# Homolytic Reactions of Ligated Boranes. Part 8.[1] Electron Spin Resonance Studies of Radicals derived from Ligated Alkylboranes

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The ligated alkylboryl radicals $L\rightarrow\dot{B}HR$ [$L = Me_3N$, $Et_3P$, or $(MeO)_3P$; $R = Me$, $Bu^t$, or $Me_2CHCMe_2$] have been generated in fluid solution, by hydrogen atom abstraction from $L\rightarrow BH_2R$ using photochemically produced t-butoxyl radicals, and studied by e.s.r. spectroscopy. The boron centre in the amine–alkylboryl radicals is pyramidal whilst that in the phosphine or phosphite complexes appears to be planar or nearly so. Unlike the isoelectronic di-t-butylmethyl radical, $Me_3N\rightarrow\dot{B}HBu^t$ is a transient species which dimerises at close to the diffusion-controlled rate at 235 K. Both amine– and phosphine–alkylboryl radicals abstract halogen rapidly from alkyl bromides, although the latter radicals are less reactive and more selective than the former. Amine–alkylboryl radicals react similarly, but more slowly, with alkyl chlorides, and halogen abstraction by the phosphine analogues was not detected by e.s.r. spectroscopy. Amine–alkylboryl radicals are highly nucleophilic and rapidly abstract an electron deficient α-hydrogen atom from a nitrile or an ester. Because of this property shown by the derived boron radicals, the amine–t-alkylboranes function as polarity-reversal catalysts for the net abstraction of electron deficient hydrogen atoms by t-butoxyl radicals. Thus, photolysis of di-t-butyl peroxide in the presence of $Me_3N\rightarrow BH_2CMe_2CHMe_2$ and a substrate affords radical products from the latter which are determined by the reactivity and regioselectivity of $Me_3N\rightarrow\dot{B}HCMe_2CHMe_2$ rather than of $Bu^tO^\bullet$. Reaction of $Bu^tO^\bullet$ with $Me_2NH\rightarrow BH_2R$ yields $Me_2NH\rightarrow\dot{B}HR$ as the product of kinetic control, but this is converted into the more stable $Me_2\dot{N}\rightarrow BH_2R$ by abstracting hydrogen from the amine–alkylborane. When R is $Bu^t$ or $Me_2CHCMe_2$, $Me_2\dot{N}\rightarrow BH_2R$ breaks down very rapidly by β-scission to give the corresponding t-alkyl radical. The aziridine–(1,1,2-trimethylpropyl)boryl radical undergoes rapid ring opening.

Previous parts in this series have reported e.s.r. studies of the formation, structures, and chemical reactions of 'primary' ligated boryl radicals of the type $L\rightarrow\dot{B}H_2$ (1), in which the ligand L can be an amine,[2–5] a phosphine,[6,7] a sulphide,[8] or an alkyl isocyanide.[1] The majority of these radicals were produced in solution by hydrogen atom abstraction from the corresponding ligated borane using photochemically generated t-butoxyl radicals [equations (1) and (2)]. When L is a secondary amine, although the amine–boryl radical is the initial (kinetically controlled) product of the reaction with t-butoxyl radicals, (1) subsequently abstracts hydrogen rapidly from the NH group of the parent amine–borane to give the more stable isomeric aminyl–borane radical (2) [equation (3)].[5]

$$\mathrm{Bu^tOOBu^t} \xrightarrow{h\nu} 2\mathrm{Bu^tO^\bullet} \qquad (1)$$

$$\mathrm{Bu^tO^\bullet} + \mathrm{L\rightarrow BH_3} \longrightarrow \underset{(1)}{\mathrm{L\rightarrow\dot{B}H_2}} + \mathrm{Bu^tOH} \qquad (2)$$

$$\mathrm{R_2NH\rightarrow\dot{B}H_2} + \mathrm{R_2NH\rightarrow BH_3} \longrightarrow \mathrm{R_2NH\rightarrow BH_3} + \underset{(2)}{\mathrm{R_2\dot{N}\rightarrow BH_3}} \qquad (3)$$

The properties of carbon-centred radicals have been studied exhaustively and shown to depend to a large extent on the nature of the substituents attached to $C_\alpha$. The work described here was carried out to determine the effects of replacing an α-hydrogen atom in (1) by an alkyl group and to compare the properties of $L\rightarrow\dot{B}HR$ with those of the isoelectronic secondary alkyl radicals.

## Results and Discussion

E.s.r. spectra were recorded during continuous u.v. irradiation (λ 240—340 nm) of liquid samples positioned directly in the microwave cavity of the spectrometer; the initial radical source was di-t-butyl peroxide (DTBP) which undergoes photolysis according to equation (1).

