203. Aminodiarylboranes and their Phosphorus and Arsenic Analogues.

By G. E. Coates and J. G. Livingstone.

Several monomeric aminodiarylboranes ($Ar_2B{\cdot}NR_2$) have been prepared, and their infrared spectra and dipole moments studied. Aminodiphenylborane ($R = H$) is dimeric and non-polar in benzene solution. The monomeric aminodiarylboranes have low dipole moments, whose direction is reversed on passing from $Ph_2B{\cdot}NMe_2$ to $Ph_2B{\cdot}NPh_2$. Phosphinodiarylboranes are monomeric and not readily hydrolyzed. Their dipole moments are generally greater than those of corresponding amino-compounds, and the phosphino-group is at the negative end of the dipole. The arsino-derivatives are similar but rather less polar. The properties of the phosphorus and arsenic compounds are interpreted in terms of weak π-donor character of phosphorus and arsenic towards boron (in contrast to the strong π-donor character of nitrogen), and the co-ordinative saturation of boron by the aryl groups.

Compounds in which an atom of acceptor character is covalently bound to one of donor character can achieve co-ordination saturation either by the formation of a double bond or by association. The first situation is exemplified by (dimethylamino)dimethylborane, $Me_2B{=}NMe_2$, since the force constant of the B–N bond is appropriate for a double bond.[1] Similarly the force constant of the B–N bonds in trisdimethylaminoborane,[2] $(Me_2N)_3B$, is $5{\cdot}5 \times 10^5$ dyne $cm.^{-1}$ which is appropriate for bonds of order 4/3. Valency expansion by the formation of a fourth σ-bond occurs in the dimeric forms of the chlorides, *e.g.*,

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[1] Becher and Goubeau, *Z. anorg. Chem.*, 1952, **268**, 133.

[2] Becher, *Z. anorg. Chem.*, 1956, **287**, 285.

$(Me_2N{\cdot}BCl_2)_2$,[3,4] and in the much studied phosphinoboranes in which cyclic trimers $(Me_2P{\cdot}BMe_2)_3$,[5] tetramers $(Me_2P{\cdot}BH_2)_4$,[5] and polymers[6] are found. No monomeric phosphino- or arsino-boranes appear to have been described, with the possible exception[5] of $PH_2{\cdot}BMe_2$.

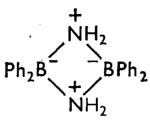
The absence of any general rule which might be used to predict whether a compound of this type would be monomeric (and presumably contain a partial double bond) or associated suggested the need to obtain further data concerning (*a*) circumstances in which aminoboranes are associated, and (*b*) the possible existence of monomeric phosphino- and arsino-boranes.

Aminoboranes.—Unsubstituted aminoborane[7] appears to be polymeric, $(H_2B{\cdot}NH_2)_n$, and unstable. The extent of association decreases as hydrogen is substituted by alkyl groups: thus *N*-methylaminoborane is trimeric,[8] $(H_2B{\cdot}NHMe)_3$, and reversible monomer-dimer equilibria may be realized with $H_2B{\cdot}NMe_2$,[9] $MeHB{\cdot}NMe_2$,[10] $Me_2B{\cdot}NHMe$,[11] and $Me_2B{\cdot}NH_2$.[12] All known tetrasubstituted aminoboranes ($R_2B{\cdot}NR'_2$; R, R′ = alkyl or aryl) appear to be monomeric.[13] Relatively few *B*-arylaminoboranes have been studied, but methylaminodiphenylborane, $Ph_2B{\cdot}NHMe$, slowly changes from monomer to dimer at room temperature;[14] all others described are monomeric.

Aminodiphenylborane has now been prepared from ammonia and chlorodiphenylborane in the presence of triethylamine,

$$Ph_2BCl + NH_3 + NEt_3 = \tfrac{1}{2}(Ph_2B{\cdot}NH_2)_2 + Et_3N,HCl$$

and is dimeric (cryoscopically in benzene and in nitrobenzene). The most likely structure (I) is centrosymmetric, and the observed electric polarization is in agreement with this. The total polarization, measured in benzene solution at 25°, was 119·9 c.c. The electron polarization, measured at six wavelengths and extrapolated to infinite wavelength, was 102·4 c.c., and the difference, 17·5 c.c., is about the expected value of the atom polarization in co-ordination compounds containing balanced dipoles [*e.g.*, the atom polarizations of *trans*-$(R_3P)_2PdAr_2$ complexes are usually about 20 c.c.[15]]. The dipole moment of compound (I) is therefore zero.



(I)

Thus the only dimeric aminodiarylboranes are those containing NH_2 or NHMe groups. Experiments with molecular models indicate that any larger groups attached to the nitrogen would cause substantial steric interference even with the hydrogen atoms in *ortho*-positions on the aryl groups.

