Competition between Different Nucleophilic Sites belonging to the Same Lewis Bases. Part I. Aminophosphines towards Borane

By **Claude Jouany** and **Jean-Pierre Laurent**, Laboratoire de Chimie de Coordination, Associé n° 160 au C.N.R.S., 38 rue des Trente-Six Ponts, 31400 Toulouse, France
Gérard Jugie,* Queen Elizabeth College, Department of Chemistry, Campden Hill, London W8 7AH

The nature of the donor–acceptor interactions in aminophosphine–borane adducts has been investigated by means of the chemical behaviour of the borane group and ^1H, ^{11}B, and ^{31}P n.m.r. spectra. The phosphorus atom appears to be a better acceptor than nitrogen towards BH_3 when these two donor atoms are linked together, such as in Me_2NPMe_2 and $(Me_2N)_2PMe$. However, when these two atoms are separated by a methylene bridge, as in $(Et_2NCH_2)_3P$, borane co-ordinates with nitrogen rather than with phosphorus. The results are explicable in terms of multiple bond behaviours and steric hindrance.

CONSIDERABLE use has been made of borane Lewis acid power to determine the basicities of Group V donors.[1] A number of studies have demonstrated that phosphorus in R_3P is a stronger base than nitrogen in R_3N, when BH_3 is used as a reference acceptor molecule. Displacement reactions, kinetic observations, and n.m.r. data [2-4] give evidence for this.

More recently this problem has been approached by studying the behaviour of the two potential donors when they are both set in the same molecules. As typical examples, we quote the work of Reetz [5] who gives evidence of the donor capacity of the phosphorus atom in tris(dialkylamino)phosphine–borane, various papers of Holmes [6] and Parry [7] concerned with different classes of phosphine such as $(R_2N)_xPF_{3-x}$ and their borane adducts, and recent work from this laboratory [8] centred on the study of halogenoborane adducts of aminophosphines (here however, the choice of bonding site of the Lewis acid is determined by the initial phosphorus–borane complex).

In all the above mentioned examples, the greater basicity of phosphorus is explicable in terms of the double bond character of the P–N bond. In order to exclude the possibility of double bonding, Miller *et al.*[9] used donor molecules where P and N atoms were separated by a methylene group; their n.m.r. results suggest that co-ordination of BH_3 is more favourable on the phosphorus site in $Me_2NCH_2PMe_2$.

In the present paper, we report our work on three new typical adducts of BH_3 with Me_2NPMe_2 (L_2); $(Me_2N)_2PMe$ (L_3); and $(Et_2NCH_2)_3P$ (L_4), where the index n in L_n may be thought of as the number of the potential donor sites in the free ligand.

RESULTS

(a) *Reactions of Free Bases* (L_2, L_3, *and* L_4) *with Triethylamine–Borane*.—When a great excess (4 : 1 mole ratio) of $Et_3N\rightarrow BH_3$ is mixed with L_2, L_3, or L_4 and slowly warmed, a strong evolution of triethylamine is observed, in good agreement with the following reaction:

$$4Et_3N\rightarrow BH_3 + L_n \longrightarrow [L_n(4-x)BH_3] + (4-x)Et_3N + xEt_3N\rightarrow BH_3$$

Immediately, a marked difference is seen here between L_2 and L_3 on one hand and L_4 on the other: while with L_2 and L_3 evolution of triethylamine occurs in slightly lower than equimolecular amount, with L_4 more than two equimolecular quantities are evolved. This suggests that, unlike L_2 and L_3, L_4 possesses more than one base site that could be used by borane fragments.

(b) *Reactions of* L_2, L_3, *and* L_4 *with* B_2H_6.—Direct introduction or *in situ* generation of diborane in L_2, L_3, or L_4 solutions gives rise to adduct formation according to the scheme:

$$L_n + z(\tfrac{1}{2}B_2H_6) \longrightarrow [L_n,xBH_3] + (z-x)(\tfrac{1}{2}B_2H_6)$$

Nevertheless, while L_2 and L_3 consume only one equimolecular amount of BH_3, L_4 consumes more than two amounts of BH_3. This observation provides an additional chemical argument to the multidonor site hypothesis for L_4.

