Homolytic Reactions of Ligated Boranes. Part 10.[1] Electron Spin Resonance Studies of Radicals derived from Ligated Arylboranes

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The ligated arylboryl radicals $L\rightarrow\dot{B}HAr$ [$L = Me_3N$, Et_3P, or $(MeO)_3P$; Ar = Ph or p-$Bu^tC_6H_4$] have been generated in oxirane solvent by hydrogen atom abstraction from $L\rightarrow BH_2Ar$ using t-butoxyl radicals produced by u.v. photolysis of di-t-butyl peroxide. The e.s.r. spectra of the phosphine- or phosphite-ligated radicals show that there is substantial conjugative delocalisation of the unpaired electron from boron onto the aromatic rings, although this delocalisation is less extensive than in comparable benzylic carbon-centred radicals. The results of *ab initio* molecular orbital calculations support the proposal that hyperconjugative delocalisation onto the phosphorus ligand competes with conjugative delocalisation onto the ring in the complexed arylboryl radicals. The e.s.r. spectra of the amine–arylboryl radicals were too weak to detect, although these radicals and $Et_3P\rightarrow\dot{B}HAr$ abstract halogen atoms readily from alkyl bromides to afford spectra of the corresponding alkyl radicals. The ligated arylboryl radicals are less reactive and more selective in bromine atom abstraction than homoleptic ligated alkylboryl radicals, presumably because the former are appreciably stabilised by conjugative delocalisation of the unpaired electron onto the aromatic rings.

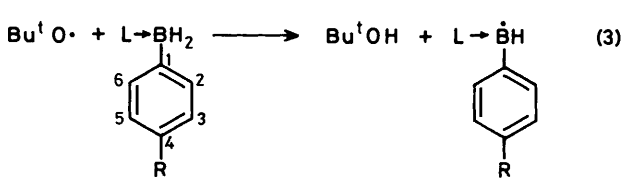
Amine– and phosphine–arylboryl radicals $R_3N\rightarrow\dot{B}HAr$ and $R_3P\rightarrow\dot{B}HAr$ are isoelectronic analogues of the benzylic radicals $R_3C–\dot{C}HAr$ and $R_3Si–\dot{C}HAr$, respectively.

In Part 9 of this series we reported that the radical chain reaction [equation (1)] between butyl iodide, ethyl acrylate, and tributylphosphine–phenylborane gives a much greater yield of ethyl heptanoate than the similar reaction in which $Bu^n_3P\rightarrow BH_2Ph$ is replaced by the unsubstituted borane complex $Bu^n_3P\rightarrow BH_3$.[1] This result suggests that hydrogen atom abstraction by $Bu^nCH_2\dot{C}HCO_2Et$ takes place more readily from $Bu^n_3P\rightarrow BH_2Ph$ than from $Bu^n_3P\rightarrow BH_3$, presumably because the B–H bond in the former is weakened by conjugative delocalisation of the unpaired electron onto the phenyl group in the phosphine–arylboryl radical $Bu^n_3P\rightarrow\dot{B}HPh$.

The aims of the present research were to use e.s.r. spectroscopy to investigate the structures, electronic configurations, and chemical reactions of ligated arylboryl radicals and to compare these species with homoleptic ligated alkylboryl radicals[2] and with benzylic carbon radicals.

$$Bu^nI + CH_2{=}CHCO_2Et + Bu^n_3P\rightarrow BH_2Ph \longrightarrow Bu^nCH_2CH_2CO_2Et + Bu^n_3P\rightarrow BHPhI \quad (1)$$

$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO\cdot \quad (2)$$



$$Bu^tO\cdot + L\rightarrow BH_2C_6H_4R \longrightarrow Bu^tOH + L\rightarrow\dot{B}HC_6H_4R \quad (3)$$

(1) $L = Me_3N$, $R = H$ (7)
(2) $L = Me_3N$, $R = Bu^t$ (8)
(3) $L = Et_3P$, $R = H$ (9)
(4) $L = Et_3P$, $R = Bu^t$ (10)
(5) $L = (MeO)_3P$, $R = H$ (11)
(6) $L = (MeO)_3P$, $R = Bu^t$ (12)

Results and Discussion

The ligated arylboryl radicals (**7**)—(**12**) were generated in oxirane solution by hydrogen atom abstraction from the corresponding arylborane complexes (**1**)—(**6**) using photochemically generated t-butoxyl radicals [equations (2) and (3)]. E.s.r. spectra were recorded during continuous u.v. irradiation of samples positioned in the microwave cavity of the spectrometer, as described previously.[2]

The amine–boranes (**1**) and (**2**) were prepared by reduction of the appropriate diethyl arylboronate [$ArB(OEt)_2$] using lithium aluminium hydride in the presence of trimethylamine,[3] according to the method described by White[4] for the preparation of (**1**). The phosphine- and phosphite-complexes (**3**)—(**6**) were prepared by displacement of trimethylamine from the corresponding amine–arylborane [equation (4; X = Et or MeO)].[5] The ^1H n.m.r. spectra of (**1**)—(**6**) exhibit ring proton chemical shifts which indicate that the $L\rightarrow BH_2$ group behaves as an electron-withdrawing substituent. For example, the ring proton resonances for (**2**) appear as an AB-quartet† with δ 7.75 (2,6-ArH), δ 7.50 (3,5-ArH), and J_{AB} 8.1 Hz. Similar chemical shifts are shown by the ring protons of 4-t-butylbenzaldehyde [δ 7.61 (2,6-ArH) and δ 7.17 (3,5-ArH)]. Boron is more electropositive than carbon and, moreover, a build-up of negative

$$X_3P + Me_3N\rightarrow BH_2Ar \longrightarrow X_3P\rightarrow BH_2Ar + Me_3N \quad (4)$$

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† The complexes (**2**), (**4**), and (**6**) each show AB-quartets in which the low-field doublet is considerably broader than the upfield doublet. However, when ^{11}B-decoupling was applied the low-field doublet sharpened and a further small doublet splitting due to coupling with ^{31}P through four bonds became apparent for (**4**) and (**6**).

