An Electron Spin Resonance Study of Phosphine-boryl Radicals; their Structures and Reactions with Alkyl Halides

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A number of phosphine-boryl radicals $X_3\overset{+}{P}\text{–}\overset{-}{B}H_2^{\bullet}$(**2**; X = MeO, CF_3CH_2O, Me_2N, Et, Bu^n, Bu^t) have been generated in solution by hydrogen abstraction from the phosphine-boranes $X_3\overset{+}{P}\text{–}\overset{-}{B}H_3$ and characterised by e.s.r. spectroscopy. The boron radical centre in (**2**) is effectively planar and the unpaired electron is contained mainly in a B-$2p_\pi$ orbital, although the low *g*-factors (*ca.* 2.0020) provide some evidence for the energetic proximity of an excited state in which the unpaired electron occupies a B–P σ^* orbital. The phosphine-boryl radicals are less reactive than the borane radical anion $H_3B^{-\bullet}$ and fail to add to benzene, ethylene, or vinyltrimethylsilane. They do abstract halogen atoms from alkyl bromides but not, in general, from alkyl chlorides, although (**2**; X = alkyl) does abstract chlorine from benzyl chloride. Selectivity in bromine abstraction increases in the order $H_3B^{-\bullet} < H_2\dot{B}CN^- \simeq$ (**2**; X = Bu^n, Me_2N) < (**2**; X = MeO) < (**2**; X = CF_3CH_2O) and the relatively high selectivity of the fluorine-containing radical is attributed to polar effects.

Very little is known about the boryl radicals ($X_2B^{\bullet}$). The prototype species $H_2B^{\bullet}$ has been well characterised in the gas phase by optical absorption spectroscopy and shown to be a non-linear σ radical.[1] The only other boryl radicals known appear to be $F_2B^{\bullet}$ [2] and $H\dot{B}O^-$,[3] which were identified on the basis of e.s.r. spectra attributed to these species trapped in rigid matrices at low temperatures.

In a preliminary communication,[4] we reported that trialkylphosphine complexes of $H_2B^{\bullet}$ can be readily generated for e.s.r. study in solution by abstraction of hydrogen from the corresponding phosphine-boranes [equation (i)] and in this

$$Bu^tO^{\bullet} + R_3\overset{+}{P}\text{–}\overset{-}{B}H_3 \longrightarrow Bu^tOH + R_3\overset{+}{P}\text{–}\overset{-}{B}H_2^{\bullet} \quad \text{(i)}$$

paper we present a full account of our investigations of the structures and reactions of these phosphine-boryl radicals.

Results

E.s.r. spectra were recorded during continuous u.v. irradiation of cyclopropane solutions containing di-t-butyl peroxide (DTBP; 15% v/v) and the phosphine-borane complex (15% v/v), while the sample was in the spectrometer cavity. The temperature range was generally *ca.* 180—250 K. With trimethyl phosphite-borane (**1**; X = MeO) the well resolved spectrum shown in Figure 1a was obtained and we assign this to the phosphine-boryl radical (**2**; X = MeO). The pattern of

$$\underset{(\mathbf{1})}{Bu^tO^{\bullet} + X_3\overset{+}{P}\text{–}\overset{-}{B}H_3} \longrightarrow \underset{(\mathbf{2})}{Bu^tOH + X_3\overset{+}{P}\text{–}\overset{-}{B}H_2^{\bullet}} \quad \text{(ii)}$$

stronger lines arises from coupling of the unpaired electron with ^{11}B (14.6 G), ^{31}P (44.0 G), and with two equivalent protons (16.6 G). The weaker lines are assigned to radicals which contain ^{10}B in natural abundance† and the computer simulation shown in Figure 1b is in good agreement with the experimental spectrum. The deuteriated analogue $(MeO)_3\overset{+}{P}\text{–}\overset{-}{B}D_2^{\bullet}$ was generated in a similar way from $(MeO)_3\overset{+}{P}\text{–}\overset{-}{B}D_3$ and showed the expected e.s.r. spectrum in which the 16.6 G triplet was replaced by a 1:2:3:2:1 quintet splitting of 2.55 G from two equivalent deuterons. However, at a given temperature the magnitudes of *a*(P) and *a*(^{11}B) were, respectively, larger and smaller than the corresponding values for $(MeO)_3\overset{+}{P}\text{–}\overset{-}{B}H_2^{\bullet}$.