(c) *Chemical Characteristics of the* L_2, L_3, *and* L_4 *Borane Adducts*.—The adducts so obtained $[L_n,xBH_3]$ may be isolated by standard procedures, such as distillation for $[L_2,xBH_3]$ and $[L_3,yBH_3]$ and fractional crystallization for $[L_4,zBH_3]$. In all cases, we obtained clearly defined compounds whose physical properties are given in Table 1.

The results of the analytical data clearly establish the nature of the compounds obtained with diborane: one BH_3 entity for each Me_2NPMe_2 or $(Me_2N)_2PMe$ and three BH_3 entities for each $(Et_2NCH_2)_3P$. However, it is still not possible from the analyses alone to determine the exact nature of the dative bonds: are they $N\rightarrow B$ or $P\rightarrow B$, or both at one and the same time? The studies of the n.m.r. spectra gave us new insight into this problem.

Nuclear Magnetic Resonance Results.—^{11}B, ^{31}P, and ^1H N.m.r. data for the free ligands and their borane adducts are summarized in Tables 2 and 3.

Me_2NPMe_2 *and* $(Me_2N)_2PMe$ *Adducts*. Strong evidence for a boron–phosphorus dative bond in these two adducts is provided by the ^{11}B, ^{31}P, and ^1H resonances. Typical

---

[1] *Cf.* T. D. Coyle and F. G. A. Stone, *Progr. Boron Chem.*, 1964, **1**, 83.

[2] W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nuclear Chem.*, 1956, **3**, 164; R. A. Baldwin and R. M. Washburn, *J. Org. Chem.*, 1961, **26**, 3549.

[3] D. E. Young, G. E. McAchran, and S. G. Shore, *J. Amer. Chem. Soc.*, 1966, **88**, 4390; S. A. Fridmann and T. P. Fehlner, *J. Phys. Chem.*, 1971, **75**, 2711.

[4] E. F. Mooney and B. S. Thornhill, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2225; D. S. Payne, *Chem. Comm.*, 1965, 327; L. K. Peterson and G. L. Wilson, *Canad. J. Chem.*, 1971, **49**, 3171.

[5] T. Reetz and B. Katlafsky, *J. Amer. Chem. Soc.*, 1960, **82**, 5036; T. Reetz, *ibid.*, p. 5039.

[6] R. R. Holmes and R. P. Carter, *Inorg. Chem.*, 1963, **2**, 1146.

[7] R. W. Parry, E. R. Alton, and S. S. Fleming, Colloque International n°191 du C.N.R.S., Paris, 141, 1970; S. Fleming and R. W. Parry, *Inorg. Chem.*, 1972, **11**, 1.

[8] G. Jugie, J. P. Laussac, and J. P. Laurent, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3455.

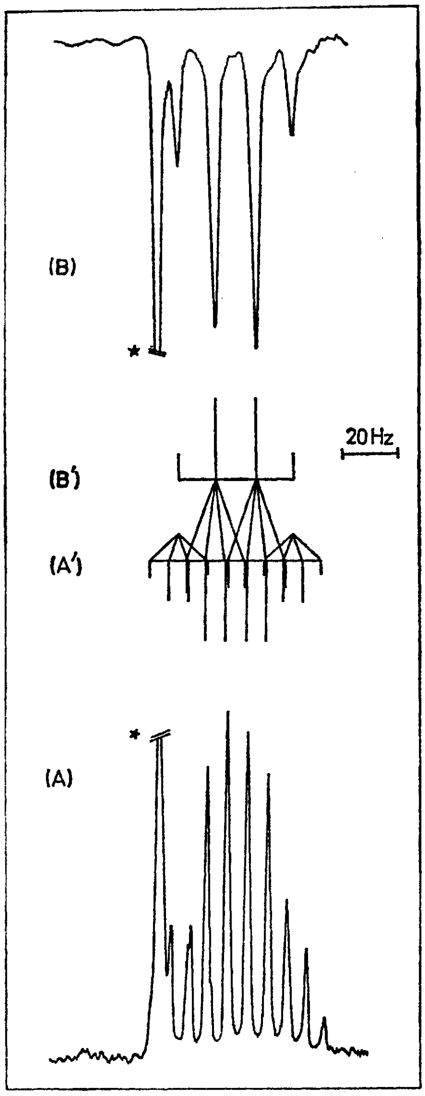
[9] K. Lunberg, R. J. Rowatt, and N. E. Miller, *Inorg. Chem.*, 1969, **8**, 1336.

