DALTON

Reversible adduct formation between phosphines and triarylboron compounds*

Donald C. Bradley, Ian S. Harding, Anthony D. Keefe, Majid Motevalli and Dao Hong Zheng

Department of Chemistry, Queen Mary and Westfield College, Mile End Road, London E1 4NS, UK

The acceptor strength of a number of Lewis-acidic fluorinated triarylboron compounds has been established and shown to depend on the amount and position of fluorine substitution. The donor strength of *tert*-butylphosphine has been found to be greater than phosphine towards these acceptor compounds; two series of adducts have been characterised and reversible adduct formation has been demonstrated for some adducts. Crystal structures of the phosphine adducts of tris(pentafluorophenyl)boron and tris(2,6-difluorophenyl)boron have been compared with those of the *tert*-butylphosphine adducts of tris(pentafluorophenyl)boron and tris(3,4,5-trifluorophenyl)boron to show a correlation between the length and the strength of the adduct bond. Mixing aryl groups in the acceptor compounds has not produced new adducts. The strong acceptor compounds have been found to form unstable adducts with water which act as drying agents ultimately producing arylboric acids; the crystal structure of (2,6-difluoropheny)dihydroxyborane has been determined.

For many years adducts have been known to form by reaction between molecules containing Group VB atoms bearing lone pairs and Group IIIB atoms. They have been the focus of renewed interest in recent years since they have been used in the growth of III–V semiconductors by metal–organic chemical vapour deposition (MOCVD). The emphasis of this work has been on the volatile trialkyls of aluminium, gallium and indium: initially to form volatile adducts which would quell the tendency of the metal alkyl towards prereaction,[1] then to form adducts which could incongruently vaporise to yield the metal alkyl when required. While the latter adducts are of little use as primary sources of metal trialkyl, they have proved very effective in purification.[2,3]

There has been far less emphasis on the chemistry of Group VB sources used in MOCVD, in part because they have been available at higher purities than the Group IIIB precursors. Typical Group VB sources are the hydrides: phosphine and arsine. Unfortunately their chemical activities are low and large overpressures are required to counteract loss of Group VB atoms from III–V semiconductors at growth temperatures. The large amounts required and existing general high purity of the Group VB hydrides has made adduct purification less attractive for them than for Group IIIB alkyls.

The tightening of safety regulations has become a driving force to find different Group VB sources and the monoalkylphosphines have proved to be safer alternatives to phosphine itself. An extra advantage is that certain alkyl groups improve the activity of phosphorus, reducing the amount of precursor required. Their syntheses are more involved, however, with more potential impurities introduced. The reduction in quantities and in purities make reversible adduct formation a viable purification route. This paper examines a set of triarylboron adducts with phosphine and *tert*-butylphosphine to determine factors important in reversible adduct formation as a purification route.

Results and Discussion

Phosphine adducts

The interaction of phosphine with a range of arylboron compounds has been studied by NMR spectroscopy. In the presence of an excess of phosphine the rate-determining step for phosphine exchange is dissociation of the adduct bond.[4] Hence the relative rate of exchange is a good probe of the order of adduct bond strengths. Proton NMR spectroscopy is a particularly good probe because a wide range of rates are revealed: exchanges faster than the NMR time-scale produce a shift in the phosphine peak position which depends on the adduct-free phosphine equilibrium (and hence the bond strength); exchanges slower than the NMR time-scale produce separate adduct and free-phosphine peaks. The coalescence temperature of these peaks is dependent on the exchange rate, while the increase in H–P coupling shows the degree of change in the orbital bonding within the phosphine moiety upon adduct formation. Details of spectra in deuteriotoluene at 223 K are listed in Table 1.

Table 1 Proton NMR data for phosphine when in excess in the presence of triarylboron compounds

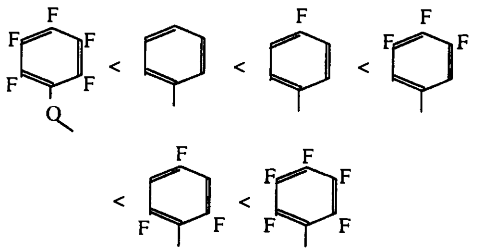
	High field		Low field	
Reactant	δ_1	$^1J_{PH}$/Hz	δ_2	$^1J_{PH}$/Hz
Free phosphine	—	—	1.56	187
Tris(pentafluorophenoxo)boron	—	—	1.56	187
Triphenylboron	—	—	1.67	204
Tris(4-fluorophenyl)boron	—	—	1.66	205
Tris(3,4,5-trifluorophenyl)boron	—	—	1.62	238
Tris(2,6-difluorophenyl)boron	3.42	395	1.58	188
Tris(pentafluorophenyl)boron	2.80	414	1.57	188

From these results it is clear that the presence of tris(pentafluorophenoxo)boron produces no change in the spectrum of phosphine, but that changes consistent with increasing interaction occur with other boron compounds down the table. Phosphine interacts *via* its lone pair with the vacant 2p orbital on boron and so these results reflect the availability of this vacant orbital to intermolecular bonding. Lone pairs on phenoxy oxygen atoms overlap with this vacant orbital to stabilise it, thus preventing reaction between tris(pentafluorophenoxo)boron and phosphine, as indicated by the lack of change in the NMR spectrum.