All the other aminodiarylboranes prepared in this investigation were monomeric in nitrobenzene solution, though often slightly associated in benzene particularly in the more concentrated solutions. The aminodiarylboranes, $Ar_2B{\cdot}NR_2$, were prepared by three methods:

$$Ar_2BCl + LiNR_2 = Ar_2B{\cdot}NR_2 + LiCl \quad (1)$$

$$Ar_2BCl + R_2NH + Et_3N = Ar_2B{\cdot}NR_2 + Et_3NHCl \quad (2)$$

$$2ArMgBr + Cl_2B{\cdot}NR_2 = Ar_2B{\cdot}NR_2 + MgCl_2 + MgBr_2 \quad (3)$$

Method (3) was particularly suitable for the preparation of dimethylaminoboranes.[13]

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[3] Wiberg and Schuster, *Z. anorg. Chem.*, 1933, **213**, 77.

[4] C. A. Brown and Osthoff, *J. Amer. Chem. Soc.*, 1952, **74**, 2340.

[5] Burg and Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 3872.

[6] Wagner and Caserio, *J. Inorg. Nuclear Chem.*, 1959, **11**, 259.

[7] Schaeffer, Adams, and Koenig, *J. Amer. Chem. Soc.*, 1956, **78**, 725.

[8] Bissot and Parry, *J. Amer. Chem. Soc.*, 1955, **77**, 3481.

[9] Wiberg, Bolz, and Buchheit, *Z. anorg. Chem.*, 1948, **256**, 285.

[10] Burg and Boone, *J. Amer. Chem. Soc.*, 1956, **78**, 1521.

[11] Wiberg and Hertwig, *Z. anorg. Chem.*, 1947, **255**, 141.

[12] Wiberg and Buchheit, F.I.A.T. Review of German Science, 1948, Inorganic Chemistry, Vol. I, p. 218.

[13] Niedenzu and Dawson, *J. Amer. Chem. Soc.*, 1959, **81**, 5553.

[14] Mikhailov and Fedotov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1959, 1482.

[15] Coates and Dixon, unpublished observations.

The ultraviolet spectrum of (diphenylamino)diphenylborane is similar in general appearance to that of tetraphenylethylene [16] (both measured in cyclohexane), absorption maxima and extinction coefficients being at 282 mμ (18,200) and 312 mμ (14,000) respectively.

The infrared spectra of these two compounds are nearly identical, the main differences being the splitting of the C_{ar}–H out-of-plane deformation bands (already reported,[17] and observed by us in all our diarylboron compounds) and the very strong band at 1372 cm.$^{-1}$ in the region in which B–N absorptions are commonly found.[13] The band due to B–N absorption was always strong and easily recognized in aminoboranes, and its frequency in the various compounds examined is given in Table 1, which also summarizes dipole moments and degrees of association in benzene and in nitrobenzene. The aminoboranes listed in Table 1 are all readily hydrolyzed by cold water; this is a general property of aminoboranes and was the basis of a method sometimes used for their analysis.

TABLE 1. *Aminodiarylboranes.*

			Degree of association			
			Benzene		Nitrobenzene	
Aminodiarylborane	B–N absorption frequency (cm.$^{-1}$)	Dipole moment (D)	Wt. %	n	Wt. %	n
$Ph_2B\cdot NH_2$	1552[b] (NH ν, 3320 and 3362)[b]	0	0·38	1·94	1·90	1·97
			0·43	1·97	3·37	1·87
			0·68	2·19	4·44	1·94
					5·27	1·93
$Ph_2B\cdot NMe_2$	1388[b]	1·6	3·49	1·08	3·06	0·85
			4·43	1·24	4·41	0·95
			7·59	1·27	5·76	1·06
			9·95	1·17	7·52	1·14
$(p\text{-}Me\cdot C_6H_4)_2B\cdot NMe_2$	1410[b]	1·1	0·63	0·93	2·07	0·98
			1·09	1·02	3·56	0·92
			1·42	1·16	4·66	1·02
			1·71	1·21	5·53	1·06
$(p\text{-}Br\cdot C_6H_4)_2B\cdot NMe_2$	1356[b]	3·1	0·346	0·96	0·209	1·01
			0·588	0·91	0·479	1·09
			0·894	0·95	0·641	1·11
			1·034	0·99	0·743	1·14
$Ph_2B\cdot NPh_2$	1372[a]	1·0	0·774	1·03	0·911	0·97
			1·152	1·31	1·431	0·94
			1·924	1·48	1·827	0·94
			2·259	1·74	2·249	1·10
$Ph_2B\cdot N(C_6H_4Me\text{-}p)_2$	1361[a]	0·8			0·417	1·04
					1·228	1·09
					1·905	1·14
					2·536	1·25
$(p\text{-}Me\cdot C_6H_4)_2B\cdot NPh_2$	1385[a]	1·6	0·424	1·02	0·579	0·99
			0·763	1·05	1·162	1·04
			1·297	1·14	1·647	1·05
			1·384	1·17	2·06	1·10

[a] In KI disc. [b] In benzene solution.