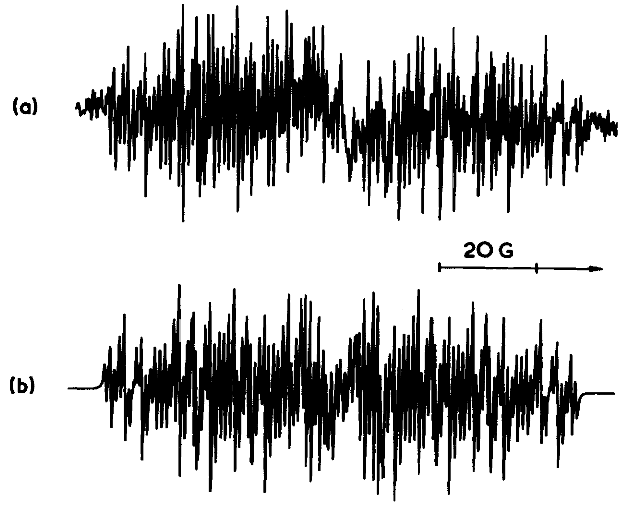
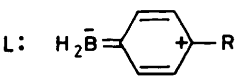


Figure 1. (a) E.s.r. spectrum of the trimethyl phosphite–phenylboryl radical (**11**) in oxirane at 230 K. (b) Computer simulation as a mixture of the ^{11}B- and ^{10}B-containing radicals present in natural abundance. The splitting constants are as given in Table 1; the linewidth is 0.40 G and the lineshape is Lorentzian

charge on boron might be expected in complexes of arylboranes with Lewis bases, as predicted by valence bond representations of the type $\overset{+}{L}-\overset{-}{B}H_2Ar$. Evidently the π-acceptor property of the boron atom in an arylborane is not satisfied by complexation with the nitrogen or phosphorus donors and the $L\rightarrow BH_2$ group behaves as a $-M$ substituent. We have noted a similar property of the $L\rightarrow BH_2$ group when attached to the nitroxide function in radicals of the type $L\rightarrow BH_2N(\dot{O})R$.[6] In valence bond terms, canonical structures of the type (**13**) contribute to the electronic configurations of (**1**)—(**6**) or, in molecular orbital language, some electron-transfer takes place from a filled ring π-orbital into the π*-group orbital of the $L\rightarrow BH_2$ substituent. These observations suggest that the ligated boryl moiety may have potential as a carbanion-stabilising substituent (perhaps leading to complete departure of L:) and a number of synthetic applications of such a property can be envisaged.



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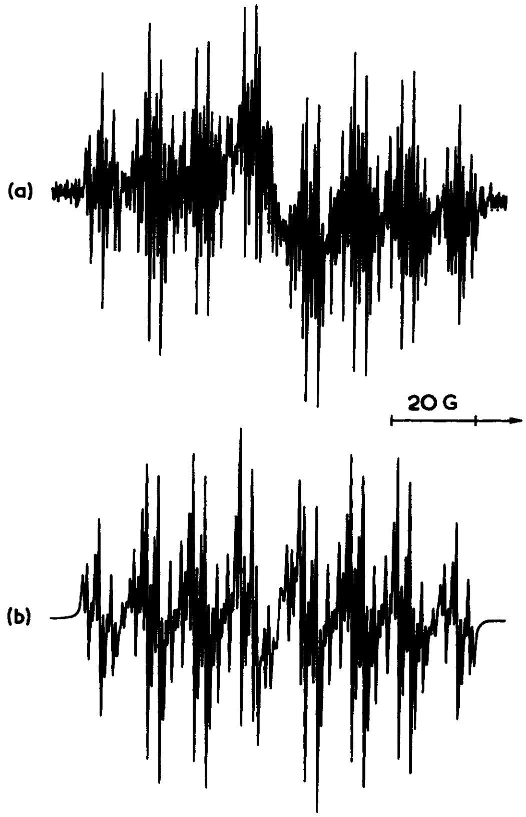


Figure 2. (a) E.s.r. spectrum of the trimethyl phosphite–4-t-butylphenylboryl radical (**12**) in oxirane at 250 K. (b) Computer simulation as a mixture of the ^{11}B- and ^{10}B-containing radicals present in natural abundance. The splitting constants are 11.14 (^{11}B), 14.00 (1 H), 37.64 (1 P), 2.86 (2 H), and 0.98 G (2 H); the linewidth is 0.60 G and the lineshape is Lorentzian

No e.s.r. spectra were detected during u.v. photolysis of di-t-butyl peroxide (DTBP) (*ca.* 15% v/v) in the presence of either (**1**) and (**2**) (0.25—0.5M) in oxirane solvent between 220 and 270 K. In the absence of amine–arylborane, a strong spectrum of the oxiranyl radical was observed, showing that t-butoxyl radicals do react rapidly with (**1**) and (**2**) presumably to give (**7**) and (**8**), respectively, the e.s.r. spectra of which are not detected. The spectrum of $Me_3N\rightarrow\dot{B}H_2$ is not easy to observe on account of its large multiplicity,[7] and the still larger number of lines expected to arise from (**7**) and (**8**) as a result of delocalisation of the unpaired electron onto the ring would certainly render detection of these spectra very difficult. A further complication could be that (**7**) and (**8**) add to the electron-deficient benzene rings of their parents to yield cyclohexadienyl radicals which would also exhibit spectra of considerable complexity; a similar problem frustrates efforts to detect e.s.r. spectra of phenylsilyl radicals in solution.[8] Indirect evidence for the formation of (**7**) and (**8**) according to equation (3) was obtained by including an alkyl bromide in the sample, when the amine–arylboryl radicals abstract halogen to produce detectable concentrations of alkyl radicals (see later).