TABLE 1

Physical and analytical data for the phosphine–borane adducts

Compounds	B.p (t/°C) [mmHg]	n_D^{20}	d_4^{20}	%C		%H		%N		%B		%P	
				Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
[L_2,BH_3]	92 [15]	1·466	0·834	40·39	40·15	12·71	12·8	11·77	11·6	9·09	9·4	26·04	26·1
[L_3,BH_3]	62 [1]	1·474	0·881	40·56	40·15	12·26	12·55	18·93	19·15	7·31	8·05	20·94	20·35
[L_4,$3BH_3$]	Solid			54·43	54·35	13·70	13·75	12·69	12·65	9·79	8·25	9·35	9·4

characteristics of these spectra are as follows: (a) the ^{21}P signal consists of a 1 : 1 : 1 : 1 quartet, the ^{31}P resonance being split by the ^{11}B nucleus ($I = 3/2$); (b) the boron-11 spectra show a 1 : 3 : 3 : 1 quartet typical of BH_3, each member of the quartet being further split into a doublet by the ^{31}P; these patterns are displaced upfield by *ca.* 40 p.p.m. from external $Et_2O \rightarrow BF_3$ as reference, into a region characteristic of $P \rightarrow BH_3$ compounds;[10] and (c) the ^1H spectra have a very similar pattern to the parent phosphines, but displaced downfield, all exhibiting a 1 : 1 : 1 : 1 quartet [^1J(BH)] each of whose members is further split into a doublet [^2J(PBH)].



100 MHz Resonance proton spectra of methylene nuclei in [$(CH_3\text{-}CH_2)_2N\text{-}CH_2]_3P,3BH_3$: (A), single resonance spectrum; (B), homonuclear double resonance spectrum, the CH_3 transitions being irradiated; (A') and (B') are the corresponding calculated line positions using text parameters; * represents P-CH_2- resonance

TABLE 2

^{31}P and ^{11}B N.m.r. data for the borane adduct

Compounds	Chemical shift, p.p.m.* $\delta^{31}P$	$\delta^{31}P$ (Free ligand)	$\Delta\delta^{31}P$	$\delta^{11}B$	Coupling constants/Hz ^1J(BH)	^1J(BP)
Me_2NPMe_2,BH_3	−51	−73	+22	−37	96	74
$(Me_2N)_2PMe,BH_3$	−20	−26	+6	−40	96	88
$(Et_2NCH_2)_3P,3BH_3$	−173	−181	+8	−12	92	
$(Et_2NCH_2)_3P,4BH_3$	−105	−181	+76	−12 −38	n.r.	n.r.

* Chemical shift values are reported in p.p.m. from the following standards: ^{31}P P_4O_6 (external) and ^{11}B $Et_2O \rightarrow BF_3$ (external); high field shifts are shown as negative values.

These data provide unequivocal arguments for the structures:

$$\underset{BH_3}{\overset{Me_2NPMe_2}{\downarrow}} \quad \text{and} \quad \underset{BH_3}{\overset{(Me_2N)_2PMe}{\downarrow}}$$

$(Et_2NCH_2)_3P,3BH_3$. In contrast, the n.m.r. spectra of this adduct exhibit no evidence of boron–phosphorus linkage: (a) the ^{11}B spectrum shows a poorly resolved quartet (1 : 3 : 3 : 1) displaced upfield 12·5 p.p.m. from $Et_2O \rightarrow BF_3$, *i.e.* situated in a region typical of $N \rightarrow BH_3$ compounds (*cf.* $Et_3N \rightarrow BH_3$, $\delta = -13$ p.p.m.[11]); moreover, no splitting of the ^{11}B signal by ^{31}P is observed; (b) the ^{31}P resonance provides further evidence for a $N \rightarrow B$ bond; not only does the ^{31}P signal show no splitting by boron, but also it is not broadened with respect to the free ligand; and (c) further evidence of nitrogen–boron bonding can be observed in proton resonance; in particular, we notice first a great enhancement of the internal shift of the ethyl group (N–CH_2–CH_3), which is $\Delta_{int} = 1{\cdot}82$ p.p.m. in [L_4,$3BH_3$] compared with a value of 1·60 p.p.m. in the parent phosphine. Secondly, while the free ligand CH_3–CH_2–N resonance consists of a trivial quartet (1 : 3 : 3 : 1) corresponding to a X_3A_2 spin system, the adduct resonance basically consists of a ten resonance spectrum whose relative intensities are not in simple ratios. Only an assignment based upon an X_3AB analysis leads to a good fit (*cf.* Figure): this present method of resolving the CH_3–CH_2–N spectra indicates a magnetic non-equivalence in the geminal protons of the methylene groups.[12] Varying temperature

---

[10] J. G. Verkade, R. W. King, and C. W. Heitsch, *Inorg. Chem.*, 1964, **3**, 884; G. Jugie and J. P. Laurent, *Bull. Soc. chim. France*, 1970, 838.

