Phosphine–Borane Derivatives. Part V.[1] Phosphine Adducts of Mixed Boron Trihalides

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The investigation by proton nuclear magnetic resonance spectroscopy of the sparingly soluble adducts formed between phosphine and boron trihalides has led to the identification of the mixed species PH_3,BX_2Y ($X \neq Y$ = Cl, Br, I) $PH_3BClBrI$, and probably PH_3BBr_2F and $PH_3,BBrF_2$. The n.m.r. parameters of PH_3,BX_3 are also reported as are those of the mixed [$^2H_3$]methylphosphine–boron trihalide adducts, CD_3PH_2,BY_2Z ($Y \neq Z$ = F, Cl, Br, I) and of CD_3PH_2,BY_3 for comparison.

THE properties of the phosphorus–boron dative bond have been the object of several recent investigations.[1-8] Attempts have been made to obtain an estimate of the strength of the P–B bond by utilising vibrational spectra in conjunction with normal co-ordinate analyses. Some of these studies have resulted in considerable differences in the values assigned to the P–B stretching force constant.[6,7] In investigations involving the use of n.m.r. spectroscopy, the trends in the changes of n.m.r. parameters have at least been fairly consistent.[1-4] This has recently been shown to be particularly true for the value of the J_{PB} coupling constant.[9,10] In addition, studies of amine adducts of mixed boron trihalides show changes in n.m.r. parameters consistent with established orders of Lewis acidity.[11,12] In view of this, we present an extension of our studies on mixed hydrogen halide adducts of boron of the type PH_3,BH_2X and PH_3,PHX_2 [2] (X = Cl, Br) to the mixed trihalide adducts PH_3,BX_2Y ($X \neq Y$ = Cl, Br, I), $PH_3,BClBrI$, PH_3,BF_2Br, and $PH_3,PFBr_2$. Also presented are the results of our parallel investigation of the analogous series CD_3PH_2,BY_2Z ($Y \neq Z$ = F, Cl, Br, I) undertaken to ascertain the effects of the stronger Lewis base on the nature of the P–B interaction.

EXPERIMENTAL

Apparatus.—Reactions were carried out in n.m.r. tubes (4 mm o.d.) with fittings to accommodate the conventional Pyrex-glass vacuum system. Greaseless stopcocks (G. Springham and Co. Ltd., Harlow, Essex; Viton A diaphragm) were used. The ^1H n.m.r. spectra of the PH_3,BX_2Y adducts dissolved in CD_3I and the CD_3PH_2,BY_2Z adducts dissolved in CH_2Cl_2 were recorded at −70 °C (in sealed tubes) on a Jeol C60HL high-resolution spectrometer. Typically, the instrument was operated at −36 db r.f. gain and 0·1 × 1 a.f. amplitude with scale setting 9 × 2 p.p.m. All chemical shifts were reported relative to tetramethylsilane as internal standard.

Starting Materials.—Phosphine (Matheson) was distilled through a trap at −126 °C and its i.r. spectrum was identical to that of the pure material.[13] Deuteriated methyl phosphine was prepared by means of the deprotonisation–methylation procedure.[14] A CD_3 content in excess of 96% was ascertained through the n.m.r. spectrum of the purified product. Boron trichloride (Matheson) and boron tribromide (Alpha Inorganics) were distilled through traps at −65 °C and −45 °C respectively; their i.r. spectra and vapour pressures indicated a high degree of purity.[15,16] Boron tri-iodide (Alpha Inorganics), in the appropriate molar quantities, was purified by agitation of a CH_2Cl_2 solution with elemental mercury in a closed vessel under moisture-free conditions. The solution was then decanted (in a dry-box) into an n.m.r. tube fitted for connection to the vacuum line. Before interaction with phosphine, the solvent was pumped away from the purified BI_3. Deuteriated methyl iodide (Stohler Isotope Chemicals, Montreal; 1% ^1H impurity) was used as obtained.