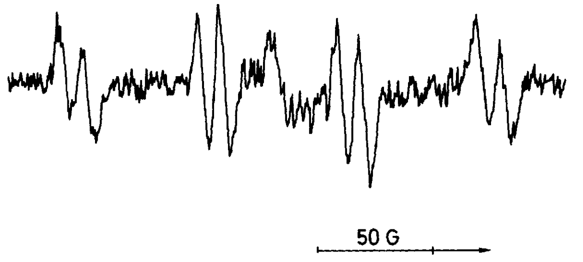

Figure 1. E.s.r. spectrum of the trimethylamine–(1,1,2-trimethylpropyl)boryl radical (4; $R = Me_2CHCMe_2$) in cyclopropane at 210 K

The spectrum shown in Figure 1 was obtained from a cyclopropane solution containing trimethylamine–(1,1,2-trimethylpropyl)borane (3; $R = Me_2CHCMe_2$; *ca.* 1M) and DTBP (*ca.* 15% v/v) and is assigned to the trimethylamine–(1,1,2-trimethylpropyl)boryl radical (4; $R = Me_2CHCMe_2$) formed by hydrogen atom abstraction from the ligated borane [equation (4)].† The pattern of eight equally intense lines arises

$$\mathrm{Bu^tO^\bullet} + \underset{(3)}{\mathrm{Me_3N\rightarrow BH_2R}} \longrightarrow \underset{(4)}{\mathrm{Me_3N\rightarrow\dot{B}HR}} + \mathrm{Bu^tOH} \qquad (4)$$

from coupling of the unpaired electron to $^{11}B$ ($I = 3/2$, natural abundance 80.2%) and to one proton; the contribution from the radical containing $^{10}B$ [$I = 3$, natural abundance 19.8%, $\gamma(^{10}B)/\gamma(^{11}B)$ 0.335] is barely discernible above the noise level under the conditions used to obtain Figure 1, although these

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† The 1,1,2-trimethylpropyl residue is commonly referred to as a thexyl group.

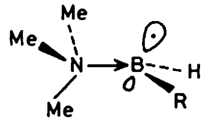
**Table 1.** E.s.r. parameters for trimethylamine–alkylboryl radicals and related species

| | | | | Hyperfine splittings (G)[b] | | |
|---|---|---|---|---|---|---|
| Radical | Solvent[a] | $T$/K | $g$-Factor[b] | $a(^{11}B)$ | $a(H_\alpha)$ | Others |
| $Me_3N\rightarrow\dot{B}HMe$ | A | 199 | 2.0020 | 61.6 | 6.1 | 14.8 (3H) |
| $Me_3N\rightarrow\dot{B}HBu^t$ | A | 177 | 2.0021 | 59.4 | 9.8 | *c* |
| | A | 230 | 2.0020 | 59.1 | 9.8 | *c* |
| | B | 235 | 2.0020 | 60.2 | 9.0 | *c* |
| $Me_3N\rightarrow\dot{B}H(CMe_2CHMe_2)$ | A | 208 | 2.0022 | 59.6 | 10.4 | *c* |
| | B | 264 | 2.0021 | 59.9 | 9.8 | *c* |
| | C | 193 | 2.0021 | 60.3 | 10.0 | *c* |
| | C | 262 | 2.0021 | 59.6 | 9.9 | *c* |
| $Me_3N\rightarrow\dot{B}H_2$[d] | D | 280 | 2.0022 | 51.3 | 9.6[e] | 1.4 (1N),<br>1.4 ($9H_\gamma$) |
| $Et_3N\rightarrow\dot{B}H_2$[d] | E | 226 | 2.0023 | 47.5 | 13.0[e] | 2.2 (1N),<br>2.2 ($6H_\gamma$) |

[a] A, oxirane; B, cyclopropane; C, cyclopropane–benzene (7:1 v/v); D, t-butyl alcohol–dimethyl ether (4:1 v/v); E, cyclopropane–tetrahydrofuran (3:1 v/v). [b] Corrected for second-order effects. The lines are broad for (**4**); splittings and $g$-factors are generally accurate to ±0.2 G and ±0.0001, respectively. [c] Not clearly resolved (see text). [d] Data from ref. 2. [e] Two equivalent protons.

lines are clearly apparent in expanded spectra. A very similar spectrum was obtained from trimethylamine–t-butylborane (**3**; R = $Bu^t$) and is attributed to the corresponding amine–alkylboryl radical. Under forcing conditions, some further splitting (presumably from $^{14}N$ and from protons in the *N*- and *B*-alkyl groups) was poorly resolved in the spectra of (**4**; R = $Bu^t$ or $Me_2CHCMe_2$), but this fine structure could not be analysed unequivocally. The spectrum of (**4**; R = Me) obtained from trimethylamine–methylborane showed an additional splitting of 14.8 G from the *B*-methyl protons and was difficult to detect because of its greater multiplicity. E.s.r. parameters for the amine–alkylboryl radicals are given in Table 1, along with data obtained previously for $Me_3N\rightarrow\dot{B}H_2$ (**4**; R = H) and for $Et_3N\rightarrow\dot{B}H_2$.

We have concluded[2] that the equilibrium geometry at boron in the trimethylamine–boryl radical is pyramidal, as shown in (**5**; R = H), on the basis of the magnitudes and temperature dependences of the $^{11}B$ and α-proton coupling constants and the effects of deuteriation at boron. The e.s.r. parameters of the



(5)

amine–alkylboryl radicals are also indicative of a non-planar configuration at the radical centre. The $^{11}B$ splittings are large and correspond to 8—9% unpaired electron population of the B 2*s* atomic orbital;[9] the small decrease in $a(^{11}B)$ with increasing temperature implies that the time-average configuration becomes more nearly planar at higher temperatures, as expected for a pyramidal equilibrium geometry and the associated double minimum potential function which would govern inversion at the radical centre.[10] The magnitudes of $a(H_\alpha)$ for (**4**; R = Me, $Bu^t$, or $Me_2CHCMe_2$) are appreciably smaller than the value (15.2 G at 253 K) for the planar or nearly-planar borane radical anion $H_3B^{\bullet -}$,[11] again in accord with a pyramidal geometry for the amine–alkylboryl radicals. The sign of $a(H_\alpha)$ for (**4**; R = alkyl) is almost certainly negative.

