165. *Bonding and Reactivity in Triphenylphosphineborane.*

By M. A. Frisch, H. G. Heal, H. Mackle, and I. O. Madden.

The enthalpies of reaction, in benzene solution, of diborane with mono-, di-, and tri-phenylphosphine have been measured by direct calorimetry. From these have been derived the enthalpies of addition of the various donors to borane (BH_3). The donor–acceptor bonding is stronger for all the phosphine donors than would be expected for σ-bonding alone. The dipole moment of triphenylphosphine–borane, and the stretching frequencies of the boron–phosphorus and boron–hydrogen bonds, give no unambiguous evidence for π-bonding between boron and phosphorus but seem compatible with it. The reactions of triphenylphosphine–borane with hydrogen chloride and iodine chloride show the borane hydrogen atoms to be electropositive, as would be expected if π-bonding occurred. Other reactions of triphenylphosphine–borane, including those with halogens, mercury(II), copper(II), and sulphur, are described, and interpreted with the help of this picture of the bonding.

The borane hydrogen atoms of the adducts of borane (BH_3) with nitrogen donors react hydridically, forming molecular hydrogen with sources of protons such as water and hydrogen halides,[1-4] but the borane hydrogen atoms in triphenylphosphine–borane do not react in this way.[5,6] In 1953 Burg and Wagner [4] proposed an explanation for the inertness of the hydrogen atoms in the phosphinoborine ring polymers which may also apply to triphenylphosphine-borane. Their suggestion was that electron density might be withdrawn from the B–H bonds into $p\pi$–$d\pi$ bonds between boron and phosphorus. This idea gains support from the observation that the adducts of borane with phosphorus trifluoride and alkylphosphines are far more stable than could be predicted on the basis of dative σ-bonding and normal inductive effects.[7] Since it is easily handled, and easily made from a Lewis base which is itself stable and easily handled, triphenylphosphine-borane seems a good subject for a more detailed study of the physical properties and chemical

[1] Schlesinger and Burg, *Chem. Rev.*, 1942, **31**, 1.
[2] Ryschkewitsch, *J. Amer. Chem. Soc.*, 1960, **82**, 3290.
[3] Nöth and Beyer, *Chem. Ber.*, 1960, **93**, 2251.
[4] Burg and Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 3872.
[5] Heal, *J. Inorg. Nuclear Chem.*, 1961, **16**, 208.
[6] Heal and Madden, *Nature*, 1962, **195**, 280.
[7] Stone, *Chem. Rev.*, 1958, **58**, 101.

behaviour associated with this presumed π-bonding. This would be more difficult with, for example, phosphorus trifluoride–borane which is partially dissociated at room temperature,[8] and the problem of distinguishing the reactions of the adduct itself from those of its dissociation products would often arise. We have found that Burg and Wagner's postulate of π-bonding is, on the whole, the most satisfactory basis for understanding triphenylphosphine–borane, though some of the physical evidence and certain chemical reactions could be explained otherwise. Our results and conclusions follow.

I. *Enthalpies of Formation.*—We have measured these from gaseous diborane and the donor in benzene solution, for the adducts of borane with triphenylphosphine and some related donors:

$$\text{Donor} + \tfrac{1}{2}B_2H_6 \longrightarrow \text{Donor–}BH_3;\ \Delta H_1 \text{ (note 1 to Table)}$$
$$\text{Donor} + BH_3 \longrightarrow \text{Donor–}BH_3;\ \Delta H_2 \text{ (note 2 to Table)}$$

Donor	$-\Delta H_1$ (kcal. mole^{-1})	$-\Delta H_2$ (kcal. mole^{-1})
Triphenylphosphine	20·2 ± 0·5	37·6 ± 3
Diphenylphosphine	16·7 ± 0·2	34·1 ± 3
Phenylphosphine	13·8 ± 0·4	31·2 ± 3

Notes: (1) ΔH_1 is the measured enthalpy of reaction of gaseous diborane with an ~0·05M-solution of the donor in benzene, at ~20°: errors are average deviations of 4—7 runs.