The B–N frequencies of all but the first compound in Table 1 fall within the range 1330—1530 reported [13] for eleven other aminoboranes. A variation in these frequencies has generally been interpreted as mainly due to a change in the multiplicity of the B–N bond,[1, 2, 13] so the high frequency (1552) observed * in the case of the dimeric compound (I), in which the B–N bonds must surely be single, may at first sight appear remarkably high. However, vibrational modes due to the stretching of B–N bonds in a ring can scarcely be expected to be closely comparable to those due to an isolated B–N bond in a monomeric compound.

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* This frequency was also observed when the substance was pressed in a potassium iodide disc.

[16] Kortüm and Dreesen, *Chem. Ber.*, 1951, **84**, 182.

[17] Bellamy, Gerrard, Lappert, and Williams, *J.*, 1958, 2412.

Although the tetramethyl compound $Me_2B{\cdot}NMe_2$ contains a double bond, the large dipole moment expected from the formula $Me_2\overset{-}{B}{=}\overset{+}{N}Me_2$ is evidently very considerably reduced by unsymmetrical electron sharing in the sense B ⟶ N owing to the electronegativity difference between boron and nitrogen. The observed dipole moment[18] is only 1·40 ± 0·03 D (1·47 ± 0·06 D in $Me_2B{\cdot}NH_2$). Both $Ph_2B{\cdot}NMe_2$ and $Ph_2B{\cdot}NPh_2$ have such small dipole moments (1·6 and 1·0 D) that it is not obvious which end of the molecule is positive. Examination of *p*-tolyl derivatives shows that the *N*-methyl compounds have polarities of different sign from those of the *N*-aryl compounds: $Ph_2\overset{\longleftarrow +}{B{-}N}Me_2$ and $Ph_2\overset{+\longrightarrow}{B{-}N}Ph_2$. This reversal of polarity could be due to the electron-repelling effect of a methyl group, whereas a phenyl group can act as an electron-attractor in such a system. The change in moment, however, is rather large ($\Delta\mu = 2{\cdot}6$ D for the two compounds just mentioned). All the observed moments are consistent with only a small or zero net polarity for the B–N bond.

Phosphinoboranes.—The only monomeric phosphinoborane previously mentioned is the not very well characterized compound $Me_2B{\cdot}PH_2$, which was described as being sensitive to hydrolysis and methanolysis and slowly forming a polymer in ether solution.[5] We find, however, that in contrast to the tri-, tetra-, and poly-meric phosphinoboranes of the type $R_2B{\cdot}PR'_2$ (R = H or alkyl, R′ = alkyl or aryl), all the phosphinodi*aryl*boranes we have prepared are monomeric. In contrast to the aminoboranes, the monomeric phosphinodiarylboranes are relatively resistant to hydrolysis The diarylphosphino-compounds are also unaffected by air.

(Diphenylphosphino)diphenylborane ($Ph_2B{\cdot}PPh_2$) was prepared by method (2), chlorodiphenylborane being added to an equimolar mixture of diphenylphosphine and triethylamine. Addition of diphenylphosphine to the other reactants gives the salt $[Et_3NH]^+[Ph_2BCl{\cdot}PPh_2]^-$, and diphenylphosphine and chlorodiphenylborane alone give a third compound $Ph_2\overset{-}{B}Cl{-}\overset{+}{P}HPh_2$. (Diphenylphosphino)diphenylborane is not only insoluble in, and undecomposed by, water but is so sparingly soluble in organic solvents that neither its molecular weight nor its dipole moment was measured. It is presumed to be monomeric or capable of reversible dissociation into monomer since it sublimed at 240° in a vacuum (dimer or trimer would contain 8 or 12 phenyl groups).

To obtain more soluble compounds, derivatives of di-*m*-tolylphosphine were prepared by a modification of reaction (1) in which the sodium derivative of di-*m*-tolylphosphine in tetrahydrofuran was added to chlorodiphenylborane in the same solvent:

$$(m\text{-}Me{\cdot}C_6H_4)_2PH + Na \xrightarrow{\text{THF}} Na^+(m\text{-}Me{\cdot}C_6H_4)_2P^- + \tfrac{1}{2}H_2 \xrightarrow{Ph_2BCl} Ph_2B{\cdot}P(C_6H_4Me\text{-}m)_2$$

The *m*-tolyl derivatives all had adequate solubility both for molecular-weight measurement in nitrobenzene and for dipole-moment measurement in benzene (in which they are sparingly soluble).