The $^{11}B$ splittings for (**4**; R = alkyl) are 15—20% larger than $a(^{11}B)$ for (**4**; R = H) under similar conditions, suggesting that the time-average configuration of the latter deviates less from planarity at boron. The value of $a(^{13}C_\alpha)$ also increases, although to a lesser extent, upon progressive alkylation of a carbon radical centre; for example the values of $a(^{13}C_\alpha)$ for $Me\dot{C}H_2$, $Me_2\dot{C}H$, and $Me_3C^\bullet$ are 39.4, 40.8, and 44.8 G, respectively, at *ca.* 195 K.[12–14]

*Radical Lifetimes.*—In fluid solution the neopentyl radical[15] ($Bu^t\dot{C}H_2$) and the isoelectronic trimethylamine–boryl radical[2] (**4**; R = H) both undergo dimerisation at close to the diffusion-controlled limiting rate. In contrast, the 2,2-dimethyl-1-t-butylpropyl (di-t-butylmethyl) radical ($Bu^t_2\dot{C}H$) is a relatively persistent species, decay of which is kinetically first-order ($t_{\frac{1}{2}}$ 58 s at 298 K in DTBP solvent) and its longevity has been attributed to steric protection of the radical centre.[16]* We hoped initially that the isoelectronic trimethylamine–t-butylboryl radical (**4**; R = $Bu^t$) and the 1,1,2-trimethylpropyl analogue would likewise be persistent, but this hope was not realised. Stationary-state radical concentrations were typical of transient species (see Figure 1) and measurements using the rotating sector technique[18,19] confirmed their short lifetimes. In cyclopropane at 235 K the steady-state concentration of (**4**; R = $Bu^t$) was proportional to the square-root of the incident light intensity and the radical decayed with second-order kinetics when photolysis was interrupted, presumably by dimerisation to give a ligated diborane(4) [equation (5)]. At 235

$$2Me_3N\rightarrow\dot{B}HBu^t \xrightarrow{2k_5} Me_3N\rightarrow B(H)(Bu^t){-}B(H)(Bu^t)\leftarrow NMe_3 \tag{5}$$

K decay from an initial concentration of $5.5 \times 10^{-7}$M occurred with a rate coefficient ($2k_5$) of $1.9 \times 10^9$ l mol$^{-1}$ s$^{-1}$, close to that expected for a diffusion-controlled reaction.

Steric repulsion falls off rapidly with the distance between interfering groups[20] and the boron atoms in a pair of trimethylamine–t-alkylboryl radicals can evidently approach readily within bonding range without causing serious repulsion between non-bonded groups. Close approach should be facilitated for (**4**; R = $Bu^t$) relative to the isoelectronic $Bu^t_2\dot{C}H$ because of the markedly pyramidal configuration at the radical centre in the former and the larger covalent radius of boron as compared with carbon.

*Phosphine–Alkylboryl Radicals.*—Triethylphosphine and trimethyl phosphite complexes of alkylboryl radicals were

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* This radical has also been reported to 'dimerise slowly, but quantitatively' to give 2,2,5,5-tetramethyl-3,4-di-t-butylhexane (1,1,2,2-tetra-t-butylethane).[17]

**Table 2.** E.s.r. parameters for phosphine–alkylboryl radicals and related species

| Radical | Solvent[a] | $T$/K | $g$-Factor[b] | Hyperfine splittings (G)[b] $a(^{11}B)$ | $a(H_\alpha)$ | $a(^{31}P)$ | Others |
|---|---|---|---|---|---|---|---|
| $Et_3P\rightarrow\dot{B}HMe$ | A | 215 | 2.0021 | 15.89 | 14.95 | 43.30 | 15.42 (3H), 0.50 (6H) |
| $(MeO)_3P\rightarrow\dot{B}HMe$ | B | 241 | 2.0022 | 12.76 | 15.65 | 41.26 | 14.60 (3H) |
| $Et_3P\rightarrow\dot{B}HBu^t$ | A | 215 | 2.0020 | 16.82 | 15.48 | 42.30 | |
| $(MeO)_3P\rightarrow\dot{B}HBu^t$ | A | 237 | 2.0019 | 13.44 | 15.48 | 39.63 | 0.92 (9H) |
| $Et_3P\rightarrow\dot{B}H(CMe_2CHMe_2)$ | A | 214 | 2.0020 | 16.58 | 15.59 | 43.17 | |
| | A | 245 | 2.0019 | 16.63 | 15.10 | 43.20 | |
| $(MeO)_3P\rightarrow\dot{B}H(CMe_2CHMe_2)$[c] | A | 228 | 2.0019 | 13.09 | 15.28 | 40.12 | 0.91 (6H) |
| $(MeO)_3P\rightarrow\dot{B}H(CMe_2CHMe_2)$[d] | A | 228 | 2.0019 | 13.20 | 15.28 | 39.80 | 1.85 (3H) |
| $(MeO)_3P\rightarrow\dot{B}D(CMe_2CDMe_2)$[c] | A | 239 | 2.0019 | 12.75 | 2.33[e] | 40.17 | 0.91 (6H) |
| $(MeO)_3P\rightarrow\dot{B}D(CMe_2CDMe_2)$[d] | A | 239 | 2.0019 | 12.85 | 2.33[e] | 39.85 | 1.85 (3H) |
| $Et_3P\rightarrow\dot{B}H_2$[f] | A | 183 | 2.0020 | 17.6 | 16.8[g] | 43.6 | |
| $(MeO)_3P\rightarrow\dot{B}H_2$[f] | A | 255 | 2.0019 | 15.1 | 16.6[g] | 43.4 | |