Formation of the Adducts PH_3,BX_3 (X = Cl, Br, I).—Equimolar quantities (typically *ca.* 0·5 mmol) of phosphine and boron trichloride or boron tribromide were distilled into an n.m.r. tube at −196 °C. (With boron tri-iodide, the purification procedure made it impossible to know the exact quantity of BI_3 present; consequently PH_3 was added in an amount to ensure that there was excess of PH_3). As the contents were allowed to warm to room temperature the formation of a white solid adduct was evident. After 1 h at ambient temperature, excess of PH_3 was pumped away. The solvent, CD_3I (*ca.* 5 mmol) and a trace of tetramethylsilane were distilled onto the product at −196 °C and the tube was then sealed. The ^1H n.m.r. spectra were then recorded from temperatures ranging from room temperature down to −70 °C. The solubility of the adducts was estimated to be *less than* 1% by comparison of the respective peak heights of the PH_3 resonance with that of the ^1H impurity of the solvent. The n.m.r. parameters are recorded (Table 1). Attempts to form an addition compound with BF_3 indicated that no such adduct formed under these experimental conditions. The variations of both J_{PH} and δ with temperature from −70 °C to +30 °C are reported (Table 2).

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Formation of Mixed Adducts PH_3,BX_2I *and* PH_3,BXI_2 (X = Cl, Br).—An estimated quantity of purified boron tri-iodide (*ca.* 0·5 mmol) was transferred to an n.m.r. tube as described under starting materials. Boron tribromide or boron trichloride (0·5 mmol) and phosphine (*ca.* 1·0 mmol) were then distilled into the n.m.r. tube at −196 °C. The contents were allowed to warm to room temperature during which time a white solid was formed. After 1 h at ambient temperature excess of reactant was pumped away, CD_3I (*ca.* 5 mmol) and a trace of tetramethylsilane were distilled onto the remaining solid at −196 °C, and the tube was sealed.

TABLE 1

Observed ^1H n.m.r. parameters (δ in p.p.m. ±0·05 p.p.m. downfield from tetramethylsilane; J_{PH} in Hz ±2 Hz) for the various boron trihalide adducts of phosphine and [$^2H_3$]methylphosphine

	Mixed		Single			Mixed		Single	
Compound [a]	δ	J_{PH}	δ	J_{PH}	Compound [b]	δ	J_{PH}	δ	J_{PH}
PH_3,BI_3	7·40	436	7·50	432	CD_3PH_2,BI_3	6·20	434	6·20	432
			7·05	434 [c]					
$PH_3,BBrI_2$	7·10	434			$CD_3PH_2,BBrI_2$	5·95	432		
$PH_3,BClI_2$	6·90	432			$CD_3PH_2,BClI_2$	5·90	430		
PH_3,BBr_2I	6·70	432			CD_3PH_2,BBr_2I	5·80	430		
$PH_3,BClBrI$	6·55	430							
PH_3,BCl_2I	6·40	430			CD_3PH_2,BCl_2I	5·60	426		
PH_3,BBr_3	6·45	428	6·45	430	CD_3PH_2,BBr_3	5·60	430	5·60	428
			6·05	432 [c]					
PH_3BClBr_2	6·30	426			$CD_3PH_2,BClBr_2$	5·50	426		
PH_3,BCl_2Br	6·00	424			CD_3PH_2,BCl_2Br	5·40	426		
PH_3,BCl_3	5·90	420	5·90	420	CD_3PH_3,BCl_3	5·35	428	5·30	422
								5·40	426 [d]
$PH_3,BFBr_2$	6·00	410			$CD_3PH_2,BFBr_2$	5·30	422		
					$CD_3PH_2,BFCl_2$	5·15	420		
PH_3,BF_2Br	5·90	404			CD_3PH_2,BF_2Br	5·00	406		
					CD_3PH_2,BF_2Cl	4·95	406		
					CD_3PH_2,BF_3	4·50	378	4·30	355

[a] Recorded at −70 °C in CD_3I. [b] Recorded at −70 °C in CH_2Cl_2. [c] Recorded at −70 °C in CH_2Cl_2. [d] Recorded at −40 °C in CD_3I.