The triarylboron compounds all show varying degrees of change; for those without *o*-fluorine atoms there is a shift in the phosphine peak positions, showing an exchange of phosphine environments (presumably free phosphine and adduct) which

---

* *Non-SI unit employed:* mmHg ≈ 133 Pa.



Scheme 1 Strength of interaction of triarylboron compounds with phosphine as a function of the aryl group

is faster than the NMR time-scale. The two triarylboron compounds with *o*-fluorine atoms show separate signals for free phosphine and adduct, showing a phosphine exchange which is slower than the NMR time-scale.

The orbital overlap which stabilises the vacant boron orbital against attack by Lewis bases must therefore be more limited when it is an aromatic π system which neighbours the boron rather than an oxygen atom. This must be due in part to the non-planar arrangement of the aromatic groups in triaryl systems compared to the flat molecular geometry of triphenoxy systems.[5,6] Furthermore, the extent of π-system overlap with the vacant boron p orbital is clearly dependent upon the extent of fluorine substitution. Increased substitution of electronegative fluorine atoms gives less overlap from a depleted π system, so a stronger interaction can form with phosphine. This is modified by the position of fluorine substitution, the closer *ortho* position being the most important.

The strength of the adduct bond in phosphine–tris(pentafluorophenyl)boron **1** is sufficient that the separate peaks for free and bonded phosphine persist even at room temperature. Below −5 °C each peak of the adduct doublet is split further into a septet by the six *o*-fluorines on the phenyl groups. The coupling constant, $^5J_{FH}$, is about 5.3 Hz which is unusually large for fluorine coupling through five bonds. The persistence of clear adduct peaks has allowed extensive study of this system by NMR spectroscopy and an activation energy of 126 kJ mol^{-1} has been determined for dissociation of this strongest adduct bond in solution.[4]

Coalescence is more prevalent in the ^{1}H NMR spectrum of phosphine–tris(2,6-difluorophenyl)boron **2** in the presence of an excess of phosphine than with **1**. Thus adduct and free phosphine peaks remain resolved at room temperature while in the case of **2** they coalesce between −40 and −20 °C. Also, the septet fine structure found in the adduct doublets of **1** does not resolve for **2**, even at −80 °C. Finally, the greater coupling between phosphorus and its protons in **1** (414 Hz) than **2** (395 Hz) shows a greater change in the phosphorus orbitals when bonding to the pentafluoro than the difluoro derivative. These all indicate the adduct bond is stronger in **1** than in **2**. These conclusions are summarised in Scheme 1.

The di- and penta-fluoro derivatives were the only two compounds to give adduct precipitates in larger-scale experiments. The adduct phosphine–tris(pentafluorophenyl)boron **1** gave phosphine in appreciable amounts at 50 °C *in vacuo*, demonstrating its potential for reversible adduct formation. The two solid phosphine adducts have been crystallised and their molecular structures determined by X-ray crystallography. Adduct **1** has been briefly reported previously,[7] but the structure of phosphine–tris(2,6-difluorophenyl)boron **2** is shown here for the first time (Fig. 1). They are both discussed more fully below.

tert-Butylphosphine adducts

As mentioned in the introduction, there has been a shift in use from phosphine itself to alkylphosphines, and *tert*-butylphosphine has been chosen here to determine general factors important in reversible adduct formation of alkylphosphines. The interaction of *tert*-butylphosphine with four arylboron compounds has been studied by ^{1}H NMR spectroscopy in a manner similar to that used for phosphine. The results are presented in Table 2.

Once again there is a dramatic change across the group of acceptor compounds. For triphenylboron there is no evidence of interaction, but all the fluorinated triarylboron compounds produce adduct and free phosphine peaks. The two highest coupling constants, $^1J_{PH}$, for the adduct peaks come from adducts with *o*-fluorine atoms, suggesting these to be the stronger adducts, with perfluorination producing the strongest adduct bond. The chemical shifts do not follow this trend, however, presumably because of solvent effects.