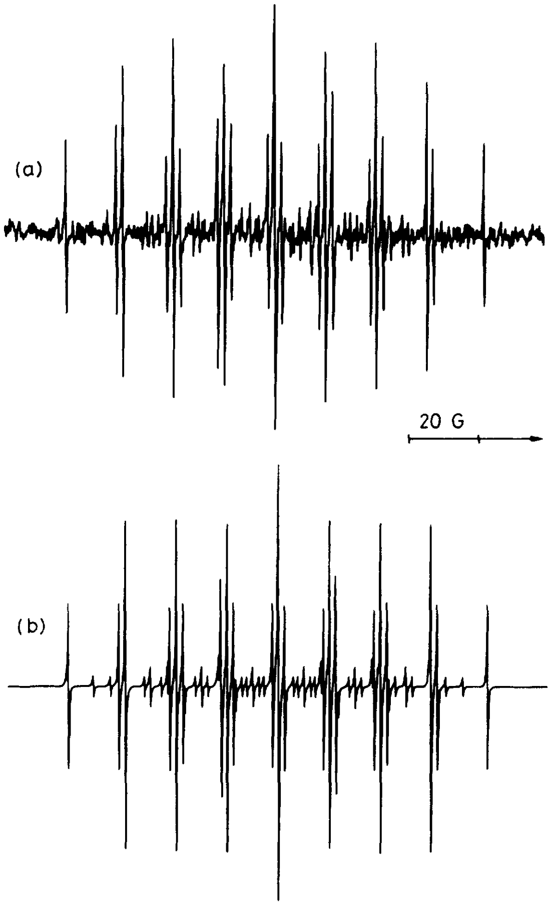

Figure 1. (a) E.s.r. spectrum of the trimethyl phosphite-boryl radical in cyclopropane at 198 K. The more intense lines are from $(MeO)_3\overset{+}{P}\text{—}^{11}\overset{-}{B}H_2^{\bullet}$, the weaker lines are from $(MeO)_3\overset{+}{P}\text{—}^{10}\overset{-}{B}H_2^{\bullet}$. (b) Computer simulation of (a) as a superposition of spectra from the ^{11}B- and ^{10}B-containing radicals present in natural abundance

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† Naturally occurring boron consists of 81.2% ^{11}B (*I* 3/2) and 18.8% ^{10}B (*I* 3): ($\gamma_{^{10}B}/\gamma_{^{11}B}$) is 0.335.

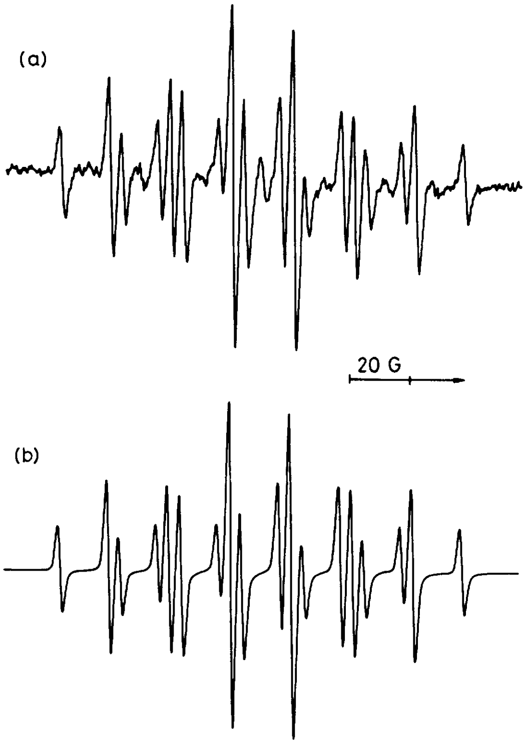


Figure 2. (a) E.s.r. spectrum of the tri-t-butylphosphine-boryl radical in cyclopropane at 181 K. (b) Computer simulation of the spectrum of $Bu^t_3\overset{+}{P}-{}^{11}\overset{-}{B}H_2^{\bullet}$; the extra weak lines present in (a) are from the ^{10}B-containing radical

The spectrum of (**2**; X = MeO) was also obtained when the DTBP was replaced with tetrakis(trimethylsilyl)hydrazine[5] as a photochemical source of hydrogen-abstracting bis(trimethylsilyl)aminyl radicals [equation (iii)], but no spectra were detected when the phosphine-borane was photolysed alone in cyclopropane.

$$(Me_3Si)_2NN(SiMe_3)_2 \xrightarrow{h\nu} 2(Me_3Si)_2N^{\bullet} \quad \text{(iii)}$$

Phosphine-boryl radicals were also generated by hydrogen-atom abstraction from several other phosphine complexes of borane and the e.s.r. parameters of (**2**; X = CF_3CH_2O, Me_2N, Et, Bu^n, and Bu^t) are given in Table 1. The spectrum of (**2**; X = Bu^t) is shown in Figure 2 together with a computer simulation for the ^{11}B-containing radical.

Detection of Phosphoranyl Radicals.—In addition to the e.s.r. spectrum of (**2**; X = MeO) a comparatively weak spectrum of the phosphoranyl radical $(MeO)_3\dot{P}OBu^t$ [a(P) 888.4 G, g 2.0019 at 203 K][6] was observed during photolysis of DTBP in the presence of $(MeO)_3\overset{+}{P}-\overset{-}{B}H_3$ between 175 and 215 K. This phosphoranyl radical was detectable immediately after beginning photolysis of a fresh sample, although its concentration did increase during continued irradiation. The radical presumably arises from addition of t-butoxyl radicals to free trimethyl phosphite,[7] although the origin of the latter is uncertain. N.m.r. spectroscopic analysis (^1H and ^{31}P) of the purified phosphine-borane showed the presence of only *ca.* 0.05% $(MeO)_3P$. However, the phosphite is highly reactive towards addition of alkoxyl radicals and further small amounts could be formed by photochemical cleavage of the B-P bond in (**1**) and/or as a breakdown product of the phosphine-boryl radical [possibly as shown in equation (iv)]. Although no spectrum which might be attributed to $H_2B^{\bullet}$ was detected between 175 and 300 K, the possibility of slow formation of $(MeO)_3P$ by this route cannot be excluded even at low temperatures.