TABLE 2

Observed ^1H n.m.r. parameters, δ_{PH} and J_{PH}, of CD_3PH_2,BF_3 [a] and PH_3,BX_3 [b] at various temperatures

	$CD_3PH_2BF_3$		PH_3,BCl_3		PH_3,BBr_3		PH_3,BI_3	
t/°C	δ_{PH}	J_{PH}	δ_{PH}	J_{PH}	δ_{PH}	J_{PH}	δ_{PH}	J_{PH}
−70	4·28	355	5·92	426	6·44	429	7·40	432
−65	4·28	350	5·90	424	6·44	429	7·40	432
−40	4·26	350	*ca.* 5·6 [c]	*ca.* 412	6·40	428	7·40	430
−20	4·22	346	*ca.* 5·4 [c]	*ca.* 400	6·34	428	7·40	430
25	3·72	301	5·37	396	6·20	424	7·26	428

[a] Recorded in CH_2Cl_2. [b] Recorded in CD_3I. [c] Estimated value of resonance located within proton impurity peak of solvent.

The ^1H n.m.r. spectra were recorded from temperatures varying from ambient to −70 °C. Both the high- and low-field resonances of the series of widely separated doublets are shown for the system PH_3–BBr_3–BI_3 (Figure 1). For convenience, only the low-field resonances are shown for the system PH_3–BCl_3–BI_3 (Figure 2). The n.m.r. parameters are displayed in Table 1.

Formation of the Mixed Adducts PH_3,BCl_2Br *and* $PH_3,BClBr_2$.—Boron tribromide (0·5 mmol), boron trichloride (0·5 mmol), and phosphine (1·0 mmol) were distilled into an n.m.r. tube at −196 °C. Essentially the same procedure was then followed as described for the PH_3,BX_2I and PH_3,BXI_2 system. The low-field resonances of the ^1H n.m.r. spectra at various temperatures are shown in Figure 3 and the n.m.r. parameters displayed in Table 1.

Formation of Mixed Adducts involving BF_3.—The same procedures as described above were carried out for the systems PH_3–BF_3–BCl_3, PH_3–BF_3–BBr_3, and PH_3–BF_3–BI_3. In all systems resonances attributable to PH_3,BX_3 (X = Cl, Br, I) were observed, although that of PH_3,BCl_3 was much less evident than that of PH_3,BI_3. Only for PH_3–BF_3–BBr_3 were two additional doublets observed attributable to PH_3,BF_2,Br and $PH_3,BFBr_2$ (Table 1).

Formation of $PH_3,BClBrI$.—The resonances attributable to this adduct (Table 1) were clearly seen in the ^1H n.m.r.