(2) ΔH_2 is the enthalpy of formation of the adduct from donor and borane calculated by using $\Delta H = 35 \pm 3$ kcal. mole^{-1} for the enthalpy of dissociation of diborane.[9]

Clearly, the phosphorus–boron bonds in these adducts are comparatively strong, in line with the view that in complexes between borane and a donor molecule involving a second-row element a special kind of π-bonding, supplementary to the normal σ-bonding, exists in the donor–acceptor bond.[10, 11] The strength of the donor–acceptor bond increases with the number of phenyl groups in the phosphine donor. Two factors probably determine this trend. In the progressive replacement of H by Ph the bond angles around the phosphorus atom widen, while the hybridization of the phosphorus moves from almost pure *p* towards the sp^3 hybridization required for adduct formation. Thus, triphenyl phosphine requires the least reorganization energy to enable it to form a co-ordinate link. Further, the positive charge that develops on the phosphorus atom when it forms the dative bond to boron may cause a delocalization of π-electrons from the aromatic rings into phosphorus *d* orbitals of the correct symmetry. Such delocalization would stabilize the adduct and increase the strength of the donor–acceptor bonds, and it would be most pronounced in the triphenylphosphine adduct.

II. *Proton Magnetic Resonance Spectra.*—We have made a preliminary study of these spectra of triphenylphosphine and its borane adduct. The borane proton resonances were not detected. The (undifferentiated) ring protons of triphenylphosphine gave a doublet at 7·26 and 7·32 p.p.m. downfield from tetramethylsilane; the splitting is caused by the phosphorus spin. In triphenylphosphine–borane, the centre of gravity of the ring-proton resonances was further downfield at 7·6 p.p.m., and the doublet structure was replaced by a multiplet, found by comparison with the spectrum of triphenylphosphine–$^{10}BH_3$ to arise from spin interaction with boron. The downfield movement may have been caused by increased delocalization of the ring π-electrons, as postulated in the previous section. We shall report these spectra more fully later.

III. *Dipole Moments.*—We find the value 4·79 ± 0·20 D for the dipole moment of triphenylphosphine–borane in benzene solution. Triphenylphosphine–boron trichloride has a moment of 7·03 D. For a valid comparison of these values, we follow a published procedure [12] and subtract from the latter value 1·18 D, an estimate of the difference between

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[8] Parry and Bissot, *J. Amer. Chem. Soc.*, 1956, **78**, 1524.

[9] Garbedian and Benson, *J. Amer. Chem. Soc.*, 1964, **86**, 176.

[10] See Mortimer, " Reaction Heats and Bond Strengths," Pergamon Press, 1962, ch. 6, for detailed arguments and references.

[11] Graham and Stone, *J. Inorg. Nuclear Chem.*, 1956, **3**, 164.

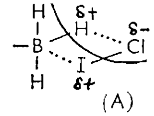
[12] Bax, Katritzky, and Sutton, *J.*, 1958, 1259.

the moments of co-ordinated boron trichloride and co-ordinated borane. The resulting figure, 5·85 D, may be said loosely to represent the moment of the phenyl groups plus the P–B bond in triphenylphosphine-boron trichloride. It is appreciably larger than the corresponding moment (4·79 D) in triphenylphosphine–borane. In order to know whether there is π-bonding in the latter, it is now necessary to subtract from each of these two values allowances for the moment of co-ordinated triphenylphosphine, leaving values for the moment of the P–B bonds. If the co-ordinated triphenylphosphine has about the same moment in the two complexes, the P–B bond is decidely less polar in triphenylphosphine–borane than in triphenylphosphine–boron trichloride. This could indicate that triphenylphosphine–borane has either weaker σ-bonding than triphenylphosphine–boron trichloride, with little or no π-bonding, or comparable or stronger σ-bonding and appreciable π-bonding. In view of the bond strengths, only the second alternative seems reasonable.

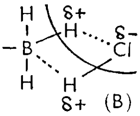
IV. *Infrared Spectra.*—We have identified the wave number of the symmetrical stretching vibration of the phosphorus–boron bond in triphenylphosphine–borane, from the effect on the infrared spectrum of replacing ordinary boron by boron-10. Its value (608 cm.$^{-1}$ for ^{11}B, 630 cm.$^{-1}$ for ^{10}B) is very near the corresponding value for phosphorus trifluoride–borane (607 cm.$^{-1}$ for ^{11}B),[13] an adduct which must be σ- plus π-bonded, since phosphorus trifluoride has negligible donor strength where only σ-bonding is possible. On the other hand, it has been found[14] that for a series of phosphite complexes ν(B–P) lies in the range 759—869 cm.$^{-1}$. Thus the significance of ν(B–P) in relation to the nature of the B–P bond is doubtful.

The wave numbers of the symmetrical and unsymmetrical boron–hydrogen stretching vibrations in triphenylphosphine–borane, identified by replacing the borane hydrogen atoms by deuterium, are, respectively, 2240 and 2400 cm.$^{-1}$; compare ν(B–H) in trimethylamine–borane[15] (2270, 2370 cm.$^{-1}$) and phosphorus trifluoride–borane[13] (2385, 2455 cm.$^{-1}$).