Table 1. E.s.r. parameters for phosphine-boryl radicals $X_3\overset{+}{P}-\overset{-}{B}H_2^{\bullet}$ in cyclopropane

			Hyperfine splittings[a] (G)			
X	*T*/K	*g*-Factor[a]	$a(^{31}P)$	$a(^{11}B)$	a(2H)	Others
MeO	175	2.0019	44.1	14.5	16.6	
	215	2.0019	43.9	14.7	16.6	
	255	2.0019	43.4	15.1	16.6	
MeO[b]	175	2.0020	44.4	13.4		2.55 (2D)
	215	2.0020	44.2	13.9		2.55 (2D)
	255	2.0019	44.0	14.2		2.55 (2D)
CF_3CH_2O	174	2.0023	42.2[c]	13.8[c]	16.3[c]	
Me_2N[d]	211	2.0020	42.5	16.7	16.3	2.0 (3N)
Et[e]	183	2.0020	43.6[c]	17.6[c]	16.8[c]	
Bu^n	168	2.0020	43.8[c]	17.4[c]	17.2[c]	
Bu^t	181	2.0021	40.2	20.5	16.2	
Ph[f]	*ca.* 293	2.0016	41.4	19.3	15.3	

[a] Calculated from line positions and the microwave frequency using Preston's program ESRLSQ (see ref. 23). The error limits for g and a are generally ±0.000 05 and ±0.05 G, except where noted otherwise. [b] Data for $(MeO)_3\overset{+}{P}-\overset{-}{B}D_2^{\bullet}$. [c] Error ±0.2 G; the lines were broad and the similarity of a(B) and a(2H) resulted in overlap. [d] In cyclopropane–benzene solvent (3:1 v/v). [e] In oxirane solvent. [f] Taken from ref. 12. Isotropic average data obtained for the radical trapped in a single crystal of $Ph_3\overset{+}{P}-\overset{-}{B}H_3$ (see text).

$$(MeO)_3\overset{+}{P}-\overset{-}{B}H_2^{\bullet} \longrightarrow (MeO)_3P + H_2B^{\bullet} \quad \text{(iv)}$$

The phosphoranyl radical $(MeO)_3\dot{P}OBu^t$ was not detectable above 220 K at which temperature, especially after prolonged photolysis, the spectrum of the t-butyl radical could be observed alongside that of (**2**; X = MeO). This alkyl radical is formed by β-scission of the phosphoranyl as shown in equation (v).[7] The spectrum of (**2**; X = MeO) was not detectable above *ca.* 270 K and reaction (iv) may now be responsible for the rapid removal of the phosphine-boryl radical, although alternative modes of decay are also possible. The boryl radical $H_2B^{\bullet}$ may well be difficult to detect in solution, because of the existence of rapid electron spin relaxation processes leading to very broad lines.

$$(MeO)_3\dot{P}OBu^t \longrightarrow Bu^{t\bullet} + (MeO)_3P{=}O \quad \text{(v)}$$

Similarly, the spectrum of the phosphoranyl radical $(CF_3CH_2O)_3\dot{P}OBu^t$[8] [$a$(P) 939.6 G, g 2.0018 at 215 K] was detected in addition to that of (**2**; X = CF_3CH_2O). Weaker spectra of two other unidentified phosphoranyl radicals [a(P) 917.7 and 914.3 G, g 2.0021 and 2.0016, respectively, at 215 K] were also observed below 220 K. However, these radicals were also detected during photolysis of a cyclopropane solution containing DTBP and tris-(2,2,2-trifluoroethyl) phosphite and their concentrations relative to that of $(CF_3CH_2O)_3\dot{P}OBu^t$ increased with time, indicating that they arise as secondary products from the reaction of $Bu^tO^{\bullet}$ with the phosphite.

Especially at higher temperatures (240—300 K) and after prolonged photolysis, e.s.r. spectra of the corresponding alkyl radicals $X^{\bullet}$ were detected alongside spectra of (**2**; X = Et, Bu^n, or Bu^t) although the origin of these alkyl radicals is also uncertain. The major source is probably alkoxydealkylation of the free trialkylphosphines [equation (vi)], the latter generated by photolysis of the phosphine-boranes or as decay products of (**2**), but it is also possible that reaction (vii) could provide an alternative route to alkyl radicals, especially at higher temperatures.

$$Bu^tO^\bullet + X_3P \longrightarrow Bu^tOPX_2 + X^\bullet \qquad \text{(vi)}$$

$$X_3\overset{+}{P}-\overset{-}{B}H_2^\bullet \longrightarrow X_2P-BH_2 + X^\bullet \qquad \text{(vii)}$$

Reactions of (**2**) *with Alkyl Halides.*—These reactions were studied by including an alkyl halide (*ca.* 1M) in the reaction mixture along with the phosphine-borane and DTBP. At low temperature (203 K) the spectrum of (**2**; X = MeO) was partially replaced by that of the corresponding alkyl radical in the presence of ethyl, n-propyl, or isopropyl bromide (RBr). t-Butyl bromide is more reactive and, under the same conditions, [(**2**; X = MeO)]/[$R^\bullet$] was much smaller although this ratio doubled when the bromide concentration was halved. At higher temperatures (≥240 K) with all bromides only the corresponding alkyl radicals were detected, but with n-propyl, isopropyl, or benzyl chlorides only the spectrum of (**2**; X = MeO)* was observed up to 293 K. The radicals (**2**; X = Me_2N, Et, Bu^n, or Bu^t) are more reactive, since with the alkyl bromides only alkyl radicals were detected even at 183 K. Although neither n-propyl nor isopropyl chloride gave alkyl radicals up to 290 K, the spectrum of (**2**; X = Bu^n) was replaced by that of the benzyl radical in the presence of $PhCH_2Cl$ (1M) even at 185 K.

