, E. Unger, and B. T. Wilkins, *J.C.S. Dalton*, 1975, preceding paper.

[2] Part IV, M. F. Lappert, M. R. Litzow, J. B. Pedley, T. R. Spalding, and H. Nöth, *J. Chem. Soc.* (*A*), 1971, 383.

[3] F. E. Brinckman and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 6235.

[4] J. C. Lockhart, *Spectrochim. Acta*, 1968, **A24**, 1205.

[5] A. Finch and J. C. Lockhart, *Chem. and Ind.*, 1964, 497.

[6] P. A. McCusker and H. S. Makowski, *J. Amer. Chem. Soc.*, 1957, **79**, 5185.

[7] J. E. Burch, W. Gerrard, M. Howarth, and E. F. Mooney, *J. Chem. Soc.*, 1960, 4916.

[8] E. W. Abel, W. Gerrard, and M. F. Lappert, *J. Chem. Soc.*, 1957, 5051.

accumulator and taking several hundred sweeps, it was possible to obtain spectra good enough for quantitative measurements even when the concentrations of mixed species formed were low. The ^{19}F n.m.r. spectra were recorded on a Varian HA 100 spectrometer operating at 94·1 MHz, using $CFCl_3$ as internal lock. The Figure shows the spectrum of $PhBF_2$–$PhBCl_2$ in methylcyclohexane at 303 K.

RESULTS AND DISCUSSION

The $PhBX_2$–$PhBY_2$ *System*.—The observed chemical shifts and coupling constants shown in Table 1 follow the expected trends.[9] Due to B–F coupling, ^{19}F n.m.r. signals were very broad and diffuse even when neat liquids ($PhBF_2$ and $PhBCl_2$) were mixed without a solvent. On account of this, there may be some doubt concerning the chemical shifts and coupling constants derived from ^{19}F spectra. A variable-temperature ^{19}F n.m.r. study of the mixture showed that as the temperature was lowered the signals became sharper without any perceptible splitting.

TABLE 1

Observed chemical shifts and coupling constants

	δ ^{11}B [a,b] ±0·2 p.p.m.	$J(^{11}B–^{19}F)$ [c] ±1 Hz	δ ^{19}F [d,e] ±0·2 p.p.m.	$J(^{11}B–^{19}F)$ [f] ± 2 Hz
$PhBF_2$	−25·5 (−24·9) [g]	62 (61) [g]	92	60
PhBFCl	−40·9 (−40·4) [g]	93 (90) [g]	51	[h]
$PhBCl_2$	−55·9 (−55·8) [g]			
PhBFBr	−42·6 (−42·8) [g]	92 (98) [g]		
$PhBBr_2$	−57·7 (−57·3) [g]			

[a] Solvent methylcyclohexane. [b] Relative to $F_3B\cdot OMe_2$ as 0·0 p.p.m. [c] From ^{11}B n.m.r. [d] Neat liquid. [e] Relative to CCl_3F as 0·0 p.p.m. [f] From ^{19}F n.m.r. [g] Values in parentheses obtained at Sussex on the R10 instrument are compared with those obtained in Munich on the HA 100. [h] Not determined due to broadness of the signal.

Results of equilibrium studies on reactions (1) and (2) are summarised in Table 2.* The variable-temperature

$$PhBF_2 + PhBCl_2 \rightleftharpoons 2PhBFCl \tag{1}$$

$$PhBF_2 + PhBBr_2 \rightleftharpoons 2PhBFBr \tag{2}$$

studies on reaction (1) are summarised in Table 3, and in each case they represent the average of at least four separate determinations. Spectra were also obtained for reaction (2) and for reaction (1) at 233 K, but due to the very low concentration of the mixed species equilibrium constants could not be obtained with a reasonable degree of accuracy. The standard enthalpy and entropy changes for reaction (1) were calculated from a second-law plot and the results are shown in Table 3. The entropy change for reaction (1) is close to the statistical value of $R\ln 4$ (2·8 cal K^{-1} mol^{-1}) as was also found for the mixed halides.[2] The enthalpy change of 1·53 kcal mol^{-1} is also compatible with previous studies. It was impossible to obtain an accurate second-law plot for reaction (2), but the entropy change would be expected to be approximately statistical in which case, using data from Table 2, $\Delta H^{\ominus}$ is *ca*. 2·0 kcal mol^{-1}.