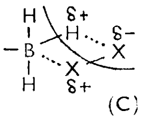
V. *Chemical Reactions.*—Triphenylphosphine–borane might enter into chemical reaction either as an intact molecule, or after dissociation to triphenylphosphine and borane, which would be the effective agents in reaction. The activation energy for dissociation cannot be much less than the enthalpy of dissociation, *viz.*, ~38 kcal. If the frequency factor for unimolecular dissociation were 10^{13} sec.$^{-1}$ (a likely order of magnitude) and the activation energy 38 kcal. mole^{-1}, it would require a temperature of 225° to bring the half-reaction time for dissociation down to one hour. Triphenylphosphine–borane was, in fact, quantitatively recovered after three hours at 150° with 3N-hydrochloric acid, showing negligible dissociation at this temperature. The reactions now to be discussed all took place far below 150°; they will therefore be treated as reactions of intact molecules of triphenylphosphine–borane.



(A)



(B)



(C)

Two reactions show that the borane hydrogen is electropositive. First, iodine monochloride in carbon tetrachloride at room temperature afforded triphenylphosphine–boron tri-iodide and hydrogen chloride, probably through the tri-iodide transition state (A). Secondly, triphenylphosphine–borane was recovered unchanged after long treatment with hydrogen chloride, bromide, or iodide in boiling toluene, but triphenylphosphine–trideuterioborane exchanged most of its deuterium for hydrogen when kept for 48 hours at room temperature with hydrogen chloride in benzene. A similar transition state with electropositive borane hydrogen breaking up as shown in (B), accounts for both observations. In contrast, the borane hydrogen atoms in the alkylamine–boranes react as if

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[13] Taylor and Bissot, *J. Chem. Phys.*, 1956, **25**, 780.
[14] Heitsch and Verkade, *Inorg. Chem.*, 1962, **1**, 863.
[15] Rice, Galiano, and Lehmann, *J. Phys. Chem.*, 1957, **61**, 1222.

they were electronegative, being replaced by chlorine in the reaction with iodine chloride, and affording molecular hydrogen with hydrogen halides.[3] These facts can be explained by the postulate that boron π-bonds to phosphorus in triphenylphosphine–borane but not to nitrogen in the alkylamine–boranes. Hydrogen is normally slightly electronegative with respect to boron (Pauling scale), and the withdrawal of electron density from the B–H bonds, which would be needed to free a boron orbital for the π-bond, would leave the hydrogen electropositive.

The conductivity of triphenylphosphine–borane in dimethylformamide solution showed negligible ionization, but its behaviour with sodium triphenylmethyl in ether gave evidence of some tendency to lose a proton; a poorly characterized, air-sensitive, buff powder with a composition approaching that of a monosodium salt was precipitated.

With three molar equivalents of chlorine or bromine in benzene solution at room temperature, triphenylphosphine–borane gave nearly quantitative yields of triphenylphosphine–borone trichloride and triphenylphosphine–boron tribromide, respectively. With less chlorine, the infrared spectrum gave no evidence for PPh_3–BH_2Cl or PPh_3–$BHCl_2$ but in the early stages of bromination there was infrared evidence for stable PPh_3–BH_2Br and PPh_3–$BHBr_2$. The monobromo-compound also resulted from the redistribution reaction:

$$Ph_3PBH_3 + BBr_3 \longrightarrow Ph_3PBH_2Br\ [+ BHBr_2]$$

but no such reaction took place with boron trichloride or trifluoride. Iodine in heptane replaced successive borane hydrogen atoms with increasing difficulty, the final stage requiring nine hours at 98°. These halogenations probably all go by way of a succession of four-centre transition states of the type (C). That the halogen might first attack and break the phosphorus–boron bond is not ruled out by the nature of the products, but seems less likely, since bromine did not react with triphenylphosphine–boron tribromide in one hour in benzene at room temperature.

In 12 hours with magnesium methoxide in refluxing methanol, triphenylphosphine–borane was 90% destroyed. The primary products were not determined, but on hydrolysis the reaction mixture gave triphenylphosphine and boric acid in good yield.

Triphenylphosphine–borane in dimethylformamide reduced mercury(II) acetate or chloride to the corresponding mercury(I) salts, which began to be precipitated almost at once at room temperature. The first step was probably a Lewis acid displacement:

$$HgX_2 + Ph_3PBH_3 \longrightarrow Ph_3PHgX_2 + BH_3$$

[likely because triphenylphosphine forms extremely stable complexes with mercury(II)], followed by a reduction,

$$BH_3 + 6HgX_2 \longrightarrow BX_3 + 3HX + 6HgX$$

The yield of mercury(I) approached that of the equation when mercury(II) was present in considerable excess.