The coalescence temperature of free and bound phosphine peaks, combined with the peak separation, can also give insights into the order of acceptor strength because it is a probe of the activation energy or dissociation.[8] Dissociation of phosphine has been established as an S_N1 process;[4] this is unlikely to be different for the more sterically hindered *tert*-butylphosphine. The activation energy of dissociation therefore corresponds closely in magnitude with the thermodynamic bond enthalpy for adduct formation and any trend in the former should therefore be directly reflected in a corresponding trend in the adduct bond strengths. Thus tris(pentafluorophenyl)boron forms the strongest adduct bond because it has the highest coalescence temperature, observed between 360 and 380 K. Both the tri- and di-fluoro derivatives have coalescence temperatures between 240 and 260 K, but tris(2,6-difluorophenyl)boron forms the stronger adduct because its coalescing peaks are initially further apart. This confirms that the order of acceptor strengths of the boron compounds, as shown in Scheme 1, is the same for both phosphines.

tert-Butylphosphine adducts of tris(pentafluorophenyl)boron **3**, tris(2,6-difluorophenyl)boron **4** and tris(3,4,5-trifluorophenyl)boron **5** have been isolated by crystallisation from light petroleum and their thermolysis behaviour has been studied. Heating all these samples at 57 °C for 120 h *in vacuo* produced no *tert*-butylphosphine from the pentafluoro derivative **3**, about 50% of the total possible from the trifluoro derivative **5** and an almost quantitative yield from the difluoro derivative **4**. The last two results show clearly that reversible adduct formation for *tert*-butylphosphine is possible. Such a thermolysis study does not give unambiguous thermodynamic data, however. For example, the change in order from that predicted from acceptor strengths may represent differences in factors that affect vaporisation kinetics, *i.e.* sample grain sizes.

The complete lack of dissociation in the pentafluorophenyl compound **3** has been confirmed by studies at other temperatures with varying background pressures. It was not possible to produce incongruent vaporisation under any conditions; even at 105 °C (10^{-2} mmHg) the compound sublimed congruently. Thus, while the general order of acceptor strength is maintained in the boron compounds, *tert*-butylphosphine is found to be a much stronger lone-pair donor than phosphine. This reflects the increase in electron density on phosphorus caused by the electroinductive *tert*-butyl group, and shows that steric bulk is not the only factor in predicting adduct bond strengths.

The structures of two of the adducts have been determined by X-ray crystallography on the samples recrystallised from light petroleum. The structure of the *tert*-butylphosphine adduct of tris(pentafluorophenyl)boron **3** is presented in Fig. 2 and that of tris(3,4,5-trifluorophenyl)boron **5** in Fig. 3.

Crystal structures of the adducts

Crystal data for the four adducts are presented in Table 3. Clearly, the molecular packing is sensitive to both fluorine substitution and the introduction of a *tert*-butyl group into the

Table 2 Proton NMR data for *tert*-butylphosphine when in excess in the presence of triarylboron compounds

	Adduct		Free PBu^tPh_2	
Reactant	δ_1	$^1J_{PH}$/Hz	δ_2	$^1J_{PH}$/Hz
tert-Butylphosphine	—	—	2.83	186
	—	—	(1.09)	(12)
Triphenylboron	—	—	2.83	186
	—	—	(1.09)	(12)
Tris(3,4,5-trifluorophenyl)boron	2.48	364	2.83	186
	(0.16)	(15)	(1.09)	(12)
Tris(2,6-difluorophenyl)boron	4.44	387	2.83	186
	(0.63)	(14)	(1.09)	(12)
Tris(pentafluorophenyl)boron	3.91	400	2.83	186
	(0.31)	(16)	(1.09)	(12)

Values for the alkyl protons are given in parentheses.

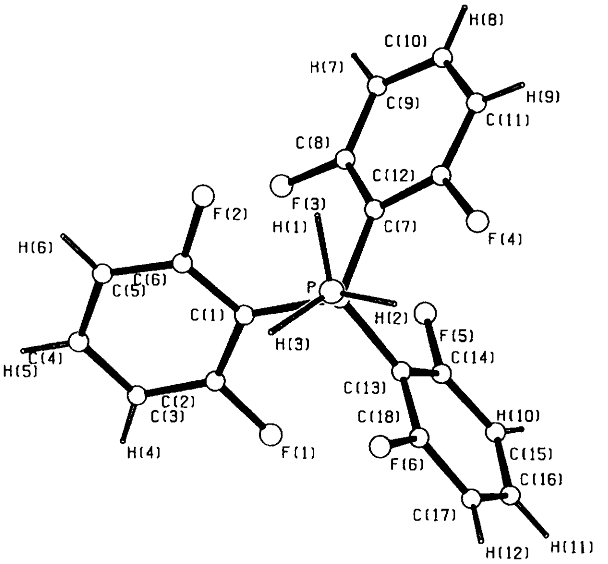


Fig. 1 Crystal structure of the phosphine adduct of tris(2,6-difluorophenyl)boron **2**

structure. The molecules in **1** all lie on three-fold axes, with three unique molecules in the unit cell. The three-fold axes pass along each adduct bond, giving the molecules C_3 symmetry. None of the other adducts has any molecular symmetry, but there are two molecules in the asymmetric unit of **3** compared to one in both **2** and **5**. Selected bond lengths and angles from these compounds are listed in Table 4.