Competition experiments were carried out at 240 K with pairs of alkyl bromides in order to obtain their relative reactivities. Provided that reactions (viii) and (ix) are the only sources of $R^{1\bullet}$ and $R^{2\bullet}$ and that these species are removed by diffusion-controlled radical–radical reactions, the relative reactivities of the competing halides will be given by equation (x).[9] The relative radical concentrations (obtained by double

$$X_3\overset{+}{P}-\overset{-}{B}H_2^\bullet + R^1Br \xrightarrow{k_1} X_3\overset{+}{P}-\overset{-}{B}H_2Br + R^{1\bullet} \qquad \text{(viii)}$$

$$X_3\overset{+}{P}-\overset{-}{B}H_2^\bullet + R^2Br \xrightarrow{k_2} X_3\overset{+}{P}-\overset{-}{B}H_2Br + R^{2\bullet} \qquad \text{(ix)}$$

$$(k_1/k_2) = ([R^{1\bullet}][R^2Br])/([R^{2\bullet}][R^1Br]) \qquad \text{(x)}$$

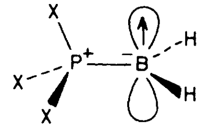
integration of suitable lines in the spectra) were extrapolated to zero photolysis time and the calculated values of (k_1/k_2), which are independent of $[R^1Br]/[R^2Br]$ within experimental error, are given in Table 2. Photolysis of solutions containing phosphine-borane and alkyl bromide, but no DTBP, gave rise to weak spectra of the alkyl radicals, but the spectra were very much stronger in the presence of the peroxide.

Other Reactions of (**2**).—As judged from the e.s.r. spectra obtained, we found no evidence for addition of any of the phosphine-boryl radicals to benzene, 2-methylpropene, or vinyltrimethylsilane (each 1.5—2M in cyclopropane) up to 270 K or to ethylene (as solvent) up to 246 K. Similarly, there was no addition of (**2**; X = MeO) to trifluoromethylbenzene (1.1M) below 270 K, although at 290 K a complex spectrum was observed which could be due to a cyclohexadienyl radical adduct, but this spectrum was too weak to be analysed.

Table 2. Relative rate constants for halogen atom abstraction from pairs of alkyl bromides in cyclopropane at 240 K

Abstracting radical	$R^1 = Pr^n, R^2 = Pr^i$		$R^1 = Bu^t, R^2 = Pr^i$	
	$[R^1Br]/[R^2Br]$	k_1/k_2	$[R^1Br]/[R^2Br]$	k_1/k_2
$(MeO)_3\overset{+}{P}-\overset{-}{B}H_2^\bullet$	0.49	0.32	0.44	3.0
	1.00	0.37		
	2.00	0.36		
$(CF_3CH_2O)_3\overset{+}{P}-\overset{-}{B}H_2^\bullet$	0.49	0.15	0.44	4.3
	1.00	0.16		
	2.00	0.12		
$(Me_2N)_3\overset{+}{P}-\overset{-}{B}H_2^\bullet$	0.49	0.43	0.44	2.9
	1.00	0.53		
	2.00	0.49		
$Bu^n{}_3\overset{+}{P}-\overset{-}{B}H_2^\bullet$	0.49	0.48	0.44	2.6
	1.00	0.47		
	2.00	0.44		
$H_3B^{-\bullet}$ [a]		1.0		1.2
$H_2\dot{B}CN^-$ [a]		0.5		2.6

[a] Data for reactions in Me_2O–Pe^tOH (1.3:1 v/v) at 203 K taken from ref. 13.



(3)

Discussion

The phosphine-boryl radical $X_3\overset{+}{P}-\overset{-}{B}H_2^\bullet$ is isoelectronic with both $X_3\overset{+}{P}-CH_2^\bullet$ and $X_3Si-CH_2^\bullet$ and examples of the latter two types of radical have been characterised by e.s.r. spectroscopy.[10,11] Prior to our work, the only known phosphine-boryl radical was (**2**; X = Ph). The anisotropic e.s.r. spectrum of this species, generated by *X*-irradiation of single crystals of $Ph_3\overset{+}{P}-\overset{-}{B}H_3$, has been reported by Berclaz and Geoffroy[12] and its spectroscopic parameters are included in Table 1. It was concluded that (**2**; X = Ph) is planar at the boron radical centre and that rotation about the P–B bond is rapid on the e.s.r. timescale at room temperature. Our results indicate that the other phosphine-boryl radicals listed in Table 1 are also effectively planar at boron and that the unpaired electron is accommodated mainly in a B-$2p_\pi$ orbital, as shown in (**3**).