PPh_3–${}^{10}BH_3$ exchanged boron with ordinary diborane to near equilibrium within a day at room temperature in benzene solution. If the rate-determining step here were the dissociation of either the complex or diborane, the reaction could not have been so fast; instead, it must have been bimolecular. The transition state may have been a complex of triphenylborane with the hydride B_3H_9; this hydride has not been isolated, but is thought to exist as an intermediate in the pyrolysis of diborane.[16]

In dimethylformamide at 100° triphenylphosphine–borane reduced copper(II) acetate or chloride to copper(I), and sulphur to hydrogen sulphide, but these reactions did not occur at room temperature. As control experiments showed that triphenylphosphine–borane also reacted with the solvent at a similar rate at 100°, those reductions may really

[16] Lipscomb, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 117; see also Brown, Stehle, and Tierney, *J. Amer. Chem. Soc.*, 1957, **79**, 2020.

have been effected by organic products, including formaldehyde, formed by the action of triphenylphosphine–borane on the solvent.

EXPERIMENTAL

Eastman Kodak triphenylphosphine was recrystallized from ethanol to constant m. p. 80°. Dr. B. C. Smith of Birbeck College kindly supplied diphenylphosphine. Monophenylphosphine of constant b. p. 160° was made by Michaelis's method.[17]

Preparation of the Complexes.—Diborane [18] was carried by nitrogen into a M-solution of triphenylphosphine in ether; triphenylphosphine–borane was precipitated and crystallized from a concentrated benzene solution on addition of spectroscopic grade hexane; it had m. p. 189°.

Direct reduction of triphenylphosphine–boron trichloride was found to be possible but less satisfactory. This compound (4·7 mmole) was suspended over a refluxing mixture of anhydrous ether (15 ml.) and lithium aluminium hydride (19 mmole, nominal; L. Light & Co.) in a semi-micro-Soxhlet apparatus. When the extraction thimble was empty (9 hr.), benzene was added and the mixture hydrolysed with 6M-hydrochloric acid. The benzene layer contained 2·3 mmoles of triphenylphosphine–borane. An attempt to make triphenylphosphine–trideuterioborane by the analogous method gave only a 6% yield, probably because the lithium aluminium deuteride (Metal Hydrides Inc.) was very pure and dissolved more readily in ether than did the hydride; it may, in consequence, have further reduced most of the complex first formed.

Deuteriodiborane, from boron trichloride, lithium aluminium deuteride, and ether,[19] was mixed with triphenylphosphine in ether *in vacuo*. The product, recrystallized in the same way as triphenylphosphine–borane, had m. p. 189° and mixed m. p. 189° with undeuterated material.

Calcium fluoride–boron trifluoride complex containing 96% of the boron as ^{10}B (Oak Ridge National Laboratory) was dried at 110° and the decomposed *in vacuo* at 250°. The resulting boron trifluoride was fractionated and treated [20] with lithium aluminium hydride in ether to give [^{10}B]diborane, which with triphenylphosphine as above, afforded triphenylphosphine–[^{10}B]borane, m. p. 189°.

Calorimetry.—Details of the apparatus and procedure will be published elsewhere.[21] AnalaR benzene was dried for at least a week over successive batches of sodium wire and was distilled from bright sodium just before use. In the calorimeter, benzene (35 ml.) was "scavenged" by feeding in diborane (~0·1 mmole) to react with any remaining impurities. An ampoule containing triphenylphosphine (~1 mmole) or other Lewis base was then crushed under the benzene. Diborane, prepared as above and fractionated *in vacuo* [22] to a purity >99% (infrared spectrum), was measured out from a mercury-operated gas-burette and injected through a needle-valve into the calorimeter in ~0·1-mmole portions, the temperature rise after each injection being plotted on a chart recorder. For all the systems examined, the heat evolved was a linear function of the amount of diborane added, showing that none of the adducts was appreciably dissociated.

Dipole Moments.—Benzene was dried as above and finally distilled from lithium aluminium hydride under nitrogen. At 25·0°, the dielectric constants (measured with a WTW Dipolmeter, type DM01) and refractive indices (BK refractometer) of benzene solutions of triphenylphosphine–borane were:

Wt. fraction	0·00326	0·00668	0·00939	0·01231
Dielectric constant	2·308	2·343	2·370	2·403
Refractive index	1·49861	1·49896	1·49937	1·49960
Dipole moment	4·79	4·78	4·72	4·86

The dipole moment values were calculated by Guggenheim's method.[23]

The Dipolmeter was calibrated with pure benzene (ε_{25} 2·274) and pure carbon disulphide (ε_{25} 2·625).