[a] A, cyclopropane; B, oxirane. [b] Corrected for second-order effects. [c] More abundant isomer (see text). [d] Less abundant isomer (see text). [e] Deuterium splitting. [f] Data from ref. 6. [g] Two protons coupling.

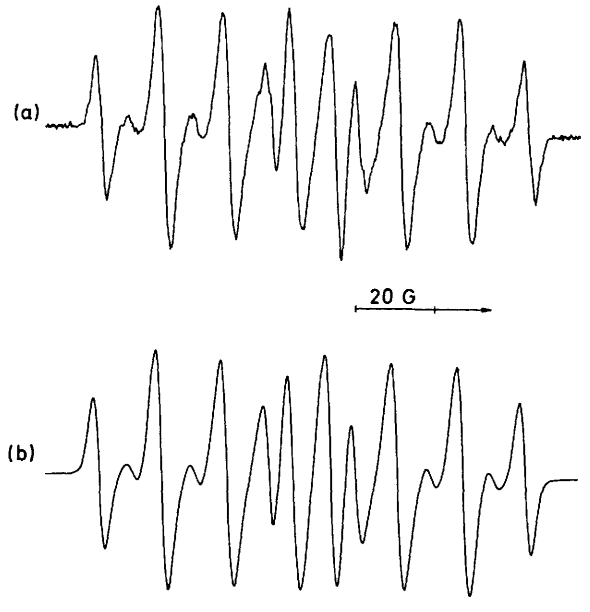


**Figure 2.** (a) E.s.r. spectrum of the triethylphosphine–(1,1,2-trimethylpropyl)boryl radical in cyclopropane at 245 K. (b) Computer simulation as a composite spectrum from the $^{11}B$- and $^{10}B$-containing radicals present in natural abundance. The coupling constants are as given in Table 2 [$a(^{10}B)$ 5.57 G], the linewidth is 3.2 G, and the lineshape is 70% Gaussian

generated by hydrogen atom abstraction from the corresponding ligated boranes [equation (6; X = Et or MeO, R = Me, Bu$^t$, or $Me_2CHCMe_2$)]. The e.s.r. spectra of $Et_3P\rightarrow\dot{B}H(CMe_2CHMe_2)$ and $(MeO)_3P\rightarrow\dot{B}HBu^t$ are shown in Figures 2 and 3, respectively, and all the spectroscopic parameters are given in Table 2.

$$Bu^tO^\bullet + X_3P\rightarrow BH_2R \longrightarrow \underset{(6)}{X_3P\rightarrow\dot{B}HR} + Bu^tOH \quad (6)$$

We have concluded previously that, unlike $R_3N\rightarrow\dot{B}H_2$, $X_3P\rightarrow\dot{B}H_2$ is close to planar at the radical centre,[6] and consideration of the values of $a(^{11}B)$, $a(H_\alpha)$, and $a(^{31}P)$ for (6) indicates that the equilibrium geometries of these radicals are also near-planar at boron. Stabilising donation of the unpaired electron from boron into an empty ligand orbital of π symmetry will be maximised in a planar configuration[6] and is probably responsible for the different geometries of amine– and phosphine–alkylboryl radicals.

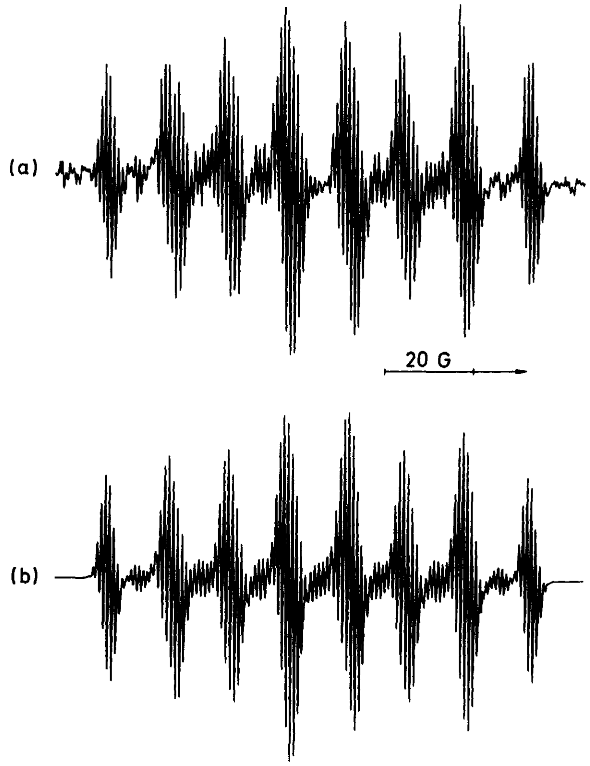


**Figure 3.** (a) E.s.r. spectrum of the trimethyl phosphite–t-butylboryl radical in cyclopropane at 237 K. (b) Computer simulation as a composite spectrum from the $^{11}B$- and $^{10}B$-containing radicals present in natural abundance. The coupling constants are as given in Table 2 [$a(^{10}B)$ 4.50 G], the linewidth is 0.38 G, and the lineshape is 100% Lorentzian