The diaryl(phosphino)boranes prepared are listed in Table 2.

The infrared spectra of the phosphorus compounds were very similar to those of their nitrogen analogues, and in all but one instance it was easy to distinguish the strong band almost certainly associated with stretching of the B–P bond. Since these bands (1400—1500 cm.$^{-1}$) are at higher frequencies than those of the B–N bands in most of the aminoboranes studied, in spite of the mass of a phosphorus being greater than that of a nitrogen atom, the boron–phosphorus bonds in the monomeric phosphinoboranes would appear to have pronounced double-bond character.

The monomeric phosphinoboranes might therefore be expected to have pronounced polar character, as indicated by the co-ordination formula (II). Moreover, since boron and phosphorus (and arsenic) have much the same electronegativity values (in the range

[18] Becher, *Z. anorg. Chem.*, 1952, **270**, 273.

TABLE 2. *Diaryl(phosphino)boranes.*

Compound	B–P absorption frequency (cm.$^{-1}$)	Dipole moment (D)	Degree of association: Benzene Wt. %	Benzene *n*	Nitrobenzene Wt. %	Nitrobenzene *n*
$Ph_2B{\cdot}PEt_2$	1440[b]	1·1	0·431	1·05	0·223	1·03
			0·801	1·12	0·509	1·12
			1·52	1·22	1·727	1·28
			1·96	1·54	2·466	1·39
$(p\text{-}Br{\cdot}C_6H_4)_2B{\cdot}PEt_2$	1412[a]	0·7	0·172	1·01		
			0·283	1·12		
			0·885	1·16		
			1·571	1·27		
$Ph_2B{\cdot}PPh_2$	1445[a]	(Not sufficiently soluble, see text)				
$Ph_2B{\cdot}P(C_6H_4Me\text{-}m)_2$	1482[a]	2·2			0·348	1·00
					0·391	1·01
					0·477	0·89
$(p\text{-}Me{\cdot}C_6H_4)_2B{\cdot}P(C_6H_4Me\text{-}m)_2$	1487[a]	2·9			0·472	1·11
					0·943	1·17
					1·266	1·03
$(p\text{-}Br{\cdot}C_6H_4)_2B{\cdot}P(C_6H_4Me\text{-}m)_2$	1480[a] or 1425[a]	0·6			0·421	0·97
					0·987	1·06
					1·19	1·15

[a] In KI disc. [b] In benzene solution.

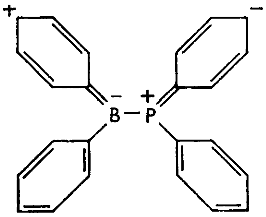
1·9—2·1, however computed; see Pritchard and Skinner's review [19]), the moment indicated in (II) should not be reduced by bond polarization as in the aminoboranes (the electronegativity of nitrogen being about 3).

$$\overset{\longleftarrow\!\!\!+}{Ar_2B=PR_2}$$

(II)

$$\overset{+\!\!\!\longrightarrow}{Ar_2B=PR_2}$$

(III)



(IV)

In fact, inspection of Table 2, with the effect of methyl and bromo-substituents on dipole moments in mind, shows that the moments of the phosphinoboranes are larger than those of the corresponding aminoboranes, and that the phosphino-group is the *negative* end of the dipole (III). From Table 2 the dipole moment of (III; Ar = R = Ph) must be about 2·5 D, that of (III; Ar = Ph, R = Et) being about 1·1 D and in the same direction.

This surprising result suggests that phosphorus is acting as a *weak* π-donor (to boron) in these compounds, possibly owing to an unfavourable relation between the " sizes " of boron 2*p*- and phosphorus 3*p*-orbitals. In all the diarylboranes some electron flow is to be expected from the aryl groups to the vacant boron 2*p*-orbital, and in $Ph_2B{\cdot}PEt_2$ this could perhaps account for the greater part of the observed dipole moment. Good evidence for such effects has been obtained from studies on the dipole moments of alkyl- and aryl-dihalogenoboranes.[20] Though the boron atom in a diaryl(diethylphosphino)-borane could thus be regarded as co-ordinatively saturated, or partly so, the phosphorus is not, and in fact the di*ethyl*phosphino-compounds add methyl iodide to form phosphonium salts $\{Ar_2B{\cdot}PEt_2Me\}I$.

In $Ph_2B{\cdot}PPh_2$ and related compounds the still larger moments would be due, in effect, to conjugation both between boron and aryl and between phosphorus and aryl, as shown in the " resonance " formula (IV). This formulation accounts in a qualitative way, not only for the observed dipole moments, but also for the lack of chemical reactivity, since both boron and phosphorus are co-ordinatively saturated (or partly so). Further, the

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[19] Pritchard and Skinner, *Chem. Rev.*, 1955, **55**, 745.