[11] J. N. G. Faulks, N. N. Greenwood, and J. H. Morris, *J. Inorg. Nuclear Chem.*, 1967, **29**, 329.

[12] R. Marty, D. Houalla, and R. Wolf, *Org. Magnetic Resonance*, 1970, **2**, 141.

and concentration has a negligible effect on the ^1H n.m.r. spectra and gives no additional information.

The above-mentioned arguments provide us with unequivocal evidence for the structure  $\underset{\substack{\downarrow \\ BH_3}}{(Et_2NCH_2)_3P}$, in which the three BH_3 groups are linked to the phosphine through its nitrogen atoms. [The i.r. spectra of these compounds have been recorded and carefully studied in the region 2000—2500 cm^{-1} in order to observe the characteristic ν(B–H) frequencies. However the shift in frequency between the $N{\rightarrow}BH_3$ and $P{\rightarrow}BH_3$ compounds[13] is not large enough to provide a clear indication of the binding sites.]

TABLE 3

^1H N.m.r. spectra[a]

Compounds	Solvents	P–CH_3 or P–CH_2– δ_{PCH}	^2J(PCH)	P–N–CH_3 or P–CH_2–N–CH_2–CH_3 δ_{NCH}	^3J(PNCH)	δ_{NCCH}	^3J(HCCH)	Δ_{int}
Me_2NPMe_2 (L_2)	Neat liquid	0·99	5·5	2·50	10·0			
Me_2NPMe_2,BH_3 [L_2,BH_3]	CCl_4, 10%	1·32	8·9	2·64	10·2			
[$Me_2N)_2PMe$ (L_3)	Neat liquid	1·14	7·0	2·64	8·9			
$(Me_2N)_2PMe,BH_3$ [L_3,BH_3]	CCl_4, 10%	1·41	9·5	2·64	8·9			
$(Et_2NCH_2)_3P$ (L_4)	CH_2Cl_2, 10%	2·68	2·8	2·60		1·00	7·1	1·60
$(Et_2NCH_2)_3P$ (L_4)	C_6H_6, 10%	2·73	2·8	2·64		1·03	7·1	1·61
$(Et_2NCH_2)_3P,3BH_3$ [$L_4,3BH_3$]	CH_2Cl_2, 10%	3·33	~0	2·99[b]		1·17	7·5	1·82
$(Et_2NCH_2)_3P,3BH_3$ [$L_4,3BH_3$]	C_6H_6, 10%	3·16	~0	2·93[b]		0·94	7·5	1·99

[a] Signals downfield from tetramethylsilane are reported as positive. Chemical shifts and coupling constants are respectively reported in p.p.m. and Hz. [b] This CH_2 resonance must be analysed as an AB system with the following parameters: $^2J(H_AH_B)$ 13·5 Hz, Δν(AB) 25·5 Hz (r.f. frequency: 100 MHz).

DISCUSSION

From the chemical and n.m.r. data cited above, two different kinds of behaviour can be observed: under normal conditions of borane generation, while L_2 and L_3 react with the borane entity through their phosphorus atom, L_4 reacts through its nitrogen atoms. Therefore, one would estimate that the order of basicity for these three ligands is:

(a) P > N in Me_2NPMe_2 (L_2)
and $(Me_2N)_2PMe$ (L_3)
and (b) N > P in $(Et_2NCH_2)_3P$ (L_4)

Observation (a) seems in good agreement with the well known hypothesis of P—N bond multiplicity[14] in compounds where trivalent phosphorus and trivalent nitrogen are linked together; the back-co-ordination of the nitrogen lone pair onto phosphorus would imply an enhancement of the phosphorus basic strength, while that of nitrogen suffers a reduction.