The value of $a(\beta\text{-C}H_3)$ for $Me_3N\rightarrow\dot{B}HMe$ (14.8 G) is much smaller than that[21] for the isoelectronic $Me_3C\text{–}\dot{C}HMe$ (25.2 G), presumably reflecting a less effective hyperconjugative interaction in the former as a result of its pyramidal geometry and the poorer energetic match between the SOMO and the filled β-$CH_3$ π group orbital. The similarity in values of $a(\beta\text{-C}H_3)$ shown by $Me_3N\rightarrow\dot{B}HMe$ and $X_3P\rightarrow\dot{B}HMe$, despite the probable smaller spin population on boron in the latter, is

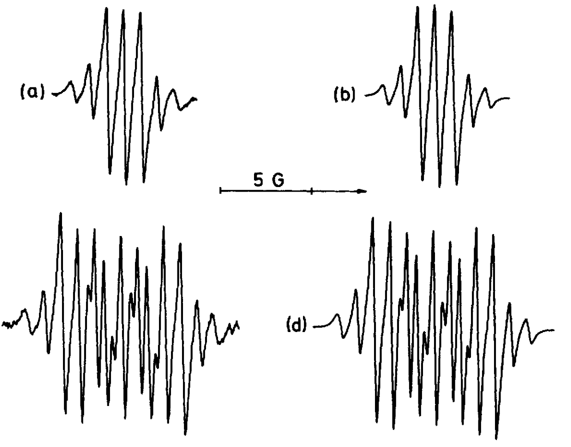
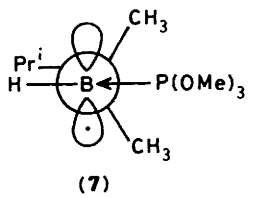


**Figure 4.** (a) Low-field multiplet from the e.s.r. spectrum of (MeO)$_3$P$\rightarrow\dot{B}$H(CMe$_2$CHMe)$_2$ (97.5 atom % $^{11}$B) in cyclopropane at 251 K. (b) Computer simulation of (a) as a superposition of a 0.91 G septet (linewidth 0.27 G, relative intensity 0.75, lineshape 90% Lorentzian) and a 1.85 G quartet (linewidth 0.38 G, relative intensity 0.25, lineshape 90% Lorentzian). (c) Low-field multiplet from the e.s.r. spectrum of (MeO$_3$)P$\rightarrow\dot{B}$D(CMe$_2$CDMe$_2$) (97.5 atom % $^{11}$B) in cyclopropane at 251 K. (d) Computer simulation as described for (b), except that each contributor has an additional splitting of 2.33 G from one deuterium nucleus

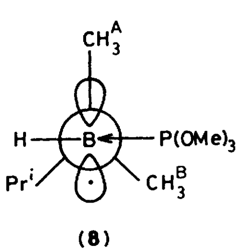
presumably a consequence of the different geometries at the radical centre.

Although the basic appearance of the spectrum of (MeO)$_3$P$\rightarrow\dot{B}$H(CMe$_2$CHMe$_2$) was similar to that of the t-butyl analogue, the fine structure present in the former could only be accounted for in terms of the presence of two conformations of the radical. Thus, although the fine structure for (MeO)$_3$P$\rightarrow\dot{B}$H(CMe$_2$CHMe$_2$) [Figure 4(a)] comprises seven lines, it is clear from the relative intensities that these cannot arise simply from coupling to two equivalent $\gamma$-methyl groups in the thexyl moiety. The corresponding multiplet for (MeO)$_3$P$\rightarrow\dot{B}$D(CMe$_2$CDMe$_2$) is shown in Figure 4(c) and can be simulated as an overlapping pattern resulting from three (MeO)$_3$P$\rightarrow\dot{B}$H(CMe$_2$CHMe$_2$) septets separated by $a$(D$_\alpha$) [Figure 4(d)]. Hence, the $\gamma$-methine proton in the protiated radical does not give rise to a resolvable splitting. The observed seven-line pattern can be simulated in terms of a binomial septet [$a$(6H$_\gamma$) 0.91 G] and a quartet [$a$(3H$_\gamma$) 1.85 G] with relative intensities 3:1 and the same centre [Figure 4(b)]. Thus, we interpret the spectrum of (MeO)$_3$P$\rightarrow\dot{B}$H(CMe$_2$CHMe$_2$) as arising from two conformations which have essentially the same $g$-factor and spectral width and do not interconvert on the e.s.r. timescale. The total composite spectrum proved difficult to simulate precisely, because its detailed appearance was very sensitive to tiny changes in the e.s.r. parameters chosen for the two conformations.