[20] Curran, McCusker, and Makowski, *J. Amer. Chem. Soc.*, 1957, **79**, 5188.

charge separation between boron and phosphorus indicated in (IV) should result in B–P stretching force constants greater than would be expected for B–P single bonds, since the B–P bond would amount to a σ-bond possibly with a small π-component but with some electrostatic attraction in addition.

The relative importance of structures analogous to (IV) in the aminoboranes is, we suggest, much less because boron and nitrogen achieve co-ordinative saturation by formation of a B=N double bond.

TABLE 3. *Arsinodiarylboranes.*

Compound	B–As adsorption frequency (cm.$^{-1}$) (KI disc)	Dipole moment (D)	Degree of association: Benzene Wt. %	Benzene n	Nitrobenzene Wt. %	Nitrobenzene n
$Ph_2B{\cdot}AsPh_2$	1369	1·3	0·333	1·09	0·447	1·04
			0·715	1·26	0·734	1·05
			1·891	1·76	1·802	0·99
			2·891	1·95	2·598	1·06
$(p\text{-}Me{\cdot}C_6H_4)_2B{\cdot}AsPh_2$	1439	2·1	0·691	0·94		
			1·23	0·99		
			2·41	1·14		
			3·33	1·37		
$(p\text{-}Br{\cdot}C_6H_4)_2B{\cdot}AsPh_2$	1370	~0·4	0·704	1·04		
			1·29	1·12		
			2·44	1·31		
			2·98	1·38		

The reason for the phosphinodiarylboranes' being monomeric, when the series $R_2B{\cdot}PR'_2$ ($R = H$, alkyl) form trimers, tetramers, or polymers, thus lies in the boron atom in the diarylborane series being already co-ordinatively saturated (or nearly so) not by π-bonding with phosphorus but by π-bonding with the aryl groups.

Arsinoboranes.—These were prepared from the chlorodiarylborane and the sodium salt of the diarylarsine in tetrahydrofuran; they are listed in Table 3. Infrared spectra again resembled those of the nitrogen and phosphorus compounds, but the tetraphenyl compound $Ph_2B{\cdot}AsPh_2$ was very much more soluble than $Ph_2B{\cdot}PPh_2$ in organic solvents. The diaryl(arsino)boranes resembled the phosphino-analogues in their resistance to water or dilute acids or alkalis at 100°, but differed in their quantitative and analytically useful reaction with aqueous-alcoholic hydrogen peroxide at room temperature:

$$Ph_2B{\cdot}PAr_2 + H_2O_2 \longrightarrow 2PhOH + H_3BO_3 + Ar_2PO_2H$$

$$Ph_2B{\cdot}AsAr_2 + H_2O_2 \longrightarrow 2PhOH + 2ArOH + H_3BO_3 + H_3AsO_4$$

The B–As absorption bands are at rather lower frequencies than those of B–P bands in analogous compounds, and in the same region as B–N bands. The arsino-group is, as in the phosphinoboranes, the *negative* end of the dipole, the moments being rather less. We conclude that the electronic situation in the arsinoboranes resembles that in the phosphinoboranes, the smaller moments of the former being due to a smaller degree of electron transfer from arsenic to the aryl groups bound to it.

Though the σ-donor character of nitrogen, phosphorus, and arsenic towards boron diminishes in that order, it seems that the π-donor character diminishes even more rapidly.

EXPERIMENTAL

Microanalyses (C, H, and halogen) are by Mr. A. Wiper and Miss V. Conway, of these laboratories.

Combustion analyses often presented the difficulties, familiar with organoboron compounds, due to the retention of carbon as boron carbide in combustion residues, leading to erratic results for carbon. More reproducible results were generally obtained when smaller samples were burnt, and when the residue after combustion was heated with an oxygen-enriched flame.

Compounds were in several instances identified by quantitative hydrolysis (for amino-) or oxidation reactions (for phosphino- and arsino-derivatives). Cryoscopic constants were determined by using biphenyl for benzene, and *p*-nitrotoluene for nitrobenzene.

Except in the case of one compound, for which refractivities were measured over a range of wavelengths, refractivities were measured at 6620 Å (Jena interference filter) and atom polarizations were taken as 10% of these refractivities.

Dipole moments were measured in benzene solution, total polarizations being derived by Halverstat and Kumler's method.[21] In spite of the apparent association of many of the compounds studied, as suggested by cryoscopic measurements, dielectric constant–weight fraction plots were always very nearly linear.

Infrared spectra were measured with a Grubb-Parsons GS2A grating spectrometer.

Chlorodiphenylborane, which was used in several preparations, has previously been described as a liquid; [22] we found it had m. p. 21·5—22·0°.