The values of $a(^{11}B)$ and $a(H_\alpha)$ for (**2**) are similar to those reported[13] for $H_3B^{-\bullet}$ [$a(^{11}B)$ 19.9, a(3H) 15.2 G at 253 K] and for $H_2\dot{B}CN^-$ [$a(^{11}B)$ 14.3, a(2H) 15.8, a(N) 3.0 G at 252 K] and both these borane radical anions are also planar at the radical centre.[3,13,14] The B-2s contribution to the SOMO of (**2**) will be greater in thermally populated out-of-plane vibrational states than in the ground state, resulting in the positive temperature coefficient observed for the ^{11}B hyperfine coupling constant shown by (**2**; X = MeO). In contrast, a(P) for this radical shows a small negative temperature coefficient. Unpaired electron density in the valence s-orbitals of H_α and P will arise mainly as a result of spin polarisation of the B–H and B–P σ bonding electrons,[10b,12] and thus the signs of both a(2H) and a(P) will be negative. An increase in population of out-of-plane vibrational states, in which the P-3s orbital will contribute directly to the SOMO, will result in an increased positive contribution to the isotropic splitting constant and thus a(P) will become less negative at higher temperatures. This interpretation is supported by the e.s.r. parameters of $(MeO)_3\overset{+}{P}-\overset{-}{B}D_2^\bullet$ in which, because of the greater mass of deuterium, the radical centre is on average closer to planarity than that in the protio analogue at a given temperature. Thus, at the same temperature the boron splitting (positive) is smaller and the phosphorus splitting (negative) is larger for $(MeO)_3\overset{+}{P}-\overset{-}{B}D_2^\bullet$ than for $(MeO)_3\overset{+}{P}-\overset{-}{B}H_2^\bullet$.

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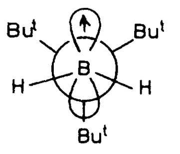
* A weak spectrum of the t-butyl radical, generated by reaction (v), was sometimes also evident.



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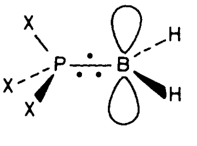

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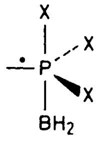

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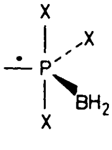

(7)

The values of $a(^{11}B)$ and $a(P)$ for (**2**; X = Bu^t) are appreciably different from those for the other trialkylphosphine-boryl radicals and the radical centre in the former is probably more easily deformed from planarity or may even be significantly pyramidal at the potential energy minimum, as shown in (**4**), because of the steric effect of the bulky t-butyl groups. To summarise, we conclude that whilst the boron centre in (**2**) is, in general, effectively planar, out-of-plane deformation probably requires little input of energy.

As deduced by Berclaz and Geoffroy[12] for (**2**; X = Ph), the extent of unpaired electron delocalisation onto phosphorus appears to be small. However, it does seem likely that some π delocalisation is present and that interaction between the unpaired electron located formally on boron and an empty π^* group orbital[15] of the X_3P moiety may be the reason why the phosphine-boryls are planar at boron whilst the analogous amine-boryls are pyramidal.[4] Thus, the values of $a(^{11}B)$ for $Et_3\overset{+}{P}\text{–}\overset{-}{B}H_2^{\bullet}$ and $Et_3\overset{+}{N}\text{–}\overset{-}{B}H_2^{\bullet}$ are 17.6 and 47.5 G at similar temperatures, implying that the radical centre in the latter is distinctly non-planar. Any stabilising interaction between the unpaired electron and a π^* X_3P orbital will be greatest when the radical centre is planar and this effect will act to counterbalance the expected[16] tendency of the electronegative phosphonium group to induce non-planarity at boron. The π^* Et_3N group orbital in $Et_3\overset{+}{N}\text{–}\overset{-}{B}H_2^{\bullet}$ should be higher in energy than the π^* Et_3P orbital in $Et_3\overset{+}{P}\text{–}\overset{-}{B}H_2^{\bullet}$ and will thus be less well suited energetically, in addition to being less well distributed spatially (because of the higher electronegativity of N compared with P), to interact with the singly occupied orbital on boron.

It is also possible that torsional and steric interactions of the type illustrated in (**4**) are partly responsible for the pyramidal structure of the radical centre in $Et_3\overset{+}{N}\text{–}\overset{-}{B}H_2^{\bullet}$, for which out-of-plane bending probably requires less energy than the analogous deformation of the isoelectronic alkyl radical $Et_3C\text{–}CH_2^{\bullet}$. The B–P and C–P bonds are longer than the corresponding bonds to nitrogen and hence torsional and steric interactions of the BH_2 group with the 'onium ligand will be smaller for $Et_3\overset{+}{P}\overset{-}{B}H_2^{\bullet}$ than for $Et_3\overset{+}{N}\text{–}\overset{-}{B}H_2^{\bullet}$.