E.s.r. spectra which we assign to the phosphine- or phosphite–arylboryl radicals (**9**)—(**12**) were observed during u.v. photolysis of DTBP (15% v/v) in the presence of the corresponding arylborane complex (**3**)—(**6**) (*ca.* 0.5M). Spectra of (**11**) and (**12**) are reproduced in Figures 1 and 2, respectively, and expanded wing regions, which show the fine structure resulting from delocalisation of the unpaired electron onto the benzene rings, are shown in Figure 3. Spectra of the phosphine–arylboryl radicals (**9**) and (**10**) were less well resolved than those of the phosphite complexes, presumably because small splittings from the methylene protons of the phosphine ligands now contribute to the linewidth. The e.s.r. parameters for (**9**)—(**12**) are collected in Table 1; all radicals were transient and their spectra decayed within the fall time of the spectrometer when u.v. irradiation was interrupted. The unpaired electron distributions in the ligated 4-t-butylphenylboryl radicals (**10**) and (**12**) are clearly very similar to those in the corresponding phenylboryl adducts (**9**) and (**11**), the hyperfine coupling constants for which are included in Figure 4 to facilitate comparisons with related radicals.

The amine–boryl radicals $R_3N\rightarrow\dot{B}H_2$ are markedly pyramidal at boron.[7] In contrast, the equilibrium geometries at boron in phosphine-[9,10] and sulphide–boryl[11] radicals $R_3P\rightarrow\dot{B}H_2$ and $R_2S\rightarrow\dot{B}H_2$ both appear to be close to planar, although out-of-plane bending is not energetically demanding and the time-average configurations at the temperatures employed are likely to deviate significantly from planarity. We

Table 1. E.s.r. parameters for phosphine- and phosphite-boryl radicals

				Hyperfine splittings/G			
Radical	Solvent[a]	T/K	g-Factor	$a(^{11}B)$	$a(H_\alpha)$	$a(^{31}P)$	Others[b]
(**9**)	A	237	2.0022	12.8	14.0	36.3	3.1 (2,6-ArH), 3.9 (4-ArH)
(**10**)	A	227	2.0022	12.7	13.7	36.2	3.1 (2,6-ArH)
(**11**)	A	230	2.0020	11.26	14.00	38.11	2.90 (2,6-ArH), 0.98 (3,5-ArH), 3.41 (4-ArH)
(**12**)	A	198		11.08	13.92	37.88	2.86 (2,6-ArH), 0.98 (3,5-ArH)
		230	2.0020	11.13	13.94	37.68	2.88 (2,6-ArH), 0.96 (3,5-ArH)
		267	2.0020	11.14	14.05	37.54	2.86 (2,6-ArH), 0.98 (3,5-ArH)
$Et_3P\rightarrow\dot{B}HMe$[c]	B	215	2.0021	15.89	14.95	43.3	15.42 (3 H), 0.50 (6 H)
$Et_3P\rightarrow\dot{B}H_2$[d]	B	183	2.0020	17.6	16.8[e]	43.6	
$(MeO)_3P\rightarrow\dot{B}HMe$[c]	B	241	2.0022	12.76	15.65	41.26	14.60 (3 H)
$(MeO)_3P\rightarrow\dot{B}H_2$[d]	B	215	2.0019	14.7	16.6[e]	43.9	

[a] A = oxirane, B = cyclopropane. [b] The pairs of *ortho*- and *meta*-protons, which will be non-equivalent if rotation about the B–C(1) bond is slow on the e.s.r. timescale, gave rise to apparently equal splittings at all temperatures examined. [c] Reference 2. [d] Reference 9. [e] Two equivalent protons.

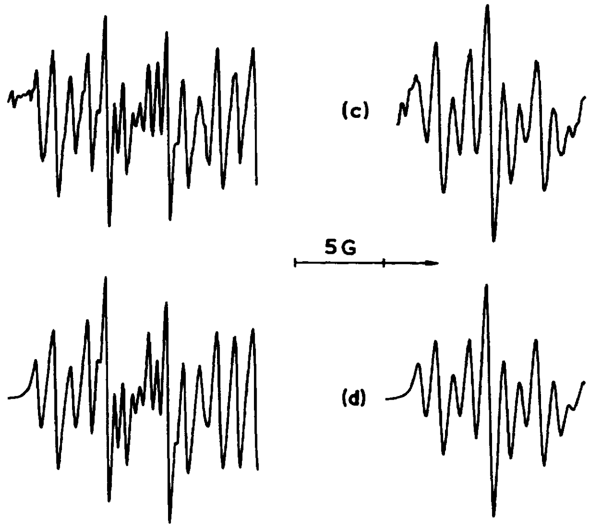


Figure 3. (a) Low-field wing region from the e.s.r. spectrum of (**11**) at 230 K. (b) Computer simulation of (a); the splitting constants are as given in Table 1, the linewidth is 0.34 G, and the lineshape is Lorentzian. (c) Low-field wing region from the e.s.r. spectrum of (**12**) at 228 K. (d) Computer simulation of (c); the splitting constants are as given in Table 1, the linewidth is 0.50 G, and the lineshape is 80% Lorentzian and 20% Gaussian