Since L_4 should be taken as a true phosphine (the phosphorus and nitrogen atoms being separated by a methylene bridge) the order (b) is in marked contrast to the usual behaviour[2] of amines and phosphines towards BH_3. This is all the more surprising, as the work of Ludberg *et al.*[9] has already demonstrated that in $Me_2NCH_2PMe_2$ the most favourable co-ordinating site is the phosphorus atom.

Consequently we tried to demonstrate the basicity of nitrogen in L_2 and L_3 or phosphorus in L_4. With this objective, we have varied the experimental conditions, although in any one of these cases, there is no difference arising from experimental factors in as much as the two dative sites belong to the same molecule. Using a great excess of borane (either gaseous B_2H_6 or co-ordinated BH_3 in $Et_3N{\rightarrow}BH_3$) with the pure ligand or solutions thereof, we obtained the following results. First, with Me_2NPMe_2 and $(Me_2N)_2PMe$, no change is noticed. ^{31}P, ^{11}B, and ^1H Magnetic spectra do not indicate $N{\rightarrow}B$ dative bond adducts; secondly, with $(Et_2NCH_2)_3P$, we characterized new bonding possibilities. Analysis of the n.m.r. spectra of samples of the reaction mixture showed the development of resonances which could be assigned to $P{\rightarrow}B$ dative bond formation. On the one hand, for instance, the ^{31}P spectra exhibited a broad resonance signal displaced downfield by *ca.* 75 p.p.m. from the resonance of the free ligand; we must compare the $\Delta\delta^{31}P$ * here observed with that characteristic of $Me_3P{\rightarrow}BH_3$ ($\Delta\delta^{31}P \simeq 55$ p.p.m.[10]). On the other hand, in the ^{11}B spectra we observed a new resonance pattern displaced *ca.* 38 p.p.m. upfield from the $Et_2O{\rightarrow}BF_3$ reference. This new resonance lies in the $\geqslant P{\rightarrow}BH_3$ area (*cf.* for instance, $\delta^{11}B = -38$ p.p.m. in $Me_3P{\rightarrow}BH_3$[10]); thirdly, by direct comparisons of the ^{31}P and ^{11}B signal intensities, we can assert that, if in the most favourable cases a certain ratio of [$L_4,4BH_3$] appears ($\simeq$60%), a quantity of [$L_4,3BH_3$] (the three borane fragments belonging to the three basic nitrogen sites) always coexists with the totally substituted adducts. Even important variations of experimental conditions did not allow us to obtain higher proportions.

Furthermore, the great stability of the $P{\rightarrow}B$ dative bond, once formed, must be remarked upon. For example, the ^{11}B and ^{31}P spectra of samples held at room temperature for several days did not show any change in the proportions of [$L_4,4BH_3$] and [$L_4,3BH_3$]. Moreover, when we add some free ligand (L_4) to the [$L_4,4BH_3$] and

---

* $\Delta\delta^{31}P = \delta^{31}P$(adduct) − $\delta^{31}P$ (free ligand).

[13] G. Jugie, R. Wolf, and J. P. Laurent, *Compt. rend.*, 1968, **266B**, 168.

[14] A. B. Burg and P. J. Slota, *J. Amer. Chem. Soc.*, 1958, **80**, 1107.

$[L_4,3BH_3]$ mixture, the ^{31}P experiments show that the intensity of the $P\rightarrow BH_3$ pattern remains unchanged; at the same time, we noticed that the ^{31}P signal of the non-BH_3 bonded phosphorus in $(Et_2NCH_2)\underset{\underset{BH_3}{\downarrow}}{P}$ moved towards the free ligand position, suggesting a redistribution of BH_3 fragments onto the newly introduced nitrogen sites.

If our first results seemed to question the usual basicity order of phosphorus and nitrogen atoms towards BH_3 in $(Et_2NCH_2)_3P$, our later observations have supported this order. Indeed they show that although it is not impossible to link the phosphorus of L_4 to borane fragments, once this dative bond is formed, it exhibits a stability of the same order as $N\rightarrow B$. Nevertheless, the particular order of basicity in L_4 may be partially rationalized by steric considerations; it appears that $[L_4,4BH_3]$ has such a configuration that the four BH_3 groups (one on the phosphorus atom and one on each of the three nitrogen atoms) are much too close together, making such an adduct hardly plausible under normal circumstances. On the other hand, in $[L_4,3BH_3]$ the position of the three borane groups does not lead to a serious hindrance between them. From models, we find that one conformation seems favourable to a dative $P\rightarrow B$ bond formation: unfortunately, in such an arrangement, the three nitrogen lone pair electrons come very close together and repel each other.