By analogy with the conclusions reached for the neopentyl and isobutyl radicals by Ingold and Walton,[22] we suggest that the two conformations of (MeO)$_3$P$\rightarrow\dot{B}$H(CMe$_2$CHMe$_2$) are similar to (**7**) and (**8**). These could interconvert slowly on the e.s.r. timescale because they also differ in conformation about the C$_\beta$–C$_\gamma$ bond to the isopropyl group, the barrier to rotation about which is likely to be substantial. We propose that (**7**) is responsible for the $\gamma$-proton septet splitting of 0.91 G, while (**8**) shows a quartet splitting of 1.85 G from CH$_3$$^A$; the splitting from CH$_3$$^B$ is unresolved but contributes to the greater linewidth for this less abundant conformation.



(**7**)



(**8**)

The e.s.r. spectra of phosphine–t-alkylboryl radicals were more intense than those of the trimethylamine complexes because the former are more persistent. Thus, the rate-coefficient for second-order decay of Et$_3$P$\rightarrow\dot{B}$HBu$^t$ from an initial concentration of *ca.* 3 × 10$^{-6}$M is 7.5 × 10$^7$ l mol$^{-1}$ s$^{-1}$ in cyclopropane at 235 K, some 25 times less than 2$k_5$ under the same conditions. The relative persistence of the phosphine complexes is presumably attributable, at least in part, to their near planarity at the sterically congested radical centre (*cf.* before).

*Reactions with Alkyl Halides.*—In common with the 'primary' ligated boryl radicals L$\rightarrow\dot{B}$H$_2$ (L = R$_3$N, R$_3$P, or R$_2$S),[2,5,6,8,11] the ligated alkylboryl radicals rapidly abstract halogen from alkyl bromides [*e.g.* equation (7)]. Thus, in

$$L\rightarrow\dot{B}HR + Pr^nBr \longrightarrow Pr^{n\bullet} + L\rightarrow BHRBr \qquad (7)$$

cyclopropane at 173 K when n-propyl, isopropyl, or t-butyl bromide (each 1.0M) was present along with (**3**; R = Me, Bu$^t$, or Me$_2$CHCMe$_2$) and DTBP, the amine–boryl radical was no longer detected and a strong spectrum of the corresponding alkyl radical was observed. In similar experiments with alkyl chlorides, a weak spectrum of (**4**; R = Bu$^t$ or Me$_2$CHCMe$_2$) was observed alongside that of the alkyl radical produced by halogen abstraction, although the relative strength of the former decreased along the series Pr$^n$Cl > Pr$^i$Cl > Bu$^t$Cl showing that the reactivity of (**4**) towards these halides increases in the opposite order.

Similar experiments with Et$_3$P$\rightarrow$BH$_2$(CMe$_2$CHMe$_2$) and alkyl halides (1M) afforded only the spectrum of the t-butyl radical with Bu$^t$Br between 157 and 220 K, but with Pr$^n$Br below 214 K the spectrum of Et$_3$P$\rightarrow\dot{B}$H(CMe$_2$CHMe$_2$) was apparent alongside that of the n-propyl radical. With Pr$^n$I between 157 and 262 K, only the n-propyl radical was detected, but with either Pr$^n$Cl or Bu$^t$Cl only the spectrum of Et$_3$P$\rightarrow\dot{B}$H(CMe$_2$CHMe$_2$) was observed between 169 and 260 K. The phosphine–alkylboryl radical is thus less reactive in halogen abstraction than the corresponding amine-ligated radical. The radical (MeO)$_3$P$\rightarrow\dot{B}$H(CMe$_2$CHMe$_2$) was still less reactive. No halogen abstraction was detected from Bu$^t$Cl or Pr$^n$Cl up to 278 K nor from Pr$^n$Br below 222 K; above this temperature a weak spectrum of Pr$^{n\bullet}$ was also evident.

Quantitative competition experiments were carried out as described previously[2,5,6,8,11] in order to determine the relative reactivities of t-butyl and n-propyl halides towards amine– and phosphine–alkylboryl radicals; the results are summarised in Table 3. With the alkyl bromides, Et$_3$P$\rightarrow\dot{B}$HR is much more selective towards the tertiary halide than is Me$_3$N$\rightarrow\dot{B}$HR, in accord with the higher reactivity of the latter. The amine–alkylboryl radicals react selectively with the tertiary chloride in competitions between Bu$^t$Cl and Pr$^n$Cl, but are very unselective in their much more rapid reactions with the corresponding bromides. In fact t-butyl bromide is slightly *less* reactive than n-propyl bromide towards the bulky amine–t-alkylboryl radicals. Although the transition state for bromine atom abstraction by (**4**; R = alkyl) would be expected to be very 'early', such that the activation energy is insensitive to the strength of the C–Br bond being broken, steric effects are evidently still important in the transition state and favour abstraction from the less encumbered primary bromide by the sterically demanding