The strength of adduct bonding determines the thermolysis behaviour of the adducts; two different behaviours have been observed. The stronger Lewis base, *tert*-butylphosphine, reacts with the strongest Lewis acid, tris(pentafluorophenyl)boron, to give an adduct **3** which vaporises congruently, a behaviour different from the other adducts, which vaporise incongruently. This is reflected in the adduct bond lengths: the two shortest, hence strongest, adduct bonds are found in **3**.

Another possible source of binding that holds phosphines in these adducts is an interaction between fluorine atoms and phosphine hydrogens in a manner akin to hydrogen bonding. While it is not typical for phosphines to hydrogen bond, adduct formation withdraws considerable electron density from the phosphorus, and hence hydrogens, making the strength of the dipolar interaction approach that of a hydrogen bond. The van der Waals radii of fluorine and hydrogen are 1.35 and 1.2 Å respectively, so non-bonding H··· F separations of less than 2.55 Å may indicate such an interaction. On this basis all the adducts show a degree of intermolecular F··· H interaction, the closest being 2.385 Å in the first molecule in the unit cell of **1**.

Intramolecular interaction must occur *via* the *o*-fluorine atoms; the shortest intramolecular separations are found in the two unique molecules of **3**, at 2.337 and 2.357 Å, with one at 2.407 Å in **2**. The uncertainty in position of the hydrogen atoms, however, means that these figures cannot by themselves show that such interactions are occurring. Both steric repulsions and intramolecular hydrogen bonds should, however, produce distortions about the adduct bond. There are no distortions expected from steric repulsions of phosphine, thus **1**, with only intermolecular F··· H interactions, retains three-fold symmetry around the adduct bond. Steric repulsion of *tert*-butylphosphine will bend back the *tert*-butyl group and the aryl ring it is repelling, resulting in one wider and two narrower angles between the adduct bond and the aryl groups, as found in **5**. The tilting produced by an attractive interaction for one of the phosphine hydrogens is different, however, producing one wide, one narrow and one intermediate angle of the aryl groups to the adduct bond, as found in both **2** and **3**.

Distortions of the aryl groups around the adduct bond can therefore be attributed to steric repulsions from the *tert*-butyl groups and attractive intermolecular F··· H interactions, combined appropriately. Also, the adduct bonds in **2** and **3**, where attractive intramolecular attractions are evident, are also shorter than in **1** and **5**, where they are not. Thus there is evidence for interaction akin to hydrogen bonding in all the appropriate structural parameters not affected by the uncertainty in hydrogen-atom positions.

Mixed arylboron compounds

Perfluorination produces such a strong acceptor compound that adducts will only dissociate if the Lewis base is a very weak donor like phosphine. For stronger Lewis bases, like the alkylphosphines, fluorination must be limited to engineer reversible adduct formation. The adducts detailed above all have a symmetric distribution of fluorine atoms but synthesis of their parent triarylboron compounds is more difficult than for either tris(pentafluorophenyl)boron or triphenylboron due to the instability of partially fluorinated arylating agents.

Limiting the fluorination by mixing phenyl and pentafluorophenyl groups on the boron is therefore a possibility. First it is necessary to investigate which intermediate compositions form stable triarylboron compounds; this has been established by an ^{11}B NMR study of mixtures of triphenylboron and tris(pentafluorophenyl)boron. Between the peaks for pure triphenylboron (at δ 67.8) and pure tris(pentafluorophenyl)boron (at δ 59.6) only one new peak appeared at δ 67.4, corresponding to a molecular formula of $BPh_2(C_6F_5)$. Other intermediate compositions produced two of these three peaks with appropriate integration. There was no evidence of a monophenyl derivative.

In the stable intermediate, electron withdrawal from the boron by one fluorinated aryl group must therefore be balanced by electron supply to it from the two phenyl groups. This