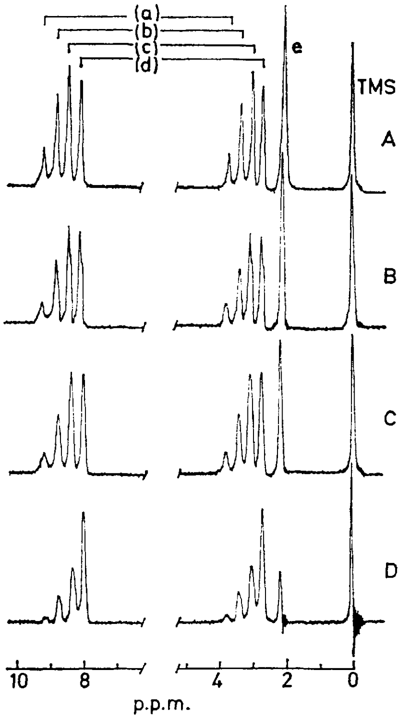

FIGURE 1 ^1H N.m.r. spectrum of the PH_3 resonances of the system PH_3–BBr_3–BI_3 at A, −70 °C; B, −30 °C; C, −10 °C; and D, +25 °C; (a), PH_3,BI_3; (b) $PH_3,BBrI_2$; (c) PH_3,BBr_2I; and (d) PH_3,BBr_3; (e) ^1H impurity of the solvent, CD_3I; TMS = tetramethylsilane spectrum recorded at −70 °C of the mixture of adducts resulting from mixing PH_3, BCl_3, BBr_3, and BI_3 in the approximate ratio of 3 : 1 : 1 : 1.

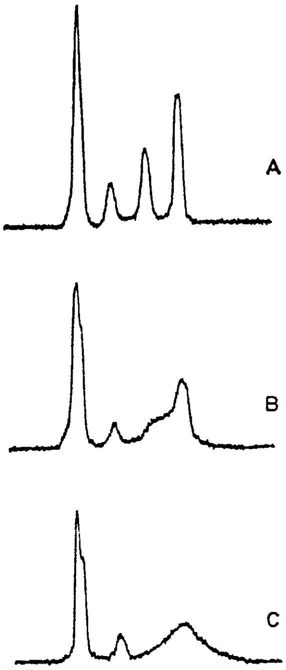

FIGURE 2 ^1H N.m.r. spectrum of the low-field PH_3 resonances of system PH_3–BCl_3–BI_3 at A, −70 °C; B, −10 °C, and C, +25 °C. Peaks, from left to right at −70 °C, are attributable to PH_3,BI_3, $PH_3,BClI_2$, PH_3,BCl_2I, and PH_3,BCl_3

Formation of the Adducts CD_3PH_2,BY_2Z ($Y \neq Z = F$, Cl, Br, I).—The single and mixed adducts of the boron trihalides with CD_3PH_2 were produced in the same manner as that described for the PH_3 system. Use of CD_3I as solvent had to be abandoned because of its tendency to solidify in the presence of these adducts at temperatures as high as −40 °C. CH_2Cl_2 was found to be a suitable solvent (*ca.* 1% molar solution) for all adducts. The n.m.r. parameters recorded at −70 °C for the entire series are displayed in Table 1.

RESULTS AND DISCUSSION

Phosphine reacts with boron trichloride, tribromide, and tri-iodide, but not the trifluoride, to form the corresponding 1 : 1 adducts (1). The resulting solid

$$PH_3 + BX_3 \rightleftharpoons PH_3BX_3\ (X = Cl, Br, I) \quad (1)$$

white adducts exhibit extremely low solubility in a wide range of solvents. This, so far, has prevented the determination of the ^{11}B n.m.r. parameters, J_{PB} and δ_{PB}. Nevertheless, the ^1H n.m.r. spectra of the complexes in very dilute solutions of deuteriated methyl iodide (*ca.* 1% molar) have been recorded. In the spectra the PH_3 resonance is observed as the widely separated doublet characteristic of four-co-ordinated phosphine bonded to boron (J_{PH} 420—436 Hz at −70 °C).[2] It is to be noted that in the spectrum of PH_3,BCl_3 a marked change occurs in the values of J_{PH} and δ_{PH} as the system is warmed from −70 °C to +25 °C (Table 2). This is consistent with the rapid equilibrium in (1) resulting in an averaging of the signals of free PH_3 and PH_3,BCl_3.[17] The PH_3,BCl_3 system is the only one in which extensive dissociation might be expected at ambient temperatures.[18] Further, the convergence of J_{PH} and δ_{PH} by −70 °C in all three systems (Table 2) suggests that these are probably the true parameters of the adducts.