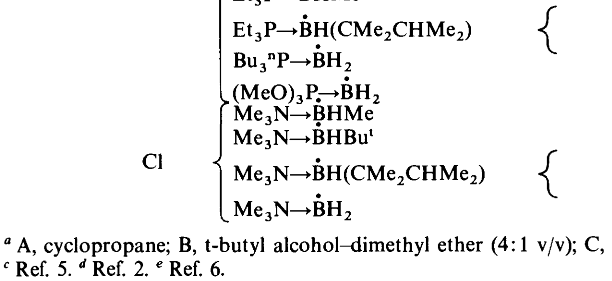
**Table 3.** Relative rate coefficients for abstraction of halogen from t-butyl and n-propyl halides by ligated boryl radicals

| Halogen | Abstracting radical | Solvent[a] | $T$/K | $k_{\mathrm{Bu^tHal}}/k_{\mathrm{Pr^nHal}}$[b] | Ref. |
|---|---|---|---|---|---|
| Br | $Me_3N\rightarrow\dot{B}HMe$ | A | 217 | 1.1 | This work |
| | $Me_3N\rightarrow\dot{B}HBu^t$ | A | 173 | 0.70 | |
| | | A | 216 | 0.87 | |
| | $Me_3N\rightarrow\dot{B}H(CMe_2CHMe_2)$ | A | 173 | 0.67 | |
| | $Me_3N\rightarrow\dot{B}H_2$ | B | 261 | 1.5 | *c* |
| | $Et_3N\rightarrow\dot{B}H_2$ | C | 246 | 1.2 | *d* |
| | $Et_3P\rightarrow\dot{B}HMe$ | A | 170 | 2.8 | This work |
| | $Et_3P\rightarrow\dot{B}H(CMe_2CHMe_2)$ | A | 170 | 3.8 | |
| | | D | 170 | 3.1 | |
| | $Bu_3{}^nP\rightarrow\dot{B}H_2$ | A | 240 | 5.6 | *e* |
| | $(MeO)_3P\rightarrow\dot{B}H_2$ | A | 240 | 8.6 | *e* |
| Cl | $Me_3N\rightarrow\dot{B}HMe$ | A | 216 | 3.5 | This work |
| | $Me_3N\rightarrow\dot{B}HBu^t$ | A | 216 | 2.5 | |
| | $Me_3N\rightarrow\dot{B}H(CMe_2CHMe_2)$ | A | 173 | 3.0 | |
| | | A | 216 | 2.7 | |
| | $Me_3N\rightarrow\dot{B}H_2$ | B | 261 | 5.0 | *c* |

[a] A, cyclopropane; B, t-butyl alcohol–dimethyl ether (4:1 v/v); C, cyclopropane–tetrahydrofuran (3:1 v/v); D, oxirane. [b] Estimated error ±10%. [c] Ref. 5. [d] Ref. 2. [e] Ref. 6.

amine–t-alkylboryl radicals. With the less reactive alkyl chlorides, the transition state will be reached further along the reaction co-ordinate and bond strength differences now outweigh steric interactions.

*Reactions with Nitriles.*—The ammonia–boryl radical adds to alkyl cyanides (RCN; R = Me, Et, or Pr$^i$) to afford the iminyl radicals (**9**) (identified by e.s.r.) which, depending on the stability of R$^\bullet$, may subsequently undergo β-scission at a detectable rate [equation (8)].[23] Tertiary amine–boryl radicals also add to acetonitrile.[2] In striking contrast, when (**4**; R = Me, Bu$^t$, or Me$_2$CHCMe$_2$) is generated in the presence of methyl, ethyl, or isopropyl cyanide the spectrum of the corresponding α-cyanoalkyl radical is observed and no evidence is found for addition to the CN group.



(8)

Although the reaction is exothermic [$DH°$(Bu$^t$O–H) and $DH°$(NCCH$_2$–H) are 440 and 389 kJ mol$^{-1}$, respectively[24]], t-butoxyl radicals abstract hydrogen only sluggishly from methyl cyanide and a very weak spectrum of $H_2\dot{C}CN$ is obtained when a cyclopropane solution containing the nitrile (1.0M) and DTBP is u.v. irradiated at 240 K [equation (9)]. If, instead, a mixture of oxirane and cyclopropane is used as the solvent, essentially only the oxiranyl radical is detected down to 164 K, showing that reaction (10)[25] is much faster than reaction (9) when the

$$Bu^tO^\bullet + MeCN \longrightarrow H_2\dot{C}CN + Bu^tOH \qquad (9)$$

$$Bu^tO^\bullet + \overline{CH_2CH_2O} \longrightarrow \cdot\overline{CHCH_2O} + Bu^tOH \qquad (10)$$

oxirane concentration is 7.5 times that of the nitrile. Only the spectrum of the amine–alkylboryl radical was observed when DTBP was photolysed in the presence of (**3**; R = Bu$^t$ or Me$_2$CHCMe$_2$) at concentrations as low as 0.1M in neat oxirane, showing the very high reactivity of (**3**) towards t-butoxyl radicals. However, when an oxirane–cyclopropane solution (2:1 v/v) containing DTBP, (**3**; R = Bu$^t$ or Me$_2$CHCMe$_2$) (0.1—1.0M) and acetonitrile (1.0M) is u.v.-irradiated 164 K, *only the spectrum of the cyanomethyl radical*[26] [$a$(2H) 21.0, $a$(N) 3.60 G, $g$ 2.0030] is observed. These results show conclusively that it is the amine–t-alkylboryl radical which reacts with the nitrile, presumably to regenerate the ligated borane (**3**) [equation (11)], which therefore functions as a *polarity reversal catalyst*,[27] accelerating the overall transformation shown in equation (9). The electrophilic alkoxyl radical is rapidly converted into the

$$Me_3N\rightarrow\dot{B}HR + MeCN \longrightarrow H_2\dot{C}CN + Me_3N\rightarrow BH_2R \quad (11)$$

nucleophilic amine–alkylboryl radical, which effects abstraction of the electron-deficient hydrogen atom from the nitrile, being itself converted back into the amine–borane catalyst.*