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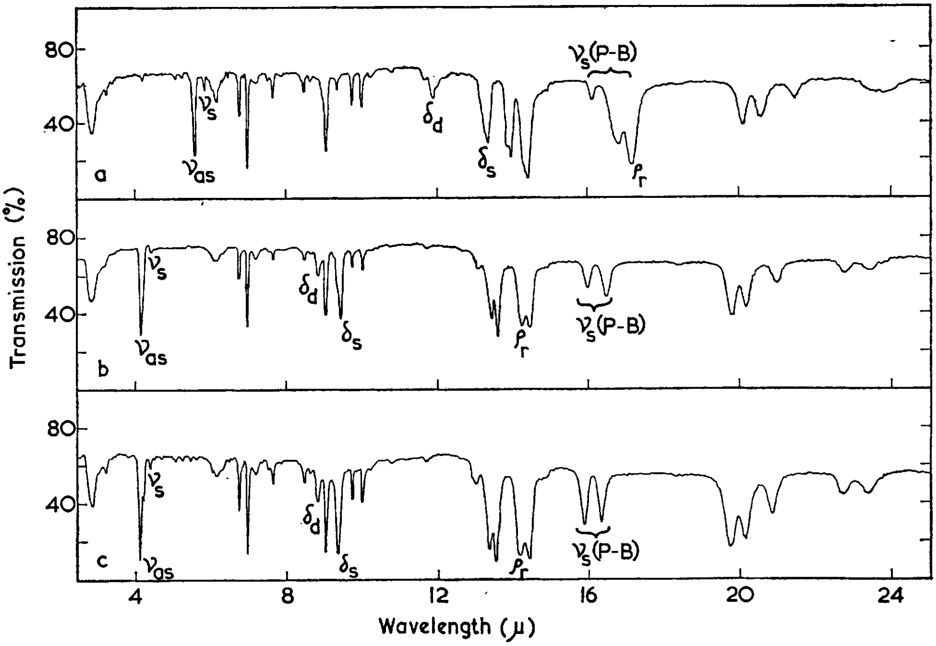
[17] Michaelis, *Annalen*, 1876, **181**, 343.
[18] Weiss and Shapiro, *J. Amer. Chem. Soc.*, 1959, **81**, 6167.
[19] Finholt, Bond, and Schlesinger, *J. Amer. Chem. Soc.*, 1947, **69**, 1199.
[20] Shapiro, Weiss, Smich, Skolnik, and Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 901.
[21] Frisch and Mackle, unpublished work.
[22] McCarty, Smith, and McDonald, *Analyt. Chem.*, 1954, **26**, 1027.
[23] Guggenheim, *Nature*, 1936, **137**, 459.

Proton Magnetic Resonance Spectra.—The proton magnetic resonance spectra of triphenylphosphine and triphenylphosphine–borane (both 0·4M in deuteriochloroform) were plotted at the University of Glasgow, with the kind co-operation of Dr. A. L. Porte, by using an Associated Electrical Industries R2 spectrometer, which was operated at 60 mc. sec.$^{-1}$ and 14,200 gauss. The spectrum was scanned from -15 to $+15$ p.p.m. from the tetramethylsilane resonance.

Infrared Spectra.—The infrared spectra were plotted with Perkin-Elmer Infracord machines covering the range 2·5—15 and 12·5—25 μ. The spectra of triphenylphosphine–borane and its isotopic substitution products, in potassium bromide discs, are shown in the Figure, with vibrational assignments expressed in the symbols used by Nakamoto.[24] The 25—40 μ region was scanned with another instrument; it contained no bands. The borane hydrogen vibrations were easily assigned on the basis of isotopic shifts. The P–B stretch gave more difficulty. Only the doublet at 15·95 and 16·45 μ in the spectrum of triphenylphosphine–borane showed any marked change in the relative intensities of its components when 96% ^{10}B replaced ordinary boron (19% ^{10}B). The ratio of wave numbers of the components (1·035) is not far from the square root of the ratio of masses of the $^{10}BH_3$ and $^{11}BH_3$ groups (1·038). If, however, this doublet be assigned to the symmetrical P–B stretch, it remains to be explained why the component of longer wavelength is still strong in the PPh_3–$^{10}BH_3$ spectrum, and why the replacement of borane hydrogen by deuterium, leaving as it does a small band near 16·1 μ does not instead completely remove both components to considerably longer wavelengths. The only explanation that occurs to us is that the P–B symmetrical stretch bands are in this region, but that they nearly coincide with another pair of bands of unknown origin, the positions of which are slightly affected by isotopic substitution. We can see no reasonable alternative assignment for the P–B stretching frequency.