Aminodiphenylborane, $(Ph_2B{\cdot}NH_2)_2$.—Chlorodiphenylborane [22] [from diphenylborinic acid [23] and trichloroborane] (10 g., 0·05 mole) in ether (100 c.c.) was saturated with ammonia at room room temperature, and triethylamine (5·1 g., 0·05 mole) in ether (50 c.c.) was slowly added. The mixture was boiled under reflux for 1 hr., cooled, and filtered under nitrogen from triethylamine hydrochloride. The filtrate was evaporated; and the colourless *product*, crystallized from benzene, had m. p. 129—130° (3·6 g., 43%) (Found: C, 79·4; H, 6·7. $C_{12}H_{12}BN$ requires C, 79·9; H, 6·6%).

Dimethylaminodiphenylborane, $Ph_2B{\cdot}NMe_2$.—To a solution of monomeric dichlorodimethylaminoborane [24] (3·2 g., 0·025 mole) in benzene (50 c.c.) was slowly added phenylmagnesium bromide (0·05 mole) in ether. The mixture was evaporated and organic product extracted with hot benzene. Vacuum-distillation of the extract yielded a clear colourless liquid *product*, b. p. 102—104°/0·05 mm. (4·1 g., 81%) (Found: C, 80·8; H, 8·0. $C_{14}H_{16}BN$ requires C, 80·4; H, 7·6%).

Dimethylaminodi-p-*tolylborane*, $(p\text{-}Me{\cdot}C_6H_4)_2B{\cdot}NMe_2$, b. p. 110—112°/0·04—0·05 mm. (76%) [Found: C, 80·0; H, 8·6. $C_{16}H_{20}BN$ requires C, 81·1; H, 8·4%). By hydrolysis, found: $(p\text{-}Me{\cdot}C_6H_4)_2B$, 81·8, 80·5; Me_2N, 18·8, 18·3. $C_{16}H_{20}BN$ requires $(p\text{-}Me{\cdot}C_6H_4)_2B$, 81·5; Me_2N, 18·6%], and *di*-p-*bromophenyldimethylaminoborane*, $(p\text{-}Br{\cdot}C_6H_4)_2B{\cdot}NMe_2$, m. p. 39—40° (from benzene–hexane) (44%) (Found: C, 46·6; H, 3·7; Br, 43·9. $C_{14}H_{14}BBr_2N$ requires C, 45·8; H, 3·8; Br, 43·7%), were similarly prepared by using *p*-tolyl- and *p*-bromophenyl-magnesium bromide respectively.

(Diphenylamino)diphenylborane, $Ph_2B{\cdot}NPh_2$.—*Method* 1. Lithium diphenylamide in dry ether was slowly added to an equivalent quantity of chlorodiphenylborane in ether at −60°. The mixture was allowed to warm to room temperature and filtered under nitrogen, and the white *product* which resulted from removing solvent from the filtrate was crystallized from benzene; it had m. p. 148—150° (66%) (Found: C, 85·8; H, 6·1; B, 3·14. $C_{24}H_{20}BN$ requires C, 86·4; H, 6·0; B, 3·26%) [0·186 g. was warmed with aqueous acetone for a few minutes, and a slight excess of ethanolamine added. The reaction mixture was poured into water, and the solid collected, dried, and sublimed in a vacuum. The sublimate (0·093 g.) was identified (infrared spectrum) as diphenylamine, and the residue (0·132 g.) was similarly identified as 2-aminoethyl diphenylborinate ($C_{24}H_{20}BN$ requires 0·096 g. and 0·128 g. respectively)].

Method 2. Diphenylamine in benzene was added to a solution containing equivalent amounts of triethylamine and chlorodiphenylborane in the same solvent. The mixture was boiled under reflux for 30 min. and filtered under nitrogen from triethylamine hydrochloride (m. p. 255—256°), and the filtrate was concentrated to crystallization (61%). The infrared spectrum of the product was identical with that of the material prepared by method (1).

(Di-p-*tolylamino)diphenylborane*, $Ph_2B{\cdot}N(C_6H_4{\cdot}Me\text{-}p)_2$, m. p. 130—132° (from benzene–hexane) [Found: C, 85·3; H, 6·5. $C_{26}H_{24}BN$ requires C, 86·3; H, 6·8%. By hydrolysis, found: Ph_2B, 45·9; $(p\text{-}Me{\cdot}C_6H_4)_2N$, 54·9. $C_{26}H_{24}BN$ requires Ph_2B, 45·8; $(p\text{-}Me{\cdot}C_6H_4)_2N$, 54·2%] was prepared by methods (1) (53%) and (2) (57%).

Diphenylaminodi-p-*tolylborane*, $(p\text{-}CH_3{\cdot}C_6H_4)_2B{\cdot}NPh_2$.—This was prepared by method (2). The *product*, crystallized from benzene–hexane (67%, had m. p. 72—73° [Found: C, 89·9;

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[21] Halverstat and Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.