When phosphine is mixed with approximately equimolar amounts of boron tribromide and boron tri-iodide the ^1H n.m.r. spectrum shows a series of four doublets attributable to the four adducts PH_3,BBr_3(d), PH_3,BBr_2I(c), PH_3B,BrI_2(b), and PH_3,BI_3(a) (Figure 1 and Table 1). It is probable that appreciable halogen exchange between BBr_3 and BI_3 occurs before adduct formation.[19] However, the peaks attributable to PH_3,BBr_3 and PH_3,BI_3 are slightly broader at room temperature than in the binary systems. This suggests that some exchange still occurs after adduct formation, possibly between adduct and free boron trihalide, because the peaks sharpen on lowering the temperature. Proton exchange at phosphorus was not observed in previous investigations of the systems PH_3,BD_3, SiH_3,PH_2BD_3, and CH_3PH_2,BD_3,[8] so it is unlikely to be a factor in these studies.

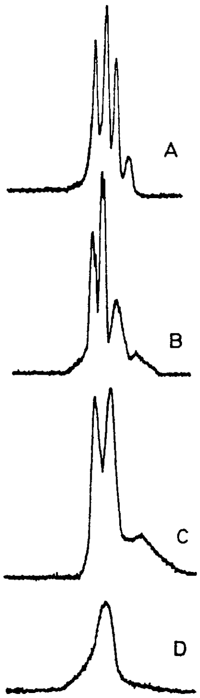

FIGURE 3 ^1H N.m.r. spectrum of the low-field PH_3 resonances of the system PH_3–BCl_3–BBr_3 at A, −70 °C; B, −30 °C; C, −10 °C; and D, +25 °C. Peaks, from left to right at −70 °C attributable to PH_3,BBr_3, PH_3BClBr_2, PH_3BCl_2Br, and PH_3,BCl_3

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In the similar system PH_3–BCl_3–BI_3 indication of line-broadening due to exchange is even more evident as is illustrated for the low-field resonances of the four doublets in Figure 2. Indeed at room temperature, the two resonances of PH_3,BCl_2I and PH_3,BCl_3 have coalesced. In the system PH_3–BCl_3–BBr_3 exchange is so rapid at room temperature than the low-field series of doublets appears as one envelope. As the system is cooled the individual peaks progressively appear: those attributable to PH_3,BBr_3 and $PH_3,BClBr_2$ at −10 °C, PH_3,BCl_2Br at −30 °C, and PH_3,BCl_3 at −70 °C.

The relative integrated peak ratios for the spectra suggest that the tendency to form the mixed species is greatest in the PH_3–BCl_3–BBr_3 system and least in the PH_3–BCl_3–BI_3 system. The integration ratios are in good agreement with those obtained in an ^{11}B n.m.r. study of boron trihalide exchange in the order BCl_3–BBr_3 > BBr_3–BI_3 > BCl_3–BI_3.[19] This supports the suggestion that in the phosphine adducts of these systems, exchange proceeds at least in part *via* free boron trihalide.

To investigate this further, an experiment was devised whereby PH_3,BI_3 and PH_3,BBr_3 were formed in separate portions of the tube and mixed in solution at −70 °C. In this way, the possibility of extensive exchange between BBr_3 and BI_3 before adduct formation was minimised. The ^1H n.m.r. spectrum was run immediately and gave no evidence for formation of the mixed adducts. The tube was warmed and the system held at room temperature for *ca.* 10 min. The spectrum run at −70 °C now exhibited small resonance peaks attributable to the formation of the mixed species.