In principal, addition of the boryl radical $H_2B^{\bullet}$ to a phosphine X_3P might give a *hypervalent* phosphoranyl radical $X_3\dot{P}BH_2$, rather than a phosphine-boryl adduct of the type (**3**), which can also be described as a *ligand-π* phosphoranyl radical.[17,18] The unpaired electron in the hypervalent phosphoranyl radical could occupy either a B–P [see (**5**)] or X–P σ^* orbital or it could be shared between phosphorus and two apical ligands in a 'trigonal bipyramidal' structure of the type (**6**) or (**7**).[18] All the hypervalent phosphoranyl radicals would exhibit very large[7] (500—1 000 G) isotropic splittings from ^{31}P and in none of our experiments did we find any evidence for the coexistence of electronic configurations other than (**3**). Apparently, transfer of the unpaired electron from the B-2p_π orbital in (**3**) to the B–P σ^* orbital as in (**5**) is energetically unfavourable, although it is noteworthy that the g-factors of the phosphine-boryl radicals are generally rather *less* than the free-spin value (2.0023). We tentatively interpret these low g-factors as evidence for mixing of the excited state (**5**) with the ground state (**3**). Since this involves promotion of the unpaired electron into the *empty* B–P σ^* orbital of (**3**) it would lead to a g factor less than 2.0023 when the external magnetic field is aligned perpendicular to the axis of the B–P bond. Figure 3 illustrates qualitatively the orbital interactions involved in the formation of (**2**; X = Me) from Me_3P and $H_2B^{\bullet}$, leading to a relatively small π–σ^* promotion energy ΔE.*

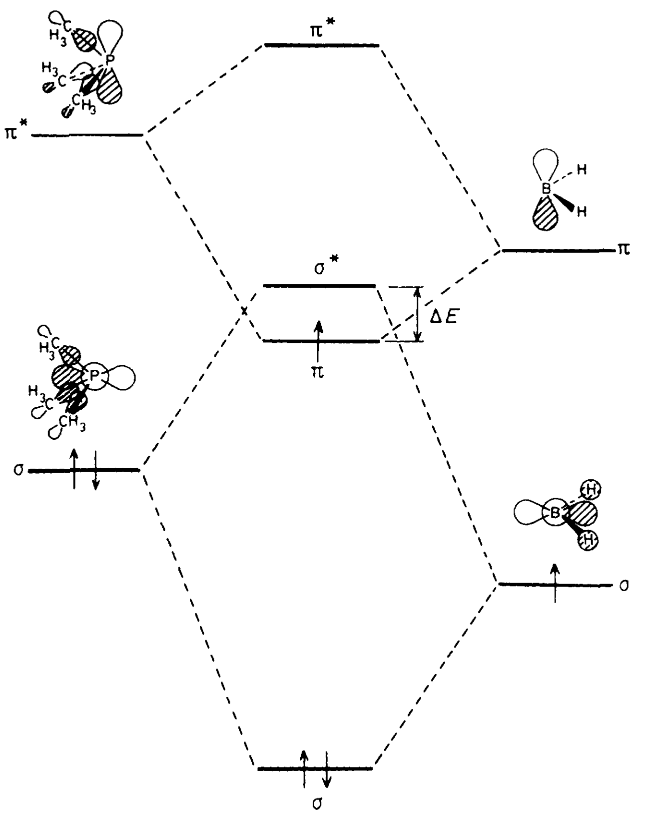

Figure 3. Qualitative molecular orbital diagram showing the important interactions between the σ SOMO and empty π orbital of $H_2B^{\bullet}$ with the lone pair orbital and empty (pseudo) π^* group orbital of Me_3P involved in the formation of the trimethylphosphine-boryl radical

The possible electronic configurations of $[X_3PBH_2]^{\bullet}$ are analogous to those of the phenylphosphoranyl radicals $[X_3PPh]^{\bullet}$,[7,17–20] and examples of both hypervalent and ligand-π [*e.g.* (**8**)] structures have been identified by e.s.r. spectroscopy. The reaction of t-butoxyl radicals with (**1**; X = CF_3CH_2O) was studied in the hope of obtaining a hypervalent species $(CF_3CH_2O)_3\dot{P}BH_2$ since $Bu^tO(CF_3CH_2O)_2\dot{P}Ph$, unlike (**8**), appears to be hypervalent.[20] However, a strong spectrum of the phosphine-boryl radical was observed at all temperatures investigated and no hypervalent phosphoranyl radicals which might be valence isomers of (**2**) were detected. Furthermore, the g-factors of (**2**; X = CF_3CH_2O) and the other phosphine-boryl radicals were all very similar.

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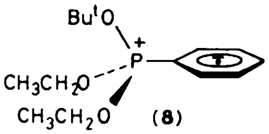
* On the basis of our experiments, it is not possible to assess the contribution of P-3d_π orbitals to the SOMO of (**2**). However, we note that an adequate qualitative description of these radicals can be obtained without the inclusion of d-orbitals.


(8)

To judge from the observed electronic configuration of (**2**; X = Ph),[12] it is less favourable for the unpaired electron to reside on a *P*-phenyl group than on a BH_2 ligand, as might be expected in view of the relative energies of the acceptor π orbitals involved.