It thus appears that in the particular case of $(Et_2NCH_2)_3P$ the formation of the $P\rightarrow B$ bond is less favoured than that of the $N\rightarrow B$ one.

We are now continuing this work by calorimetry in order to find further evidence of the different behaviour of these two bonds.

EXPERIMENTAL

Materials and Techniques.—Owing to their reactivity towards atmospheric reagents, ligands and adducts were handled under an inert atmosphere.

Dimethyl(dimethylamino)phosphine (L_2) was obtained from (dimethylamino)dichlorophosphine and methylmagnesium bromide in ether according to the method of Burg and Slota [14] (b.p. 96 °C, $n_D^{20} = 1{\cdot}449$, $d_4^{20} = 0{\cdot}824$). *Methylbis(dimethylamino)phosphine* (L_3) was obtained from methyldichlorophosphine and an excess of dimethylamine in ether [15] (b.p. 141 °C, $n_D^{20} = 1{\cdot}462$, $d_4^{20} = 0{\cdot}881$). *Tris(diethylaminomethyl)phosphine* was obtained from the Aldrich Chemical Co. ($n_D^{20} = 1{\cdot}480$, $d_4^{20} = 0{\cdot}881$). Its purity was checked by n.m.r. tests. Diborane (B_2H_6) was generated by Schlesinger's method [16] using boron trifluoride–diethyl ether and sodium borohydride in glyme. The so-evolved diborane was introduced into the free ligand solutions by a capillary tube or a small sintered glass.

Unless noted otherwise, all n.m.r. spectra were obtained on Perkin-Elmer R10 and R12 spectrometers operated at the following frequencies: ^1H, 60·00; ^{31}P, 24·29; ^{11}B, 19·25 MHz.

Dimethyl(dimethylamino)phosphine–Borane.— Triethylamine–borane (23 g, 0·2 mol) and dimethyl(dimethylamino)phosphine (10·5 g, 0·1 mol) were mixed under argon and gradually heated to boiling. Triethylamine was displaced and gently distilled through a Vigreux column (b.p. 90 °C). The triethylamine so evolved was titrated with 1N-sulphuric acid solution and we noticed that the displacement reaction stopped only when *ca.* 0·1 mol of Et_3N was removed. A distillation was then carried out *in vacuo* and 11·8 g of Me_2NPMe_2,BH_3 (80% of theoretical) was obtained (b.p. 92 °C, 15 mmHg; $n_D^{20} = 1{\cdot}466$; $d_4^{20} = 0{\cdot}834$).

Methylbis(dimethylamino)phosphine–Borane.—This adduct could be obtained by Reetz's method.[5] In a typical experiment, sodium borohydride (7·6 g, 0·2 mol) was added to methylbis(dimethylamino)phosphine (13·4 g, 0·1 mol) in tetrahydrofuran (100 ml). Then carbon dioxide was introduced into the mixture at room temperature until no further absorption was observed. The reaction product was filtered and the filtrate was evaporated. Distillation of the liquid residue yielded $(Me_2N)_2PMe,BH_3$ (8·1 g, 55% of theoretical) as a colourless liquid (b.p. 62 °C, 1 mmHg; $n_D^{20} = 1{\cdot}474$; $d_4^{20} = 0{\cdot}881$).

Tris(diethylaminomethyl)phosphine–Borane. A great excess of diborane, generated as indicated above, was introduced by bubbling into a flask containing a benzene solution of tris(diethylaminomethyl)phosphine (14·5 g, 0·05 mol). The solution was maintained at room temperature and magnetically stirred. A white crystalline precipitate appeared which was filtered and washed by pentane. The precipitate was then dried *in vacuo* and recrystallized from methylene chloride or benzene. $(Et_2NCH_2)_3P,3BH_3$ Appeared as colourless crystals which decompose before melting.

The main data (physical and n.m.r.) are given in the Tables for the free phosphines and their BH_3 adducts.

[3/2448 *Received, 29th November, 1973*]

---

[15] R. R. Holmes and R. P. Wagner, *J. Amer. Chem. Soc.*, 1962, **84**, 357.

[16] H. C. Brown and P. A. Tierney, *J. Amer. Chem. Soc.*, 1958, **80**, 1552.