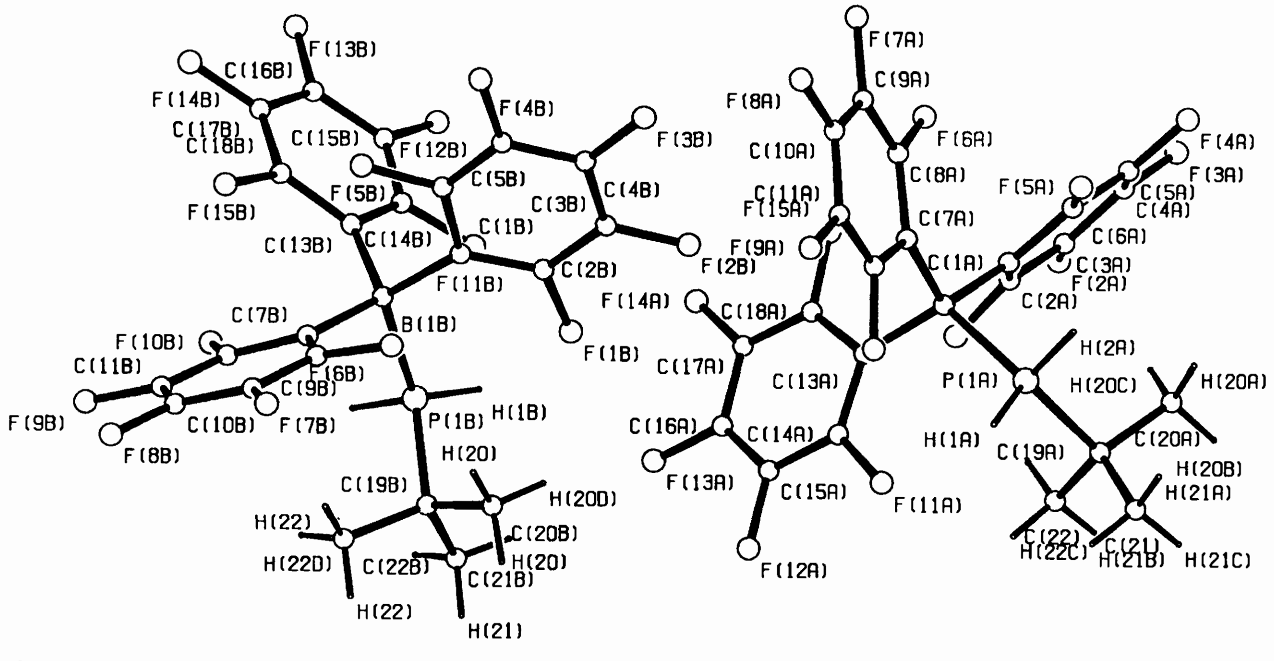


Fig. 2 Crystal structure of the *tert*-butylphosphine adduct of tris(pentafluorophenyl)boron **3**

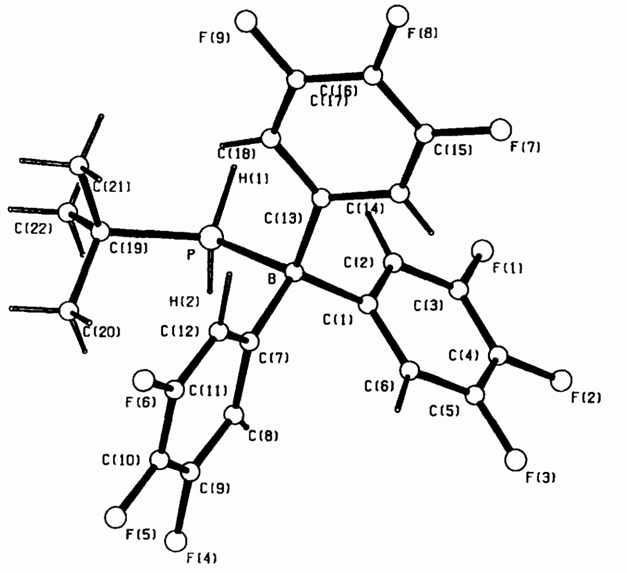


Fig. 3 Crystal structure of the *tert*-butylphosphine adduct of tris(3,4,5-trifluorophenyl)boron **5**

balance would presumably be lost when two fluorinated alkyl groups compete against one phenyl group. Thus stable intermediates can only form when delocalisation provides sufficient electron density to the nominally vacant p orbital on boron, as found in the reactant triphenylboron.

Control over delocalisation into the boron p orbital has been demonstrated in (pentafluorophenyl)diphenylboron. On adding an equimolar amount of *tert*-butylphosphine to this boron compound two peaks were found in the ^{11}B NMR spectrum; one at δ 56.1 associated with triphenylboron in the presence of *tert*-butylphosphine and the other, a sharp peak at δ −16.9, identified as the tris(pentafluorophenyl)boron adduct of *tert*-butylphosphine. This suggests that the arylboron compound rearranges in the presence of *tert*-butylphosphine. This was confirmed by removing the solvent from this solution; about 60% of the *tert*-butylphosphine was removed with the solvent and a ^1H NMR spectrum of the residue showed the ratio of phenyl protons to *tert*-butyl protons to be 10:3. These results would be expected for the reaction sequence in Scheme 2. From this scheme it is clear that using mixed aryl groups to reduce the fluorination does not give a convenient approach to reversible adduct formation. This is because a Lewis base is an additional source of electron density for the boron p orbital, which no longer needs adjacent phenyl groups to counter the effect of fluorine. The most stable situation becomes a return to the extremes: boron is stabilised in the first case by electron donation from *tert*-butylphosphine, which more than balances that lost to three pentafluorophenyl groups, and in the second case by electron donation from three phenyl groups, which produces a delocalised structure with no need for the extra electron density an adduct bond could supply.

$$3BPh_2(C_6F_5) + 3PBu^tH_2$$

$$\downarrow$$

$$2(BPh_3{\cdot}PBu^tH_2) + (C_6F_5)_3B{\cdot}PBu^tH_2$$

weak adduct strong adduct

$$\Big\downarrow \text{remove volatiles}$$

$$2BPh_3 + (C_6F_5)_3B{\cdot}PBu^tH_2$$

proton ratio: 30 9

Scheme 2

Hydrolysis of triarylboron compounds

It is important to study the hydrolysis of triarylboron compounds because water is a likely impurity in alkylphosphines. With the vapour pressure of alkylphosphines reduced compared to that of phosphine itself, standard distillation becomes a far less effective drying method for new precursors. Group VB precursors must be dry, however, because any residual water would severely complicate the MOCVD process. Reversible adduct formation may therefore be a route for drying if the triarylboron compounds do not form a complex with water, form a strong adduct with water or hydrolyse to give either involatile or very volatile decomposition products.