Reactions of Phosphine-boryl Radicals.—It is noteworthy that P–X bond homolysis is not a major decay pathway for (**2**), although it may take place to some extent at the higher temperatures. In contrast, hypervalent phosphoranyl radicals of the types $R_3\dot{P}OR$ and $(Me_2N)_3\dot{P}OR$ undergo very rapid α-scission to give $R^{\bullet}$ and $Me_2N^{\bullet}$, respectively.[7] Loss of alkyl radicals from trialkylamine-boryl radicals[4,21] [*e.g.* equation (xi)] occurs more readily than from $R_3\overset{+}{P}{-}\overset{-}{B}H_2^{\bullet}$, probably because cleavage of the latter is less favourable thermodynamically. As indicated in equation (xi),[21] there is appreciable π bonding between boron and nitrogen in an aminoborane, but the analogous stabilising interaction will be present to a much smaller extent in a phosphinoborane ($R_2\overset{+}{N}{=}\overset{-}{B}H_2$ is isoelectronic with $R_2C{=}CH_2$, $R_2\overset{+}{P}{=}\overset{-}{B}H_2$ is similarly related to $R_2Si{=}CH_2$).

$$\mathrm{Pr^i{}_2Et\overset{+}{N}{-}\overset{-}{B}H_2{}^{\bullet}} \longrightarrow \mathrm{Pr^{i\bullet}} + \begin{array}{c}\mathrm{Pr^iEt\ddot{N}{-}BH_2}\\ \updownarrow \\ \mathrm{Pr^iEt\overset{+}{N}{=}\overset{-}{B}H_2}\end{array} \qquad \text{(xi)}$$

The phosphine-boryl radicals are generally less reactive than $H_3B^{-\bullet}$ and no addition of (**2**) to benzene, ethylene, trifluoromethylbenzene, or vinyltrimethylsilane could be detected by e.s.r. below 270 K. In contrast, $H_3B^{-\bullet}$ adds readily to all four compounds, although $H_2\dot{B}CN^-$ adds only to $Me_3SiCH{=}CH_2$ under the same conditions.[13] The lower reactivity of (**2**) may be attributed to both polar and thermodynamic effects, since replacement of H in $H_3B^{-\bullet}$ by X_3P^+ will both stabilise the radical and render it less nucleophilic.

All the phosphine-boryl radicals (**2**) studied rapidly abstract halogen from alkyl bromides, but react much more slowly with alkyl chlorides. Preliminary experiments indicate that the amine-boryl radical $Et_3\overset{+}{N}{-}\overset{-}{B}H_2^{\bullet}$ is rather more reactive than (**2**; X = alkyl).[4] Thus, the amine-boryl abstracts chlorine from n-propyl chloride (*ca.* 1.5M) sufficiently rapidly for $Pr^{n\bullet}$ to be detectable by e.s.r. spectroscopy at 200 K. The borane radical anion $H_3B^{-\bullet}$ abstracts halogen readily from both bromides and chlorides, while the reactivity of $H_2\dot{B}CN^-$ is similar to that of (**2**).[13] The relative reactivities of $H_3B^{-\bullet}$ and $H_2\dot{B}CN^-$ towards pairs of alkyl bromides are included in Table 2 and it may be seen that selectivity increases in the order $H_3B^{-\bullet} < H_2\dot{B}CN^- \simeq$ (**2**; X = Bu^n, Me_2N) < (**2**; X = MeO) < (**2**; X = CF_3CH_2O).

It is likely that the transition state for dehalogenation of an alkyl bromide by $H_3B^{-\bullet}$ involves a large degree of electron transfer from the borane radical anion to the halide, whereas the corresponding reaction with (**2**) is probably better regarded as an atom abstraction process and the energy of the transition state will be much more dependent on the strength of the C–Br bond being broken. However, polar effects are still important for debromination by (**2**) and the selectivity of the latter appears to increase with its ionisation potential, the fluorine-containing radical (**2**; X = CF_3CH_2O) being the most selective (and probably the least reactive) species.

Experimental

E.s.r. Spectroscopy.—Spectra were recorded using Varian E-4 or E-109 instruments operating at *ca.* 9.2 GHz. The techniques used for sample preparation and for the detection of transient free radicals generated photochemically in the spectrometer cavity have been described previously.[5,13,18]

g-Factors and hyperfine splitting constants were computed from the measured microwave frequency and line positions, the latter determined using an n.m.r. gaussmeter and corrected for the field difference between the sample and the n.m.r. probe using the pyrene radical anion (*g* 2.0027 1) as standard.[22] Best-fit spectroscopic parameters were obtained using Preston's program ESRLSQ which employs an exact solution of the isotropic Hamiltonian and an iterative least-squares fitting procedure.[23]

Materials.—Tri-n-butylphosphine-borane was obtained commercially (Aldrich) and distilled before use. The borane complexes of trimethyl phosphite,[24] tris(dimethylamino)phosphine,[25] and triethylphosphine[26] were prepared according to published methods. The complex $(MeO)_3\overset{+}{P}{-}\overset{-}{B}D_3$ was prepared from $NaBD_4$ by the method used for the unlabelled compound.[24] Although the borane complexes of tris-(2,2,2-trifluoroethyl) phosphite[27] and tri-t-butylphosphine[28] have been mentioned previously in the literature, their preparation and characterisation have not been reported in detail. We prepared these compounds by passing a small excess of diborane into a solution of the appropriate phosphine in tetrahydrofuran (THF) as described below.