Infrared spectra of (a) PPh_3–BD_3 (0·8 mg. in 330 mg. of KBr), (b) PPh_3–BH_3 (0·5 mg. in 300 mg. of KBr), and (c) PPh_3–$^{10}BH_3$ (0·8 mg. in 300 mg. of KBr). Assigned frequencies are for BH_3 except that marked ν_s (P–B).

Conductivity at 20°.—Dimethylformamide, purified by distillation from barium oxide,[25]

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[24] Nakamoto, " Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York and London, 1963, p. 145.

[25] Thomas and Rochow, *J. Amer. Chem. Soc.*, 1957, **79**, 1843.

had a specific conductivity of $1{\cdot}4 \times 10^{-6}$ ohm-cm.$^{-1}$ (Mullard E7566 bridge). A 0·03M-solution of triphenylphosphine–borane in the same dimethylformamide also had conductivity $1{\cdot}4 \times 10^{-6}$ ohm-cm.$^{-1}$.

Reaction with Triphenylmethylsodium.—An ether solution of triphenylmethylsodium was standarized.[26] Under nitrogen, 2 mmoles were slowly siphoned into a stirred solution of triphenylphosphine–borane (2 mmoles) in ether (100 ml.; dried over several batches of sodium). The triphenylmethylsodium was decolourized at once, and a flocculent brown precipitate appeared. The solution was expelled through a filter-stick under nitrogen. The precipitate quickly became sticky in air, and the batches gave variable analyses (For the best, found: C, 75·0; H, 6·6; B, 2·8; Na, 5·6. Calc. for $C_{18}H_{17}BNaP$: C, 72·5; H, 5·7; B, 3·7; Na, 7·7%.)

Methanolysis.—Triphenylphosphine–borane (0·47 mmole) was refluxed for 12 hr. under nitrogen with magnesium ribbon (1·67 mmoles) dissolved in methanol (6 ml.). Shaking with carbon tetrachloride and 6M-hydrochloric acid gave an organic layer containing triphenylphosphine (0·32 mmole; identified by infrared and elemental analysis), triphenylphosphine–borane (0·02 mmole; infrared) and a water layer containing boric acid (0·41 mmole).

Chlorination.—(1) In a typical experiment, triphenylphosphine–borane (1·73 mmoles) was stirred with spectroscopic-grade carbon tetrachloride (10 ml.) under nitrogen. Chlorine (5·2 mmoles) in carbon tetrachloride (20 ml.) was added from an all-glass dropper in 35 min., and the mixture was stirred for 30 min.; the volatile materials were then driven from the mixture into water by means of a stream of nitrogen. The water layer contained 4·90 mmoles of H^+ (acidimetric), 4·90 mmoles of Cl^- (gravimetric as silver chloride), and no boric acid. Three runs gave, respectively, per mole of triphenylphosphine–borane, 2·84, 3·06, and 2·75 moles of hydrochloric acid. The white crystals left on evaporation of the carbon tetrachloride gave the same infrared spectrum as authentic triphenylphosphine–boron trichloride, and the same hydrolysis products. (Hydrolysed by refluxing in air with carbon tetrachloride and water: found, per mole of presumed triphenylphosphine–boron trichloride, 3·00, 3·00, 3·03 moles of hydrochloric acid, and 0·94, 1·03, 1·01 mole of boric acid; 0·98, 1·00, 0·91 mole of triphenylphosphine oxide, m. p. 153°.)

(2) Chlorine diluted with nitrogen was passed at 0·046 mmole min.$^{-1}$ into triphenylphosphine–borane (0·7 mmole) in anhydrous benzene (10 ml.). The infrared B–H stretching band at 4·18 μ diminished progressively, and no new bands appeared near it. After 2·1 mmoles of chlorine had been admitted, the infrared spectrum of the solution was that of triphenylphosphine–boron trichloride, with the addition of a band at 4·18 μ (undecomposed triphenylphosphine–borane, about 20% of the original amount) and another at 3·65 μ (dissolved hydrogen chloride).