TABLE 2

Equilibrium constants for the redistribution $PhBX_2 + PhBY_2 \rightleftharpoons 2PhBXY$ in methylcyclohexane solvent at 33·5 °C

		Total boron/mol %				
X	Y	$PhBX_2$	PhBXY	$PhBY_2$	K/l mol^{-1}	$\Delta G^{\ominus}$/kcal mol^{-1}
F	Cl	42·5	21·6	35·9	0·308	
		27·1	20·8	52·1	0·306	
		56·5	21·3	22·2	0·365	0·72
		55·5	20·1	24·4	0·298	±0·01
		44·5	21·7	33·8	0·314	
		31·4	19·5	49·1	0·246	
					Mean 0·306 ± 0·02	
F	Br	35·7	16·1	48·2	0·174	
		50·5	13·8	35·7	0·105	1·20
		57·8	14·3	27·9	0·127	±0·01
		32·8	17·0	50·2	0·175	
		43·7	14·5	41·8	0·114	
					Mean 0·139 ± 0·03	

TABLE 3

Variation (with temperature) of the equilibrium constant for the reaction $PhBF_2 + PhBCl_2 \rightleftharpoons 2PhBFCl$ in methylcyclohexane

T/K	K/l mol^{-1}
306·7	0·306 ± 0·02
303	0·260 ± 0·03
273	0·214 ± 0·015

$\Delta H^{\ominus}$ 1·53 kcal mol^{-1}, $\Delta S^{\ominus}$ 2·52 cal K^{-1} mol^{-1}.

For the system $PhBCl_2$–$PhBBr_2$, we observed only a single ^{11}B resonance even when operating at 32·1 MHz. The width of the line indicates the predominant formation of the mixed species PhBClBr. In view of the fact that separate signals have been observed for the components of the mixtures $PhBF_2$–$PhBCl_2$, $PhBF_2$–$PhBBr_2$, and BCl_3–BBr_3, it is hardly likely that in the $PhBCl_2$–$PhBBr_2$ system discrete resonance lines were not observed due to rapid averaging of ^{11}B environments, as has been previously assumed.[5] In our view, the anomaly is best explained by the inadequate resolution obtainable in this type of ^{11}B n.m.r. spectrometer and the small differences in the chemical shifts (Table 1).

The $PhBX_2$–BY_3 *System*.—^{11}B N.m.r. study showed that equilibria (3) and (4) lie entirely to the right. When

$$3PhBF_2 + 2BCl_3 \rightleftharpoons 3PhBCl_2 + 2BF_3 \tag{3}$$

$$3PhBF_2 + 2BBr_3 \rightleftharpoons 3PhBBr_2 + 2BF_3 \tag{4}$$

BCl_3 or BBr_3 was used in excess, no peak due to $PhBF_2$ or the mixed species was detected. When $PhBF_2$ was used in excess, no BBr_3 or BCl_3 peak appeared. It was also found that $PhBCl_2$ and BF_3 do not exchange in methylcyclohexane solutions even after heating at 75—80 °C for 24 h. There was very slight halogen exchange in the $PhBBr_2$–BF_3 system in methylcyclohexane which was not enhanced by heating the mixture at 80 °C for 12 h. Peaks other than those due to $PhBBr_2$ or BF_3 were not prominent, although the shape

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* 1 cal = 4·184 J.

[9] M. F. Lappert, M. R. Litzow, J. B. Pedley, and A. Tweedale, *J. Chem. Soc.* (*A*), 1971, 2426.