Tris-(2,2,2-*trifluoroethyl*) *phosphite-borane.*—Diborane, generated by addition of freshly distilled boron trifluoride-dimethyl ether (1.34 g, 11.8 mmol) in dry diglyme (10 ml) to a stirred solution of sodium borohydride (0.34 g, 9.0 mmol) in diglyme (15 ml), was carried in a slow stream of dry argon into a solution of tris-(2,2,2-trifluoroethyl) phosphite (3.5 g, 10.7 mmol) in dry THF (50 ml) at 0 °C. After addition of $F_3B{\cdot}Me_2O$ during 30 min, the diborane generator was heated at 60—70 °C for 1 h to complete the reaction. THF was removed under reduced pressure and the *phosphine-borane* was purified by distillation, b.p. 52—53 °C at 6 Torr (Found: C, 21.5; H, 2.6; P, 8.8. $C_6H_9BF_9O_3P$ requires C, 21.1; H, 2.7; P, 9.1%). The n.m.r. spectrum (Varian XL-200; C_6D_6 solvent) showed: ^{31}P (85% H_3PO_4 external standard) δ 123.5 (J_{B-P} 75 Hz); ^{11}B ($F_3B{\cdot}Et_2O$ external standard) δ −45.5 (J_{B-P} 75, $^1J_{B-H}$ 100 Hz).

Tri-t-butylphosphine-borane was prepared in the same way from the phosphine (2.9 g, 14.3 mmol) as a crystalline solid which was purified by vacuum sublimation, m.p. 250 °C (with apparent decomposition) (Found: C, 66.3; H, 13.9; P, 14.4. $C_{12}H_{30}BP$ requires C, 66.7; H, 14.0; P, 14.3%). The n.m.r. spectrum (C_6D_6) showed ^{31}P, δ 58.5 (J_{B-P} 59 Hz); ^{11}B, δ −40.8 (J_{B-P} 58, $^1J_{B-H}$ 94 Hz).

The alkyl halides were carefully distilled middle fractions. For the competitive experiments, a stock mixture of the two alkyl bromides was made up by weight and portions of this were used for sample preparation. The sealed samples were stored frozen in liquid nitrogen and thawed at 195 K immediately prior to recording the spectra at 240 K. Relative radical concentrations, obtained by double integration of non-overlapping lines recorded repeatedly as the photolysis progressed, were extrapolated to zero photolysis time in order to circumvent problems arising from selective consumption of one of the two halides.

References

1 G. Hertzberg and J. W. C. Johns, *Proc. R. Soc. London. Ser. A*, 1967, **298**, 142.

2 W. Nelson and W. Gordy, *J. Chem. Phys.*, 1969, **51**, 4710.

3 R. C. Catton, M. C. R. Symons, and H. W. Wardale, *J. Chem. Soc. A*, 1969, 2622.

4 J. A. Baban and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1983, 1224.

5 J. C. Brand, B. P. Roberts, and J. N. Winter, *J. Chem. Soc., Perkin Trans. 2*, 1983, 261.

6 B. P. Roberts and K. Singh, *J. Organomet. Chem.*, 1978, **159**, 31.

7 B. P. Roberts, *Adv. Free Radical Chem.*, 1980, **6**, 225.

8 A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1972, 2224.

9 A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1971, 1823.

10 (*a*) E. A. C. Lucken and C. Mazeline, *J. Chem. Soc. A*, 1966, 1074; 1967, 439, (*b*) A. Begum, A. R. Lyons, and M. C. R. Symons, *ibid.*, 1971, 2388.

11 P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1969, **91**, 6161; A. Hudson and H. A. Hussain, *J. Chem. Soc. B*, 1969, 793.

12 T. Berclaz and M. Geoffroy, *Mol. Phys.*, 1976, **32**, 815.

13 J. R. M. Giles and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1699; 1983, 743.

14 E. D. Sprague and F. Williams, *Mol. Phys.*, 1971, **20**, 375.

15 W. L. Jorgensen and L. Salem, 'The Organic Chemist's Book of Orbitals,' Academic Press, New York, 1973.

16 L. Pauling, *J. Chem. Phys.*, 1969, **51**, 2767.

17 B. P. Roberts and J. C. Scaiano, *J. Chem. Soc., Perkin Trans. 2*, 1981, 905.

18 J. R. M. Giles and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1211.

19 G. Boekestein, E. H. J. M. Jansen, and H. M. Buck, *J. Chem. Soc., Chem. Commun.*, 1974, 118.

20 A. G. Davies, M. J. Parrott, and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1974, 973.

21 J. A. Baban and B. P. Roberts, unpublished results.

22 B. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **43**, 4191; R. Allendorfer, *ibid.*, 1971, **55**, 165.

23 D. Griller and K. F. Preston, *J. Am. Chem. Soc.*, 1979, **101**, 1975.

24 T. Reetz, *J. Am. Chem. Soc.*, 1960, **82**, 5039.

25 T. Reetz and B. Katlafsky, *J. Am. Chem. Soc.*, 1960, **82**, 5036.

26 R. A. Baldwin and R. M. Washburn, *J. Org. Chem.*, 1961, **26**, 3549.

27 T. Reetz, U.S. P. 3104253 (1963) (*Chem. Abstr.*, 1964, **60**, 557g).

28 G. Jugie, C. Jouany, L. Elegant, J.-F. Gal, and M. Azzaro, *Bull. Soc. Chim. Fr.*, 1976, 1; C. H. Bushweller and J. A. Brunelle, *Tetrahedron Lett.*, 1974, 893.

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