Bromination.—(1) The reaction with 3 mol. of bromine in carbon disulphide at −40° to give triphenylphosphine–boron tribromide has been reported.[6]

(2) Measured weights of a standard, fresh solution of bromine in benzene were added dropwise to a stirred solution of (1·13 mmoles) triphenylphosphine–borane in anhydrous benzene (10 ml.) under nitrogen. 1·13 mmoles of bromine replaced the B–H peak at 4·18 μ by new peaks at 4·05 (hydrogen bromide) and 4·14 μ, and eliminated the B–P stretching bands at 15·9 and 16·5 μ. 2·26 mmoles introduced new bands in the B–P stretching region at 16·9 and 18·4 μ. 3·39 mmoles gave the same spectrum as authentic triphenylphosphine–boron tribromide, with one strong band in this region at 15·9 μ. The residue left on evaporation of the benzene was recrystallized from acetone by addition of cold water.* This gave 0·93 mmole of triphenylphosphine–boron tribromide (identified by quantitative hydrolysis in refluxing water–benzene). In another similar experiment, the triphenylphosphine–boron tribromide was satisfactorily purified by precipitation with hexane from benzene solution.

In the brominations in benzene, the first molar equivalent of bromine reacted at once; the remainder required a few minutes for reaction.

Iodination.—(1) In a typical experiment, powdered triphenylphosphine–borane (3·1 mmoles) was refluxed with dry n-heptane (15 ml.), while iodine (9·4 mmoles) in the same solvent were gradually added. After 9 hr. 9·4 mmoles of hydrogen iodide (swept out by nitrogen,

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* Analysis of the aqueous solution showed that only 0·04 mmole (about 4%) of the triphenylphosphine–boron tribromide had been hydrolysed in this operation.

[26] Renfrew and Hauser, *Org. Synth.*, Coll. Vol. II, 1943, p. 607.

absorbed in water, and determined acidimetrically and gravimetrically as silver iodide) had been evolved, and gas evolution was complete. The heptane was distilled away. The brown gum that was left gave on recrystallization from ethyl acetate 2·5 mmoles of ivory-coloured triphenylphosphine–boron tri-iodide, m. p. 220°, identified by comparing its infrared spectrum and the quantities of its hydrolysis products with those of an authentic sample.

(2) 1 mol. of iodine under similar conditions reacted quickly. In the infrared spectrum of the white solid product (not analysed) peaks at 4·03 and 4·13 μ replaced the 4·17 μ B–H stretching band of triphenylphosphine–borane.

2 mol. of iodine similarly gave a product with one B–H stretching band at 4·00 μ, probably triphenylphosphine–di-iodoborane (Found: C, 41·9; H, 3·4; B, 2·1; I, 52·4; P, 6·3. Calc. for $C_{18}H_{16}BI_2P$: C, 41·0; H, 3·0; B, 2·1; I, 48·3; P, 5·9%).

Reaction with Iodine Chlorine.—Under nitrogen, iodine monochloride (3·47 moles) in spectroscopic-grade carbon tetrachloride (20 ml.) was added in 1 hr. to a stirred suspension of triphenylphosphine–borane (1·15 mmoles) in the same solvent (5 ml.). The volatile products, swept out by nitrogen and collected in water, gave 3·02 mmole of H^+ (acidimetric) and 3·02 mmoles of Cl^- (gravimetric as silver salt). On recrystallization from ethyl acetate, the brown gum left in the reaction vessel gave 2·70 mmoles of triphenylphosphine–boron tri-iodide (identified by its infrared spectrum; hydrolysed to 0·90 mmole of triphenylphosphine oxide, 0·91 mmole of boric acid, and 2·70 mmoles of hydrogen iodide). A second experiment again gave silver chloride from the aqueous solution of the volatiles, and silver iodide from the hydrolysate of involatiles.

Redistribution Reaction with Triphenylphosphine–Boron Tribromide.—Triphenylphosphine–borane (3·6 mmoles) were kept for 6 hr. at 0° with boron tribromide (3·6 mmoles) *in vacuo*. The volatile materials were distilled off and, on hydrolysis, gave 3·4 mmoles of boric acid and 7·5 mmoles of Br^-. The infrared spectrum of the residue had twin B–H peaks at 4·06 and 4·16 μ, thus resembling the product from triphenylphosphine–borane and one mol. of bromine.

Triphenylphosphine–borane did not react with boron trichloride or boron trifluoride under similar conditions.

Reaction with Hydrogen Halides.—Hydrogen chloride (79 mmoles) were carried in a stream of dry nitrogen through a refluxing solution of triphenylphosphine–borane (1·57 mmoles) in toluene (15 ml.) in 6 hr. Evaporation under nitrogen then left triphenylphosphine–borane (1·56 mmoles), identified by its infrared spectrum and m. p. (188°).

After similar treatment of triphenylphosphine–borane (1·98 mmoles) with hydrogen bromide (100 mmoles) free from bromine (made by dropping concentrated bromine-free hydrobromic acid into phosphoric acid and phosphorus oxide), 1·96 mmoles were recovered. 1·54 mmoles of an original 1·60 mmoles of triphenylphosphine–borane were recovered after similar treatment with 80 mmoles of hydrogen iodide similarly generated.