have attributed these different structural preferences to the existence of stabilising hyperconjugative delocalisation of the unpaired electron from boron into a low-energy empty π^*-group orbital of the phosphine or sulphide moiety, since this will be maximised in the planar configuration. As judged from the hyperfine splitting constants,[9] the time-average configuration at boron in the phosphite-boryl radical (**15**) (see Figure 4) is more nearly planar than that in the phosphine-boryl radical (**14**) [$|a(^{11}B)|/|a(H_\alpha)|$ = 0.87 and 1.05 respectively, at *ca.* 180 K]. This suggests that conjugative electron delocalisation from boron onto the X_3P ligand is greater for (**15**) than for (**14**), in accord with the lower reactivity shown by the former.[9]

Replacement of an α-hydrogen atom in (**14**) or (**15**) by a phenyl group would be expected to result in further delocalisation of the unpaired electron from boron onto the ring and to increase the preference for planarity at boron. Comparison of the e.s.r. parameters for (**11**) with those of (**15**) shows that phenylation at boron causes $a(^{11}B)$, $a(H_\alpha)$, and $a(^{31}P)$ to decrease by 23, 16, and 13%, respectively. The corresponding decreases on going from (**14**) to (**9**) are 27, 17, and 17%. Phenylation at the carbon radical centres in (**16**) and (**17**) brings about reductions of 28 and 25%, respectively, in the magnitude of $a(H_\alpha)$.

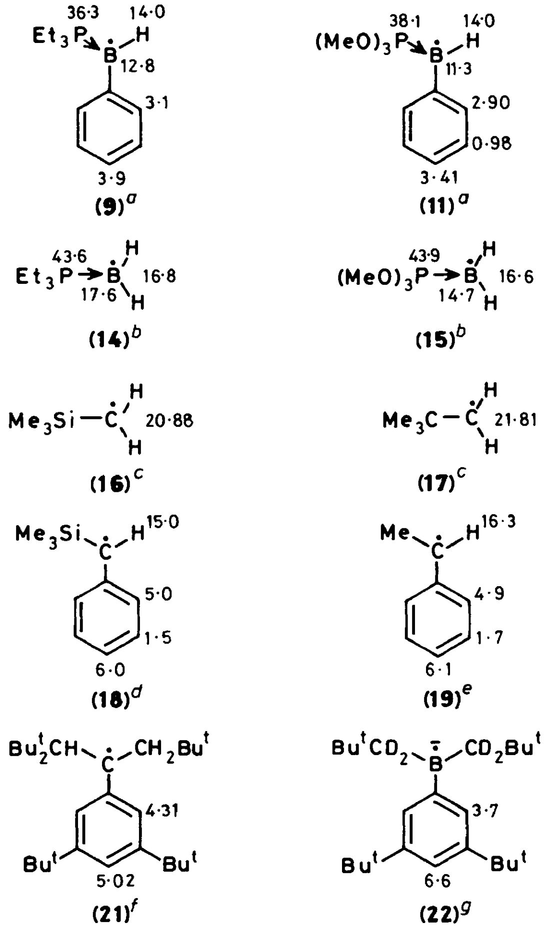


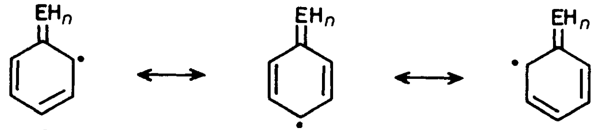
Figure 4. Hyperfine splitting constants (in G) for boron- and carbon-centred radicals. [a] This work. [b] Reference 9. [c] P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1969, **91**, 6161. [d] A. Hudson and H. A. Hussain, *J. Chem. Soc. B*, 1969, 793. [e] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1972, 786. [f] A. Berndt and K. Schreiner, unpublished results reported in 'Landolt-Börnstein, Magnetic Properties of Free Radicals, New Series,' vol. 9b, eds. H. Fischer and K.-H. Hellwege, Springer, Berlin, 1977. [g] K. Schlüter and A. Berndt, unpublished results reported in 'Landolt-Börnstein, Magnetic Properties of Free Radicals, New Series,' vol. 9d1, eds. H. Fischer and K.-H. Hellwege, Springer, Berlin, 1980

Taking $2a$(2,6-ArH) + a(4-ArH) ($\equiv P$) as an approximate

Table 2. Results of *ab initio* m.o. calculations for phosphine–boryl and silylmethyl radicals

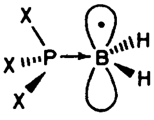
Radical	X	Total energy/Hartree		SOMO composition[a]		
		UHF	ROHF/STO-3G	c^2(B- or C_α-$2p_\pi$)	c^2(P- or Si-$3p_\pi$)	Σc^2(X_3P or X_3Si)[b]
(**23**)	H	−368.236 865[c,d]	−364.076 053	0.909	0.030	0.117
	Me	−479.854 099[e]	−479.850 514	0.919	0.024	0.101
	HO	−585.605 549[e]	−585.602 324	0.873	0.052	0.129
(**24**)	H	−329.651 626[c,f]	−325.858 653	0.978	0.001	0.029
	Me	−441.648 662[e]	−441.644 255	0.975	0.002	0.032

[a] The squares of the atomic orbital coefficients in the ROHF/STO-3G SOMO are given. [b] The valence atomic orbitals of P or Si and of the directly bonded atom of X are included. [c] 6-31G** Basis set. [d] Structure (**14**) in ref. 11. [e] STO-3G Basis set. [f] Bond lengths (Å): CH 1.078, CSi 1.860, $SiH_{eclipsed}$ 1.480, SiH 1.478. Bond angles (°): HCSi 122.6, $H_{eclipsed}$ SiC 111.7, HSiC 110.0, HSiH 109.0.