of the spectra definitely suggests slight exchange. The situation here contrasts with that in the RBF_2–BCl_3 (R = Me, Et, or vinyl) system where equilibrium was established on approaching from either side, by heating the mixture at 90 °C for 12 h. Some interesting semi-quantitative conclusions may, however, be drawn from the fact that equilibria (3) and (4) lie ' completely ' to the right within experimental error. In quantitative terms this means that the concentrations of BCl_3 and $PhBF_2$ in equation (3) are probably less than 1% of the concentrations of $PhBCl_2$ and BF_3, and similarly for (4). This situation corresponds to equilibrium constants greater than 10^{10} and $\Delta G^\ominus$ values more negative than -15 kcal mol^{-1}. The value of $\Delta S^\ominus$ should be negligible, whence $\Delta H^\ominus$ should be more negative than -15 kcal mol^{-1}. Using the following data ($\Delta H_f^\ominus$/kcal mol^{-1}), heats of reaction, $\Delta H^\ominus$, were derived for (5)—(8): BCl_3 (g), $-96{\cdot}3$;[10] BBr_3 (g), $-48{\cdot}8$;[10] Ph_2BCl (g), $-22{\cdot}0$;[11] Ph_2BBr (g), $-1{\cdot}7$;[11] $PhBCl_2$ (g), $-63{\cdot}6$;[11] $PhBBr_2$ (g), $-30{\cdot}9$;[11] and Ph_3B (g), $+31{\cdot}1$.[11] These

$$2Ph_3B\ (g) + BCl_3\ (g) \longrightarrow 3Ph_2BCl\ (g),\quad \Delta H^\ominus\ -31{\cdot}9\ \text{kcal mol}^{-1} \qquad (5)$$

$$2Ph_3B\ (g) + BBr_3\ (g) \longrightarrow 3Ph_2BBr\ (g),\quad \Delta H^\ominus\ -18{\cdot}5\ \text{kcal mol}^{-1} \qquad (6)$$

$$Ph_3B\ (g) + 2BCl_3\ (g) \longrightarrow 3PhBCl_2\ (g),\quad \Delta H^\ominus\ -29{\cdot}3\ \text{kcal mol}^{-1} \qquad (7)$$

$$Ph_3B\ (g) + 2BBr_3\ (g) \longrightarrow 3PhBBr_2\ (g),\quad \Delta H^\ominus\ -26{\cdot}2\ \text{kcal mol}^{-1} \qquad (8)$$

substantial heats of redistribution are characteristic of mixed trigonal B compounds, BX_2Y, with π systems, *e.g.* X, Y = NMe_2,Cl or OEt,Cl,[12] but differ from mixed-halide situations (X and Y are different halogens) when redistribution heats are negligible.[2]

Assuming that enthalpies of solution are small and the enthalpies of vaporisation (in kcal mol^{-1}) of BF_3 (l) (4·0, estimated), BCl_3 (l) (5·6),[10] BBr_3 (l) (7·30),[10] $PhBF_2$ (l) (8·0, estimated), $PhBCl_2$ (8·1),[11] and $PhBBr_2$ (10·5),[11] $\Delta H^\ominus$ for reactions (3) and (4) in the *gas phase* is *more* negative than -15 kcal mol^{-1}. Subtracting equations (3) and (4) from (7) and (8) gives $\Delta H^\ominus$ *less* negative than -15 kcal mol^{-1} for reaction (9). Evidently, the re-

$$Ph_3B\ (g) + 2BF_3\ (g) \longrightarrow 3PhBF_2\ (g) \qquad (9)$$

distribution reaction (9) is considerably less exothermic than those involving BCl_3 and BBr_3. The appreciable stabilisation which occurs when Cl or Br and Ph groups are mixed around a B atom does not apply to mixtures of F atoms and Ph groups. This effect may be due in some way to incompatibility of π delocalisation of the F atom with the phenyl group *via* the empty B p_π atomic orbital.

Halogen exchange was observed in (10) from whichever side the equilibrium was approached. Equilibrium con-

$$2PhBCl_2 + 2BBr_3 \rightleftharpoons 3PhBBr_2 + 2BCl_3 \qquad (10)$$

stants could not be evaulated because discrete resonance lines were not observed for $PhBCl_2$, $PhBBr_2$, and PhBBrCl (*cf.* previous section).

We thank Professor H. Nöth for kindly providing the 32·1 MHz data and the U.S. Air Force Office of Scientific Research for support.

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[10] JANAF Thermochemical Tables, Office of Standard Reference Data, National Bureau of Standards, Washington, D.C. 20234, 1971.

[11] *Cf.* J. D. Cox and G. Pilcher, ' Thermochemistry of Organic and Organometallic Compounds,' Academic Press, New York, 1970.

[12] *Cf.* H. A. Skinner, *Adv. Organometallic Chem.*, 1964, **2**, 49.