[22] Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.

[23] Povlock and Lippincott, *J. Amer. Chem. Soc.*, 1958, **80**, 5409.

[24] J. F. Brown, *J. Amer. Chem. Soc.*, 1952, **74**, 1219.

H, 7·0. $C_{26}H_{24}BN$ requires C, 89·1; H, 7·0%). By hydrolysis, found: $(p\text{-Me}\cdot\text{C}_6\text{H}_4)_2\text{B}$, 53·8, 53·7; Ph_2N, 46·8, 46·4. $C_{26}H_{24}BN$ requires $(p\text{-Me}\cdot\text{C}_6\text{H}_4)_2\text{B}$, 53·4; Ph_2N, 46·6%].

(Diethylphosphino)diphenylborane, $\text{Ph}_2\text{B}\cdot\text{PEt}_2$.—n-Butyl-lithium (0·025 mole) in benzene was added to a solution of diethylphosphine [25] (2·3 g., 0·025 mole) in benzene at room temperature. Sufficient tetrahydrofuran was added to dissolve the pale yellow precipitate (LiPEt_2), and to this solution was slowly added chlorodiphenylborane (5 g., 0·025 mole) in benzene (50 c.c.). Water (100 c.c.) was added to the mixture. The benzene layer, when separated, dried (MgSO_4), and evaporated, gave a colourless *product*, m. p. 192° (from benzene) (5·3 g., 84%) (Found: C, 75·8; H, 7·9; B, 4·4; P, 12·0. $C_{16}H_{20}BP$ requires C, 75·6; H, 7·9; B, 4·25; P, 11·8%).

*Di-*p*-bromophenyl(diethylphosphino)borane*, $(p\text{-Br}\cdot\text{C}_6\text{H}_4)_2\text{B}\cdot\text{PEt}_2$, was similarly prepared from (di-*p*-bromophenyl)chloroborane, and crystallized from benzene–hexane; it had m. p. 202° (49%) (Found: C, 45·9; H, 4·3; Br, 38·1. $C_{16}H_{18}BBr_2P$ requires C, 46·5; H, 4·4; Br, 38·9%). Addition of methyl iodide to a solution of the phosphinoborane in benzene gave an immediate white precipitate of *methiodide*, m. p. 310—312° (decomp.) (Found: I, 23·1, 23·3. $C_{17}H_{21}BBr_2IP$ requires I, 22·9%).

(Diphenylphosphino)diphenylborane, $\text{Ph}_2\text{B}\cdot\text{PPh}_2$.—Chlorodiphenylborane (5 g.) in benzene (50 c.c.) was added at room temperature to a mixture of diphenylphosphine (4·2 g.) and triethylamine (2·5 g.) in benzene (50 c.c.). Part of the resulting thick white precipitate was dissolved by addition of water, and the rest was separated, washed several times with ether, and dried, and the *phosphinoborane* collected by sublimation ($240°/10^{-3}$ mm.; 5·4 g., 61%) (Found: C, 78·9; H, 5·6. $C_{24}H_{20}BP$ requires C, 82·3; H, 5·7%). [0·1906 g. was warmed with aqueous-alcoholic hydrogen peroxide, and the phenol separated by steam distillation afforded tribromophenol, 0·348 g. ($C_{24}H_{20}BP$ requires 0·359 g.). Diphenylphosphinic acid (m. p. 195—196°) was isolated, but not quantitatively, from the steam-distillation residue].

This compound was also prepared by method (1), from the sodium derivative of diphenylphosphine and chlorodiphenylborane in 2,5-dioxahexane at $-60°$, but in lower yield (51%). The infrared spectrum of the water-insoluble solid product showed the presence of P–H bonds. The pure product was separated by vacuum-sublimation.

Chloro(diphenylphosphino)diphenylborane, $\text{BClPh}_2\text{,PHPh}_2$.—Diphenylphosphine (4·2 g.) in benzene (25 c.c.) was slowly added to chlorodiphenylborane (5 g.) in benzene (20 c.c.). The white crystalline and very hydroscopic *adduct* (7·3 g., 75%), m. p. 83—85°, was filtered off (Found: Cl, 9·04, 9·08. $C_{24}H_{21}BClP$ requires Cl, 9·18%).

Triethylammonium Chloro(diphenylphosphino)diphenylborate, $\text{Et}_3\text{NH}^+\ \text{BPh}_2\text{Cl}\cdot\text{PPh}_2^-$.—Diphenylphosphine (4·2 g.) in benzene (25 c.c.) was added to a mixture of chlorodiphenylborane (5 g.) and triethylamine (2·5 g.) in benzene (25 c.c.). The colourless precipitated *salt* (77%), m. p. 152—153°, was collected (Found: C, 72·4; H, 7·7; B, 3·71; Cl, 6·9; Et_3N, 19·8. $C_{30}H_{36}BClNP$ requires C, 73·5; H, 7·4; B, 3·24; Cl, 7·1; Et_3N, 20·1%).