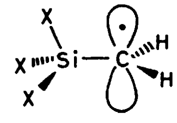


(**20a**) (**20b**) (**20c**)

measure of the extent of π-unpaired electron population on the benzene rings, conjugative delocalisation onto the phenyl group in (**18**) (*P* = 16.0 G) is fairly similar to that in (**19**) (*P* = 15.9 G). However, the π-spin population on the phenyl group in the α-silylbenzyl radical (**18**) is about 1.7 times greater than that in the phosphite–phenylboryl (**11**) (*P* = 9.2 G) and about 1.6 times greater than that in the phosphine–phenylboryl (**9**) (*P* = 10.1 G). These differences are larger than the factor of *ca.* 1.2—1.3 which might be predicted on the basis of extrapolation to (the unknown) $Ph\dot{B}H_2^-$ of the trend in *P* observed across the isoelectronic series PhO• (23.3 G) > $Ph\dot{N}H$ (20.6 G) > $Ph\dot{C}H_2$ (16.6 G).[12] This change in the value of *P* can be associated with the decreasing importance of structures of the type (**20a**—**c**) on going across the Periodic Table from oxygen to carbon, as the strength of the E=C bond relative to the E–C bond decreases. In fact, the magnitudes of the ring proton splittings reported for the benzylic radical (**21**) and for the arylborane radical anion (**22**) (see Figure 4) indicate that the unpaired electron populations on the aromatic rings are very similar in these two species. Hence, it seems likely that a contributory cause of the small ring proton splittings observed for the ligated arylboryl radicals (**9**)—(**12**) is that an X_3P substituent removes more unpaired electron population from boron than does an X_3Si substituent when attached to a carbon radical centre, leaving less to be delocalised onto the ring in the ligated arylboryl radicals.



(**23**)



(**24**)

Molecular Orbital Calculations.—In order to compare the importance of delocalisation in phosphine–boryl and silylmethyl radicals, we have carried out *ab initio* molecular orbital calculations for the radicals (**23**; X = H, Me, or HO) and (**24**; X = H or Me) using the GAUSSIAN 82 series of programs.[13]

The geometry at the radical centres was constrained to be planar and one P–X or Si–X bond was forced to eclipse the axis of the B- or C_α-$2p_\pi$ atomic orbital; remaining structural parameters were optimised within C_s symmetry using the UHF method. The structure (**23**; X = H) of the prototype phosphine–boryl radical has been optimised previously,[11] using the 6-31G** basis set, to give a stationary point on the potential energy surface.* The geometry of the silylmethyl radical (**24**; X = H) was also optimised using this basis set, but the remaining radicals were treated at the UHF/STO-3G level. The 6-31G**-optimised geometry of (**24**; X = H) showed all real harmonic vibrational frequencies; the zero-point vibrational energy (ZPVE) is 131.0 kJ mol^{-1}. Spin-restricted minimal basis set calculations (ROHF/STO-3G) were then performed for the optimised structures and the composition of each semi-occupied molecular orbital (SOMO) is shown in Table 2.

Although the absolute values for the orbital populations derived from such calculations would not be expected to be very reliable, more weight can be attached to the predicted trends. The results given in Table 2 strongly support the contention that the extent of unpaired electron delocalisation onto the X_3P ligand in (**23**) will be greater than onto the X_3Si substituent in (**24**). The mechanism of spin delocalisation is hyperconjugation, donation of the unpaired electron from the $2p_\pi$ orbital at the radical centre into the X_3P or X_3Si π*-group orbital. The greater delocalisation onto the phosphite group in (**23**; X = HO) compared with the phosphine moiety in (**23**; X = Me) can be associated with the larger P-$3p_\pi$ contribution to the $(HO)_3P$ π*-group orbital because of the greater electronegativity of oxygen relative to carbon. (Compare the relative effectiveness with which phosphine and phosphite ligands enter into π back-bonding with transition metals.[14]) The smaller extent of hyperconjugative delocalisation in (**24**) is presumably a consequence of the poorer energetic match between the donor C_α-$2p_\pi$ orbital and the π* X_3Si group acceptor orbital because of the lower electronegativities of boron compared with carbon and of silicon compared with phosphorus.