The hydrolysis reaction was investigated by adding an equimolar amount of water to a solution of tris(pentafluorophenyl)boron, in a manner analogous to the formation of the phosphine adducts. In pentane a white precipitate formed which was isolated; the solution reaction, however, was monitored by NMR spectroscopy using deuteriated toluene as a solvent.

The infrared spectrum of the precipitate shows several differences from that of the parent boron compound.

Table 3 Crystal data for the adducts **1**–**3** and **5** and the arylboric acid **6**

	1[7]	**2**	**3**	**5**	**6**
Empirical formula	$C_{18}H_3BF_{15}P$	$C_{18}H_{12}BF_6P$	$C_{22}H_{11}BF_{15}P$	$C_{22}H_{17}BF_9P$	$C_6H_5BF_2O_2$
M	545.98	384.06	602.09	494.14	157.91
Crystal system	Trigonal	Orthorhombic	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{3}$	$P2_12_12_1$	$P\bar{1}$	$P2_12_12_1$	$P2_1/n$
a/Å	15.065(1)	9.478(1)	11.154(1)	10.345(1)	23.631(3)
b/Å	15.065(1)	12.983(2)	12.459(1)	13.996(1)	5.498(10)
c/Å	14.614(1)	13.315(2)	17.456(2)	14.674(1)	5.033(10)
α/°			86.94(1)		
β/°			82.27(1)		91.61(1)
γ/°			76.82(1)		
U/Å	2872.4(3)	1638.4(4)	2339.8(4)	2124.6(3)	654(2)
Z	6	4	4	4	4
D_c/Mg m^3	1.894	1.557	1.709	1.545	1.605
μ(Mo-Kα)/mm^{-1}	0.292	0.230	0.248	0.215	0.151
F(000)	1596	776	1192	1000	320
Independent reflections, n	3375	1670	8206	2135	1322
Observed reflections	5588	1709	8892	2217	1144
Parameters, p	329	250	731	336	120
R[a]	0.0374	0.0432	0.0402	0.0480	0.0428
R[b]	0.0987	0.0981	0.0987	0.1081	0.1092
Goodness of fit[c]	1.056	0.840	1.064	0.909	1.097

[a] For $I > 2\sigma(I)$, $R = \Sigma|F_o - F_c|/\Sigma|F_o|$. [b] $R' = [\Sigma(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. [c] $[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$. $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$.

Table 4 Selected bond lengths (Å) and angles (°) for adducts **1**–**3** and **5**

	1[7]	**2**	**3**[a]	**3**[b]	**5**
B–P	2.046(5)[c] 2.046(5)[d] 2.055(5)[e]	2.038(6)	2.015(3)	2.034(3)	2.048(6)
P–H(1)	1.29(3)[c]	1.31(7)	1.30(3)	1.32(2)	1.36(4)
P–H(2)	1.35(3)[d]	1.24(6)	1.28(2)	1.26(2)	1.35(6)
P–H(3)	1.33(3)[e]	1.34(6)			
B–P–H(1)	114.5(14)[c]	109(3)	115.8(12)	115.4(11)	109(2)
B–P–H(2)	117.0(11)[d]	117(3)	104.7(11)	105.2(10)	109(2)
B–P–H(3)	117.7(12)[e]	119(3)			
B–P–C			123.6(1)	124.8(1)	128.2(2)
P–B–C(1)	104.1(2)[c]	101.7(4)	99.6(2)	114.9(2)	103.2(3)
P–B–C(7)	104.8(2)[d]	104.0(4)	106.6(2)	100.8(2)	102.6(4)
P–B–C(13)	104.0(2)[e]	108.6(4)	113.4(2)	106.1(2)	111.2(4)

[a] Parameters for first molecule in unit cell. [b] Parameters for second molecule in unit cell. [c] Parameters for first molecule with three-fold symmetry in unit cell. [d] Parameters for second molecule with three-fold symmetry in unit cell. [e] Parameters for third molecule with three-fold symmetry in unit cell.

Assignment of these changed peaks is difficult because many of them are to be expected in the same region, *viz* the B–C stretches (influenced by a change in symmetry about boron), the new B–O stretch and the H–O–H bends will all occur between 1600 and 800 cm^{-1}. Fortunately, the symmetric and asymmetric O–H stretching frequencies can be clearly identified as two sharp peaks at 3501 and 3558 cm^{-1} respectively. The presence of two such peaks shows that the water molecules remain intact in the precipitate, which can thus be identified as an adduct. The ^{1}H NMR spectrum shows a single peak at δ 4.80 corresponding to the water in this adduct.