*(Di-*m*-tolylphosphino)diphenylborane*, $\text{Ph}_2\text{B}\cdot\text{P}(\text{C}_6\text{H}_4\cdot\text{Me-}m)_2$.—A solution of the sodium derivative of di-*m*-tolylphosphine (4·2 g.) in tetrahydrofuran (20 c.c.) was added to chlorodiphenylborane (4·0 g.) in ether (20 c.c.) at room temperature. Most of the solvent was then removed by evaporation, and the residue was extracted with hot benzene. Evaporation of the benzene solution gave the colourless *phosphinoborane* (5·1 g., 67%), m. p. 123—124° (Found: C, 81·9; H, 6·3. $C_{26}H_{24}BP$ requires C, 82·4; H, 6·4%).

*Di-*m*-tolylphosphinodi-*p*-tolylborane*, $(p\text{-CH}_3\cdot\text{C}_6\text{H}_4)_2\text{B}\cdot\text{P}(\text{C}_6\text{H}_4\cdot\text{CH}_3\text{-}m)_2$, m. p. 257—258° (from benzene–hexane; 67%) (Found: C, 80·9; H, 6·9. $C_{28}H_{28}BP$ requires C, 82·8; H, 6·9%), and *di-*p*-bromophenyldi-*m*-tolylphosphinoborane*, $(p\text{-BrC}_6\text{H}_4)_2\text{B}\cdot\text{P}(\text{C}_6\text{H}_4\text{Me-}m)_2$, m. p. 281° (from benzene–hexane; 66%) (Found: C, 60·2; H, 4·1; Br, 30·1. $C_{26}H_{22}BBr_2P$ requires C, 58·1; H, 4·1; Br, 29·9%), were similarly prepared from the sodium derivative of di-*m*-tolylphosphine and the appropriate chlorodiarylborane.

(Diphenylarsino)diphenylborane, $\text{Ph}_2\text{B}\cdot\text{AsPh}_2$.—Diphenylarsine (5·8 g., 0·025 mole) was converted into its sodium derivative by reaction with excess of sodium wire in tetrahydrofuran (50 c.c.) at room temperature. The ruby-red solution was decanted under nitrogen from the excess of sodium and slowly added to chlorodiphenylborane (5 g., 0·025 mole) in tetrahydrofuran at $-60°$, the red colour being immediately discharged. The mixture was allowed to warm to room temperature, then filtered under nitrogen from precipitated sodium chloride, and the

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[25] Issleib and Tzschach, *Chem. Ber.*, 1959, **92**, 704.

filtrate was evaporated. The residue, crystallized from benzene, gave the colourless *arsinoborane* (5·8 g., 57%), m. p. 202—204° (Found: C, 72·6; H, 5·1. $C_{24}H_{20}AsB$ requires C, 73·1; H, 5·1%) [0·0944 g. was boiled (10 min.) with aqueous-alcoholic hydrogen peroxide; and the phenol, separated by steam-distillation, was converted into tribromophenol, 0·2966 g. ($C_{24}H_{20}AsB$ requires 0·3190 g.). The aqueous residue was boiled a few minutes with a trace of platinum black to remove excess of peroxide, then filtered, and boric and arsenic acid were estimated volumetrically (Found: B, 3·61; As, 18·6. $C_{24}H_{20}AsB$ requires B, 3·68; As, 19·0%)].

The same compound (identical mixed m. p. and infrared spectrum) was obtained in 67% yield by the triethylamine method.

*(Diphenylarsino)di-*p*-tolylborane,* (p-Me·$C_6H_4)_2B$·$AsPh_2$, (69%), m. p. 224—225° (from benzene–hexane) (Found: C, 73·6; H, 5·6. $C_{26}H_{24}AsB$ requires C, 74·0; H, 5·7%), and the p-*bromophenyl analogue,* (p-$BrC_6H_4)_2B$·$AsPh_2$, m. p. 244—245° (67%) (from benzene–hexane) (Found: C, 52·3; H, 3·4. $C_{24}H_{18}AsBBr_2$ requires C, 51·2; H, 3·3%), were both prepared from the sodium derivative of diphenylarsine and the appropriate chlorodiarylborane.

The authors thank the Department of Scientific and Industrial Research for a maintenance grant (to J. G. L.), Borax Consolidated Ltd. for a gift of trimethoxyboroxine and Dr. G. Kohnstam for comments.

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[*Received, August* 17*th*, 1960.]