Similar back donation, now of a π-lone pair of electrons, onto phosphorus occurs in compounds of the type $X_3P \rightarrow O$ and $X_3P \rightarrow CH_2$.[15,16] Originally, vacant P-$3d_\pi$ orbitals were thought to receive the electron pair, but more recently the involvement of *d*-orbitals has been questioned and the X_3P π*-group molecular orbital is favoured as the acceptor.[16] Certainly it is not *necessary* to include *d*-orbitals in the basis set to account adequately for the experimental observations. In accord with our proposal that the $(MeO)_3P$ group is a more effective acceptor of the unpaired electron from boron than the Et_3P

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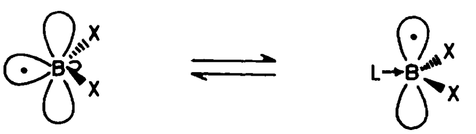
* The radical (**23**; X = H) was referred to as (**14**) in reference 11; Table 3 in this paper indicates that the optimised structure possesses one imaginary normal harmonic vibrational frequency. This is a typographical error; all vibrational frequencies are in fact positive and the ZPVE (6-31G**) is 127.9 kJ mol^{-1}. The barrier to rotation about the P→B bond is computed to be extremely small.

group, the strength and stretching frequency of the P→O bond in $(MeO)_3P{\rightarrow}O$ are both greater than the corresponding values for $Me_3P{\rightarrow}O$.[17,18]

It follows that out-of-plane deformation at boron is likely to require a smaller input of energy for the phosphine–arylboryl radicals (**9**) and (**10**) than for the phosphite-ligated analogues (**11**) and (**12**). Since $Me_3N{\rightarrow}\dot{B}HAr$ was not detected by e.s.r. spectroscopy it is not possible to determine the geometry at boron. However, it is likely that these radicals are more nearly planar at boron than $Me_3N{\rightarrow}\dot{B}H_2$ or the amine–alkylboryl radicals because of unpaired electron delocalisation onto the ring.

Finally, it is interesting to note that the ligation–deligation process [equation (5)] for a planar π-radical of the type $L{\rightarrow}\dot{B}X_2$ is symmetry forbidden in the sense[19,20] that the complexed boryl radical does not correlate with ground-state ligand and the ground state of $X_2B^{\bullet}$ provided that this is a σ-radical, as it is for $H_2B^{\bullet}$, $F_2B^{\bullet}$, and $Cl_2B^{\bullet}$.[21–23] Neither the forward nor the backward reaction has been observed experimentally.



(5)

Reaction with Alkyl Halides.—Although no e.s.r. spectra were detected during u.v. irradiation of oxirane solutions containing the amine–arylboranes (**1**) or (**2**) (*ca.* 0.25M) and DTBP (15% v/v) (see before), when n-propyl or t-butyl bromide (*ca.* 1M) was also present a spectrum of the corresponding alkyl radical was observed between 175 and 233 K. These results indicate that the amine–arylboryl radicals (**7**) and (**8**) are being produced and subsequently abstract halogen from the alkyl bromides [equation (6; $L = Me_3N$)], as do the trimethylamine–boryl[7] and –alkylboryl[2] radicals under similar conditions. With n-propyl chloride (1M) and (**1**), no spectrum of $Pr^{n\bullet}$ was detected up to 264 K; with t-butyl chloride (1M) a weak spectrum of $Bu^{t\bullet}$ was visible at 173 K and this gained in strength as the temperature was raised to 270 K.

The phosphine–arylboryl radicals (**9**) and (**10**) are less reactive in halogen abstraction. The spectrum of the t-butyl radical was observed between 173 and 233 K during u.v. irradiation of DTBP (15% v/v), t-butyl bromide (1M), and (**4**) (0.5M) in oxirane and that of the phosphine–arylboryl radical (**10**) was not detected. However, when the Bu^tBr was replaced by an equal concentration of n-propyl bromide, spectra of both $Pr^{n\bullet}$ and (**10**) were observed below *ca.* 240 K and the value of $[(\mathbf{10})]/[Pr^{n\bullet}]$ increased as the temperature was lowered to 173 K. In similar experiments with t-butyl chloride, only the spectrum of (**10**) was detected up to 265 K. The phosphite–arylboryl radicals (**11**) and (**12**) were still less reactive; with n-propyl bromide no halogen abstraction was detected up to 266 K. Below 260 K with t-butyl bromide, only the the spectrum of the radical (**12**) was observed initially when a fresh sample was photolysed.

These results demonstrate that the ligated arylboryl radicals abstract halogen atoms from alkyl halides significantly less rapidly than the correspondingly ligated boryl[7,9] or alkylboryl[2] radicals under similar conditions. This lower reactivity of the *B*-aryl radicals is paralleled by higher selectivity. Relative rates of bromine atom abstraction from t-butyl and n-propyl bromides were determined by generation of the ligated arylboryl radical in the presence of mixtures of the two halides. Making the usual assumptions,[9] the relative reactivities of the two bromides (k_{Bu^tBr}/k_{Pr^nBr}) were calculated from the values of $[Bu^{t\bullet}]/[Pr^{n\bullet}]$ measured during continuous u.v. irradiation; the results are given in Table 3.

Table 3. Relative reactivities of t-butyl and propyl bromides towards ligated boryl radicals

Abstracting radical	Solvent[a]	T/K[b]	k_{Bu^t}/k_{Pr^nBr}	Ref.
(**7**)	A	173	8.0	*c*
		238	4.9	*c*
(**8**)	A	173	5.3	*c*
		238	4.0	*c*
$Me_3N{\rightarrow}\dot{B}HMe$	B	217	1.1	*d*
$Me_3N{\rightarrow}\dot{B}H_2$	C	261	1.5	*e*
(**9**)	A	173	13	*c*
		238	8.0	*c*
(**10**)	A	173	9.9	*c*
		238	6.7	*c*
$Et_3P{\rightarrow}\dot{B}HMe$	B	170	2.8	*d*
$Bu^n_3P{\rightarrow}\dot{B}H_2$	B	240	5.6	*f*

[a] A = oxirane, B = cyclopropane, C = Bu^tOH–Me_2O (4:1 v/v). [b] The solubilities of the ligated arylboranes are significantly greater in oxirane–alkyl bromide mixtures than in oxirane alone. [c] This work. [d] Ref. 2. [e] I. G. Green and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1597. [f] Ref. 9.