In the free boron trihalide systems, the mixed BF_2Cl, $BFCl_2$, BF_2Br, and $BFBr_2$ species were observed but not BF_2I or BFI_2.[20] It is not surprising therefore that attempts to form the mixed adducts PH_3,BF_2I and PH_3,BFI_2 are unsuccessful. There is also no evidence for the formation of the mixed complexes PH_3,BF_2Cl and $PH_3,BFCl_2$, but since PH_3,BF_3 itself does not form, this is not surprising. However, peaks are discerned in the mixed PH_3–BF_3–BBr_3 system which suggests that Lewis acidity is sufficiently enhanced by bromine substitution to allow for the formation of PH_3,BF_2Br and $PH_3,BFBr_2$. With this in mind it seemed appropriate to study a system in which a BF_3 adduct could be formed. Methylphosphine is assumed to be a stronger Lewis base than PH_3 and therefore should form the adduct $MePH_2,BF_3$. To avoid complex spectra, n.m.r. parameters are obtained for deuteriated methylphosphine adducts. As can be seen (Table 1) all the binary adducts CD_3PH_2,BY_3 (Y = F, Cl, Br, I) are obtained and also the mixed species as with phosphine. In addition, CD_3PH_2,BF_2Cl and $CD_3PH_2,BFCl_2$ are obtained thereby confirming that CD_3PH_2 exhibits greater Lewis basicity in these systems than does PH_3. The complexes CD_3PH_2,BF_2I and CD_3PH_2,BFI_2 are not observed although both CD_3PH_2,BF_3 and CD_3PH_2,BI_3 are seen in the system. This lack of mixed fluoride–iodide adducts is consistent with the study previously cited.[20]

The n.m.r. parameters (Table 1) are an interesting study of regular trends. It was found necessary to use different solvents for the two systems. The CD_3PH_2,BY_2Z systems solidify in CD_3I solution at −40 °C so a change of solvent to CH_2Cl_2 is necessary. Equally unfortunately, the PH_3,BCl_3 systems are not sufficiently soluble in CH_2Cl_2 to warrant its use in the phosphine system. Parameters were obtained in selected cases in both solvents for comparison (Table 1).

The spectra of PH_3,BBr_3–BI_3 system (Figure 1) neatly illustrate the successive chemical shifts to low field and the increase in the value of the J_{PH} coupling constant (Table 1) as the halogen changes from bromine to iodine. These trends are remarkably consistent for all of the adducts within the series PH_3,BCl_3 (δ_{PH} 5·90) to PH_3,BI_3 (δ_{PH} 7·40). There is a similar trend in the more extensive series starting at CD_3PH_2,BF_3 (δ_{PH} 4·50) to CD_3PH_2,BI_3 (δ_{PH} 6·20). Apparently, an increase in Lewis acidity of the boron halide results in a deshielding of the proton on phosphorus in both series so that the order of decreasing Lewis acidity, relative to these bases, is $BI_3 > BBrI_2 > BClI_2 > BBr_2I > BClBrI > BCl_2I \simeq BBr_3 > BClBr_2 > BCl_2Br > BCl_3 > BFBr_2 > BFCl_2 > BF_2Br > BF_2Cl > BF_3$. This corresponds to the order suggested with respect to amines.[11,21] The relative chemical shifts of the comparable PH_3,BX_3 and CD_3PH_2,BX_3 adducts suggest that there is a consistent shift to high field with the stronger Lewis base.

The increase in the value of J_{PH} coupling constant from 179 Hz in free phosphine [22] to 420 Hz in PH_3,BCl_3 is dramatic. As we suggested previously,[2] by analogy with $J(^{13}C$–$H)$ coupling,[23] this apparently reflects a marked increase in *s*-character of the phosphorus orbital bound to hydrogen. The trend from PH_3,BCl_3 to PH_3BI_3 also suggests that as the Lewis acidity of the boron adducts increases there is a further slight increase in the *s*-character of the P–H bonds. This is analogous to observations in terms of $J(^{13}C$–$H)$ where its value increases as the electronegativity of the moiety attached to carbon increases.[24] Thus for this series at least the assumption that the Fermi contact term is predominant seems to be fully justified.

In the CD_3PH_2,BY_2Z series there is a similar regular increase in the values of J_{PH}. However, it is surprising that the value of J_{PH} is not very different in the corresponding adducts CD_3PH_2,BX_3 and PH_3,BX_3. This suggests that the overall effect of substituting a CD_3 group is to leave the *s*-character in the remaining P–H bonds essentially unaltered.

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