The adduct itself is not thermally stable, however. In the ^{1}H NMR, two new signals of approximately equal intensity appear when the solution is heated to 70 °C which persist when the solution is cooled. These are a complex multiplet between δ 5.75 and 5.90 and a quintet at δ 6.30 (J = 1.7 Hz). The former is the signal from pentafluorobenzene, indicating elimination of one of the aryl groups and formation of a hydroxoboron species. The hydroxoboron species is therefore the other group; the coupling indicates four equivalent nearby fluorines on the boron aryls, suggesting two pairs of *o*-fluorine atoms in a monomer: hydroxobis(pentafluorophenyl)boron.

Such a decomposition is confirmed in the solid. While the solid adduct can be sublimed at 70 °C (10^{-2} mmHg), and its melting point can be established as 114–115 °C by quick heating under nitrogen, when it is heated to 90 °C for half an hour, cooled, then placed *in vacuo*, it gives off pentafluorobenzene and water (identified by NMR spectroscopy). A mass spectrum of the residue shows only the presence of tris(pentafluorophenyl)boron, indicating any hydroxoboron species produced during decomposition must be less volatile than this acceptor compound (at least in the mass spectrometer).

The triarylboron compounds may thus act as final drying agents for alkylphosphines when they are hot (around 90 °C) which will occur during a recrystallisation of the adduct from toluene. All decomposition products (except pentafluorobenzene, which will remain with the solvent) are less volatile than tris(pentafluorophenyl)boron and so will not contaminate the alkylphosphine during thermolysis of its adduct.

Monohydroxyarylboranes are susceptible to further hydrolysis. Exposure to air produces extra O–H stretches in the infrared while slow hydrolysis of solutions can yield crystals of arylboric acids. One such has been characterised by X-ray crystallography. The structure of (2,6-difluorophenyl)dihydroxyborane **6** is presented in Fig. 4 and selected bond lengths and angles are listed in the Experimental section. Arylboric acids are also much less volatile than the corresponding triarylboron species, so once again will not interfere with the dehydration process during reversible adduct formation.

Conclusion

tert-Butylphosphine has been shown to undergo reversible adduct formation with partially fluorinated triarylboron compounds. This fact, combined with the discovery of dehydrating properties in the triarylboron compounds, indicates the adducts show great promise as agents for the purification of alkylphosphines for MOCVD.

Experimental

All compounds are air and moisture sensitive and were handled under inert atmospheres using standard Schlenk techniques. Light petroleum (b.p. 60–80 °C) (Analar, BDH) was dried by heating under reflux over the sodium ketyl of benzophenone, then distilled prior to use. Deuteriated toluene was dried over molecular sieves (3 Å). Phosphine (Air Products) and *tert*-

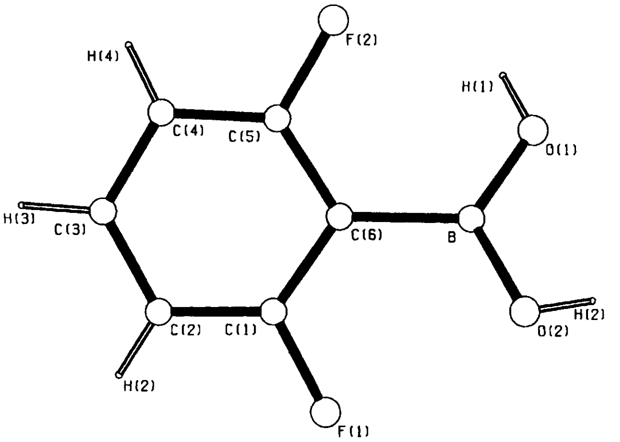


Fig. 4 Crystal structure of (2,6-difluorophenyl)dihydroxyborane **6**

butylphosphine (Epichem) were used as supplied. The preparation of triarylboron compounds[9] and their adducts phosphine–tris(pentafluorophenyl)boron **1** and –tris(2,6-difluorophenyl)boron **2**[7] has been detailed elsewhere. The NMR spectra at room temperature were recorded on a Bruker WP80, the variable-temperature spectra and ^{11}B on a Bruker WP250 spectrometer, all recorded in deuteriated toluene. Mixtures of adduct and phosphine had the phosphine in approximately two- to five-fold excess. Infrared spectra were recorded on a Perkin-Elmer 1720 X spectrometer.