The lower reactivities and higher selectivities of the amine–arylboryl radicals (**7**) and (**8**) compared with $Me_3N{\rightarrow}\dot{B}H_2$ or $Me_3N{\rightarrow}\dot{B}HMe$ may be attributed to the decreased exothermicity of halogen atom abstraction because of stabilisation of the ligated arylboryl radicals by conjugative delocalisation of the unpaired electron onto the benzene ring. The somewhat lower selectivity of (**8**) compared with (**7**) may be ascribed to a polar effect; the former radical is probably more nucleophilic and reactive than the latter. Analogous explanations may be offered for the differences in reactivities and selectivities observed for the phosphine–boryl radicals.

Reactions with Nitriles and Esters.—We have reported previously that while the amine–boryl radicals $R_3N{\rightarrow}\dot{B}H_2$ (R = H, Me, or Et) undergo addition to the cyano group of acetonitrile to form iminyl radicals, the amine–alkylboryl radicals $Me_3N{\rightarrow}\dot{B}HR$ (R = Me, Bu^t, or Pr^iMe_2C) preferentially abstract hydrogen from the nitrile to give $^{\bullet}CH_2CN$.[2] The amine–alkylboryl radicals react similarly with acetate esters to yield alkoxycarbonylmethyl radicals.[2]

In contrast, u.v. irradiation of an oxirane solution containing the amine–arylborane (**2**) (*ca.* 0.25M), DTBP (*ca.* 15% v/v), and acetonitrile (1.0M) at 233 K afforded no e.s.r. spectrum. When the temperature was raised to 264 K, unidentified signals (which did not include the spectrum of $^{\bullet}CH_2CN$) appeared. A similar experiment with the phosphine–arylborane (**4**) (0.5M) showed only the spectrum of (**10**) at 216 K. When the nitrile was replaced by an equal concentration of ethyl acetate, there was no evidence for α-hydrogen atom abstraction by the amine–arylboryl radical (**8**) between 218 and 273 K since no e.s.r. spectra were observed.

We conclude that the lower reactivity towards nitriles and esters shown by amine–arylboryl radicals is also a consequence of their stabilisation relative to amine–boryl and –alkylboryl radicals by delocalisation of the unpaired electron onto the aromatic ring.

Experimental

E.s.r. spectra were obtained using a Varian E-109 instrument operating at *ca.* 9.1 GHz. The techniques employed were as described previously.[2]

Table 4. Microanalytical, ^{11}B-, and ^{31}P-n.m.r. data and melting points for ligated arylboranes

Compound	M.p./°C	Elemental composition Found % (calculated %)				δ/p.p.m. (*J*/Hz)	
		C	H	N	P	^{11}B	^{31}P[a]
(1)	71—72[b]					−0.4 (t) (97 BH)	
(2)	138—140	76.2 (76.1)	12.1 (11.8)	6.9 (6.8)		−0.5 (t) (99 BH)	
(3)	52—53	69.3 (69.3)	10.5 (10.7)		14.4 (14.9)	−27.5 (d, t) (92 BH, 52 BP)	12.3 (q) (50 PB)
(4)	37—38	72.5 (72.7)	11.2 (11.5)		12.0 (11.7)	−27.8 (d, t) (92 BH, 47 BP)	12.2 (q) (46 PB)
(5)	*c*	50.7 (50.5)	7.4 (7.5)		 (14.5)	−29.9 (q) (94 BH, 90 BP)[d]	105.8 (q) (89 PB)
(6)	69—70	58.2 (57.8)	8.9 (9.0)		11.2 (11.5)	−30.1 (q) (92 BH, 89 BP)[d]	106.0 (q) (89 PB)

[a] ^{1}H Decoupled. [b] Lit., m.p. 68—69 °C (ref. 4). [c] Compound is an oil at room temperature. [d] Determined with the aid of proton decoupled spectra.

Materials.—N.m.r. spectra (C_6D_6 solvent) were obtained using Varian XL-200 or VXR-400 instruments (200 or 400 MHz for ^{1}H), with tetramethylsilane internal standard (^{1}H) or $Et_2O{\rightarrow}BF_3$ or 85% aqueous H_3PO_4 external standards (^{11}B or ^{31}P, respectively); all ^{31}P n.m.r. spectra were proton decoupled. Preparations of ligated arylboranes, all of which contained ^{11}B ($I = 3/2$) and ^{10}B ($I = 3$) in natural abundance [80.2 and 19.8%, respectively; $\gamma(^{10}B)/\gamma(^{11}B) = 0.335$], were conducted under dry nitrogen or argon; all solvents were dried before use, except oxirane (BDH) which was used as received, as was 4-t-butylbenzaldehyde (Lancaster Synthesis).

Diethyl phenylboronate[3] and trimethylamine–phenylborane (1)[4] were prepared by published methods. Preparations of new compounds are described below; melting points, microanalytical results, and ^{11}B and ^{31}P n.m.r. spectroscopic data for the ligated arylboranes are given in Table 4.