Isotopic Exchange with Hydrogen Chloride.—Triphenylphosphine–trideuterioborane (0·077 mmole) in dry benzene (3 ml.) was saturated with dry hydrogen chloride. The solution was then evaporated under nitrogen; practically unchanged complex was left (infrared). Benzene (3 ml.) was added, and the flask again filled with hydrogen chloride, stoppered, and left for 48 hr. Evaporation as before then gave a residue with a conspicuous B–H peak at 4·18 μ, about 57% as intense as the same amount of triphenylphosphine–borane would have given. At equilibrium, about 67% of the deuterium would be replaced by hydrogen.

Isotopic Exchange with Diborane.—$PPh_3{}^{10}BH_3$ (0·405 mmole), benzene (2 ml.), and ordinary diborane (0·203 mmole) were enclosed in an evacuated 10-ml. bulb. After 24 hr. at 20° the volatile materials were pumped off. The residue had a broad infrared peak in the P–B stretching region, with a flat top extending from 16·31 to 16·44 μ. The labelled complex had a sharp peak at 16·31 μ, and that with ordinary boron a sharp peak at 16·44 μ. There was no doubt that exchange had occurred, but with the spectral resolution available its extent could only be crudely estimated. The shape of the P–B stretching band was consistent with complete equilibration.

Reaction with Mercury(II).—Triphenylphosphine–borane and mercury(II) chloride in anhydrous dimethylformamide [24] at 20° immediately began to precipitate mercury(I) chloride (Found: Hg, 84·0; Cl, 14·7. Calc. for Hg_2Cl_2: Hg, 85·0; Cl, 15·0%). Triphenylphosphine–borane (0·8 mmole) in dimethylformamide (5 ml.) gave with the stated amounts (per mole of complex) of mercury(II) chloride, the following amounts of mercury(I) chloride:

$HgCl_2$ added (mol.)	3·0	4·0	7·0	10·0	16·1	30·0	50·0
HgCl precipitated (mol.)	1·35	1·82	3·42	4·76	5·00	5·60	5·86

The precipitate* was grey in the first two experiments of the series, indicating some reduction to mercury.

Triphenylphosphine–borane and anhydrous mercury(II) acetate (1·155 mmoles) in dimethylformamide (3 ml.) precipitated crystalline mercury(I) acetate (0·887 mmole) (Found: C, 9·3; H, 1·2; Hg, 77·9. Calc. for $C_2H_3HgO_2$: C, 9·3; H, 1·2; Hg, 77·2%). Precipitation seemed complete after an hour but, when the filtrate was diluted with water, a precipitate containing 4% of the original amount of complex was formed, as shown by infrared analysis.

Reaction with Dimethylformamide.—Starting in each case with ~0·3 mmole of triphenylphosphine–borane in pure [24] dimethylformamide (5 ml.), there was no decomposition of the triphenylphosphine–borane in 1½ hr. at 20°, 5·2% in the same time at 50°, and 72·9% in the same time at 100°. The undecomposed triphenylphosphine–borane was precipitated with water and determined in benzene solution by infrared analysis (4·18 μ band).

Reaction with Sulphur.—In four runs triphenylphosphine–borane (0·4—0·8 mmole) and rhombic sulphur (8 mg.-atoms per mmole of triphenylphosphine–borane) were kept at 100° in pure dimethylformamide (5 ml.). The hydrogen sulphide evolved was carried by a slow stream of nitrogen into standard iodine solution. No more was formed after 3 hr. Per mole of complex, the yields of hydrogen sulphide were 1·72, 1·65, 1·77, 1·73 mmoles.

Reaction with Copper(II).—Copper(II) was estimated iodometrically or spectrophotometrically. At 100°, dimethylformamide alone slowly reduced copper(II) chloride, 0·655 mmole in 5 ml. leaving 0·575 mmole after 1 hr. With this corrected for, triphenylphosphine–borane at a concentration of 0·3 mmole per 5 ml. reduced in 1 hr. at 100° 3·7 equiv. of copper(II) of 6·9 added, and 4·3 of 10·5 added.

Copper(II) acetate was not reduced by dimethylformamide at 100°. In the same conditions as for the chloride, triphenylphosphine–borane reduced 2·5 of 5·6 equiv. added, 3·4 of 8·4 added, and 2·8 of 10·3 added.

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* Mercury(I) chloride was found to have negligible solubility (<0·25 mg./per ml.) in dimethylformamide at 20°.