Synthesis

***tert*-Butylphosphine adducts 3–5.** A solution of *tert*-butylphosphine (0.39 g, 4.33 mmol) in light petroleum (20 cm^3) was added to an equimolar amount of the triarylboron compound in light petroleum (20 cm^3). The solution was stirred for 48 h and the resulting white precipitate isolated by decanting the supernatant and drying *in vacuo*. Further crystals were grown from the supernatant by cooling. The combined yields were near quantitative. Their exact thermal behaviour in nitrogen was dependent on the rate of heating, but decomposition to a liquid at 140 °C was typical. Owing to the chemical composition of these compounds it was not possible to obtain reliable elemental analyses of the adducts. However, heating **4** or **5** *in vacuo* to temperatures below the decomposition temperature (*i.e.* < 140 °C) generated a vapour of *tert*-butylphosphine which was distilled off slowly to leave the appropriate acceptor compound: $\text{PBu}^t\text{H}_2\cdot\text{B(C}_6\text{F}_5)_3$ **3**, sublimes at 105 °C (10^{-2} mmHg), δ_H(80 MHz, solvent $\text{C}_6\text{D}_5\text{CD}_3$, 295 K) 0.48 (9 H, d, J_PH 16, Bu^t) and 4.28 (2 H, d, J_PH 394, PH$_2$); $\text{PBu}^t\text{H}_2\cdot\text{B(C}_6\text{F}_2\text{H}_3)_3$ **4**, δ_H(80 MHz, solvent $\text{C}_6\text{D}_5\text{CD}_3$, 295 K) 0.76 (9 H, d, J_PH 14, Bu^t), 4.68 (2 H, d, J_PH 375, PH$_2$) and 6.62 (9 H, m, $\text{C}_6\text{F}_2\text{H}_3$); $\text{PBu}^t\text{H}_2\cdot\text{B(C}_6\text{F}_3\text{H}_2)_3$ **5**, δ_H(80 MHz, solvent $\text{C}_6\text{D}_5\text{CD}_3$, 295 K) 0.44 (9 H, d, J_PH 15, Bu^t), 3.33 (2 H, d, J_PH 318 Hz, PH$_2$) and 6.67 (6 H, m, $\text{C}_6\text{F}_3\text{H}_2$).

Crystallography

The crystal structure of compound **1** has been detailed previously.[7] Data from this crystal structure are presented here for comparison with the other adducts. The clear, colourless crystals of **2**, **3** and **5** were mounted under nitrogen in Lindemann capillaries, as was a crystal of (2,6-difluorophenyl)-dihydroxyborane **6**, assumed to be air-sensitive until it was characterised. Data for all crystal structures were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-Kα radiation (λ 0.710 69 Å) over a θ range from 1.5 to 25°. Unit-cell parameters were determined by least-squares analysis of 25 automatically centred reflections in the range $10 < \theta < 15°$ (refinement based on F). The data were corrected for Lorentz-polarisation and absorption effects.

Structures were solved and refined using the programs SHELXS 86 and SHELXL 93.[10] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were geometrically idealised and refined isotropically (riding model). The crystal data are compared in Table 3. Important structural parameters of compound **6**, a hydrolysis product of a sample of **4**, are B–O(1) 1.351(4), B–O(2) 1.341(4), B–C(6) 1.578(4) Å, O(1)–B–O(2) 118.1(2), O(1)–B–C(6) 122.5(2) and O(2)–B–C(6) 119.5(2)°.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/205.

Acknowledgements

We thank Air Products Ltd. (D. H. Z.), the Link scheme 'Alternative phosphorus precursors for MOCVD growth of InP and related materials' (I. S. H., A. D. K.), the SERC for financial support and Epichem Ltd. for supply of *tert*-butylphosphine.

References

1 R. H. Moss and J. S. Evans, *J. Cryst. Growth*, 1981, **55**, 129.
2 D. C. Bradley, H. Chudzynska, M. M. Faktor, D. M. Frigo, M. B. Hursthouse, B. Hussain and L. M. Smith, *Polyhedron*, 1988, **7**, 1289.
3 A. H. Moore, M. D. Scott, J. I. Davies, D. C. Bradley, M. M. Faktor and H. Chudzynska, *J. Cryst. Growth*, 1986, **77**, 19.
4 D. C. Bradley, G. E. Hawkes, P. R. Haycock, K. D. Sales and D. H. Zheng, *Philos. Trans. R. Soc. London, Ser. A*, 1994, **384**, 315.
5 D. B. Cook and P. Palmieri, *Chem. Commun.*, 1969, 1327.
6 S. X. Xiao, W. C. Trogler, D. E. Ellis and Z. Berkovitch-Yellin, *J. Am. Chem. Soc.*, 1983, **105**, 7033.
7 D. C. Bradley, M. B. Hursthouse, M. Motevalli and D. H. Zheng, *J. Chem. Soc., Chem. Commun.*, 1991, 7.
8 H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 1956, **25**, 1228.
9 A. G. Massey and A. J. Park, *J. Organomet. Chem.*, 1964, **2**, 245.
10 G. M. Sheldrick, SHELXS 86, University of Göttingen, 1986; SHELXL 93, University of Göttingen, 1993.

Received 2nd April 1996; Paper 6/02313D