Diethyl 4-t-Butylphenylboronate.—4-t-Butylphenylmagnesium bromide [prepared from the bromoarene (100.0 g, 0.47 mol) and magnesium (12.0 g, 0.49 mol)] in ether (250 cm^3) was added dropwise during 2 h to a vigorously stirred solution of trimethyl borate (52.0 g, 0.50 mol) in ether (250 cm^3) cooled in a solid CO_2–acetone slush bath. After the addition was complete, the mixture was allowed to warm to room temperature and left to stand overnight. It was then cooled in an ice–water-bath and stirred during dropwise addition of 2M-hydrochloric acid (250 cm^3). The ethereal solution was separated, washed with water (3 × 100 cm^3), and dried ($MgSO_4$); the solvent was removed under reduced pressure to give crude 4-t-butylphenylboronic acid (50.0 g).

A mixture of the crude boronic acid (37.0 g), benzene (200 cm^3), and absolute ethanol (100 cm^3) was slowly distilled through a 30 cm Vigreux column to remove the ternary water–ethanol–benzene azeotrope boiling at 65—66 °C, followed by the excess of ethanol and benzene. The residue was distilled under reduced pressure to yield *diethyl 4-t-butylphenylboronate* (28.5 g; b.p. 84—88 °C at 0.01 Torr). δ_H 1.16 (t, *J* 7.1 Hz, *Me*CH$_2$O), 1.25 (s, Bu^t), and 4.04 (q, *J* 7.1 Hz, MeC*H*$_2$O); the ring protons gave rise to an AB-quartet, δ 7.34 (3,5-ArH) and 7.74 (2,6-ArH), J_{AB} 8.4 Hz.

Trimethylamine–4-t-Butylphenylborane (**2**).—A mixture of lithium aluminium hydride (5.4 g, 0.14 mol) and ether (450 cm^3) was stirred under reflux for 1 h. The solution so formed was cooled in an ice-bath and the reaction flask was equipped with a condenser containing solid CO_2–acetone slush. An excess of trimethylamine (45.0 g) was allowed to evaporate into the reaction flask, the contents of which were then further cooled to −30 to −40 °C and stirred during dropwise addition of diethyl 4-t-butylphenylboronate (28.2 g, 0.12 mol) in ether (90 cm^3). After the addition, the reaction mixture was allowed to stand at room temperature overnight before being re-cooled in an ice-bath during cautious addition of water (10.3 cm^3, 0.57 mol). The resulting suspension was filtered, the filtrate was dried ($MgSO_4$), and the ether was partially removed under reduced pressure. The residue was cooled to *ca.* −20 °C in a freezer, when the *amine–arylborane* (**2**) (7.8 g) separated as a crystalline solid, δ_H 1.32 (s, Bu^t) and 1.84 (s, MeN); the ring protons gave rise to an AB-quartet, δ 7.75 (2,6-ArH) and 7.50 (3,5-ArH), J_{AB} 8.1 Hz.

Triethylphosphine–phenylborane (**3**) was prepared by stirring trimethylamine–phenylborane (1.0 g, 6.7 mmol) and an excess of triethylphosphine (1.0 g, 8.5 mmol) in benzene (5 cm^3) for 3 h under reflux. The solvent and excess of phosphine were removed under reduced pressure and the crude product was purified by h.p.l.c. on silica using light petroleum (b.p. 40—60 °C)–ethyl acetate (4:1 v/v) as eluant. δ_H 0.67 (d, t, J_{HH} 7.8, J_{HP} 14.6 Hz, *Me*CH$_2$P) and 1.02 (d, q, J_{HH} 7.8, J_{HP} 9.0 Hz, MeC*H*$_2$P); the ring protons give rise to a multiplet, δ 7.1—7.7.

Triethylphosphine–4-t-butylphenylborane (**4**) was prepared in a similar way from (**2**) and purified by h.p.l.c. δ_H 0.70 (d, t, J_{HH} 7.9, J_{HP} 14.6 Hz, *Me*CH$_2$P), 1.02 (d, q, J_{HH} 7.9, J_{HP} 8.8 Hz, MeC*H*$_2$P), 1.33 (s, Bu^t), 7.45 (d, *J* 8.4 Hz, 3,5-ArH), and 7.70 (d, d, J_{HH} 8.4, J_{HP} 2.7 Hz, 2,6-ArH).

Trimethyl phosphite–phenylborane (**5**) was prepared by stirring trimethylamine–phenylborane (2.2 g, 14.8 mmol) with an excess of trimethyl phosphite (4 cm^3) in ether (5 cm^3) at 30 °C for 2 h. The solvent and excess of phosphite were removed under reduced pressure and the same exchange procedure was repeated twice more. The crude phosphite–phenylborane was purified by h.p.l.c. on silica using light petroleum (b.p. 40—60 °C)–dichloromethane (3:1 v/v) as eluant. δ_H 3.17 (d, J_{HP} 10.5 Hz, MeOP); the ring protons gave rise to a multiplet, δ 7.1—7.8.

Trimethyl phosphite–4-t-butylphenylborane (**6**) was prepared by stirring the trimethylamine complex (**2**) (1.0 g, 4.9 mmol) and trimethyl phosphite (2 cm^3) in ether (5 cm^3) at 50 °C for 7 h. The solvent and excess of phosphite were removed under reduced pressure and the crude product was purified by h.p.l.c. as described for (**5**). δ_H 1.34 (s, Bu^t), 3.18 (d, J_{HP} 10.6 Hz, MeOP), 7.44 (d, *J* 8.4 Hz, 3,5-ArH), and 7.82 (d, d, J_{HH} 8.4, J_{HP} 2.5 Hz, 2,6-ArH).

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