A similar reaction with [$^2H_3$]acetonitrile afforded the spectrum of $D_2\dot{C}CN$ [$a$(2D) 3.25, $a$(N) 3.60 G at 173 K] and competition experiments showed that CH$_3$CN is 28 times more reactive than CD$_3$CN towards (**4**; R = Me$_2$CHCMe$_2$) at 173 K in oxirane–cyclopropane as solvent (2:1 v/v). This kinetic isotope effect is within the range expected for H/D atom abstraction at low temperatures and provides support for reaction (11) as opposed to a route involving single-electron transfer from (**4**) to the nitrile. It is interesting that hydrogen atom abstraction from acetonitrile by a photoexcited nitroxide radical shows almost no deuterium isotope effect at 310 K.[28] We suggest that this result may indicate that electron transfer from the excited nitroxide is rate-determining [equation (12)].

$$R_2\dot{N}O^* + CH_3CN \longrightarrow [R_2\overset{+}{N}{=}O][CH_3CN]^{\bullet-} \longrightarrow R_2NOH + H_2\dot{C}CN \quad (12)$$

When n-propyl bromide and acetonitrile were present in equal concentration (1.0M) along with (**3**; R = Me$_2$CHCMe$_2$)

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* Neither $Me_3N\rightarrow BH_3$ nor dimethyl ether performed a similar catalytic function. Thus, $MeO\dot{C}H_2$ did not react detectably with MeCN up to 259 K and $Me_3N\rightarrow\dot{B}H_2$ (like the triethylamine complex[2]) underwent addition to give an iminyl adduct [$a$(N) 9.5, $a$($^{11}$B) 21.8 G, $g$ 2.0026 at 240 K in oxirane–cyclopropane].

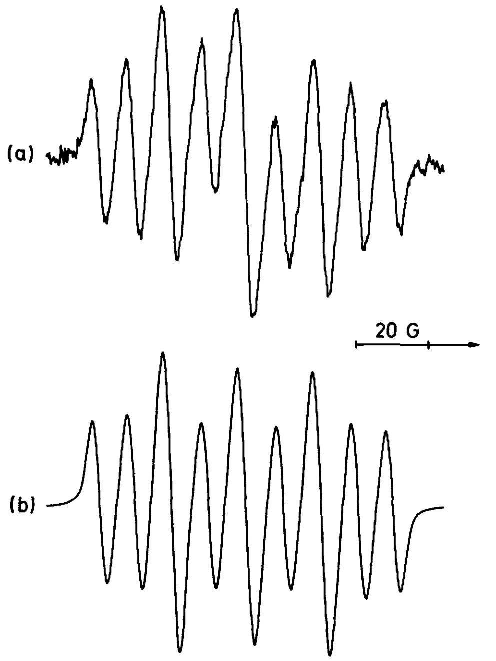

**Figure 5.** (a) E.s.r. spectrum of the iminyl radical adduct $Me_3N{\rightarrow}BHMeC(CD_3){=}N^{\bullet}$ in oxirane–cyclopropane (2:1 v/v) at 173 K. (b) Computer simulation of (a) as a composite spectrum from the $^{11}B$- and $^{10}B$-containing radicals present in natural abundance. The coupling constants are as given in the text [$a(^{10}B)$ 6.89 G], the linewidth is 4.0 G, and the lineshape is 60% Lorentzian

and DTBP, only $Pr^{n\bullet}$ was detected at 178 K, but in a similar experiment with n-propyl chloride only the spectrum of $H_2\dot{C}CN$ was observed. The rate coefficient for reaction (11) thus lies between those for halogen abstraction by (**4**) from the two alkyl halides. An oxirane–cyclopropane solution (2:1 v/v) containing n-propyl bromide and isopropyl cyanide (each 1.0M) in addition to (**3**; R = $Me_2CHCMe_2$) and DTBP gave rise only to the spectrum of $Pr^{n\bullet}$, showing that even with this relatively reactive nitrile the cyanoalkyl radical is formed indirectly by way of (**4**) and not *via* direct abstraction by $Bu^tO^{\bullet}$.

The radical (**4**; R = Me) also abstracts hydrogen from $CH_3CN$ and no iminyl adduct was detectable. However, with $CD_3CN$ at 173 K addition was observed [$a(^{11}B)$ 20.6, $a(N)$ 9.5 G, $g$ 2.0026] (see Figure 5), presumably because abstraction of the α-deuterium atom is relatively slow (see before) and because addition to the internal carbon is more favourable for the less bulky *B*-methyl radical. Although the increasing tendency of $Me_3N{\rightarrow}\dot{B}HR$ to abstract an α-hydrogen atom rather than to add to the CN group along the series R = H < Me < $Bu^t$, $Me_2CHCMe_2$ is probably mainly steric in origin, polar effects may also play a part since a *B*-alkyl group should render the boron radical more nucleophilic and increase the rate of abstraction of electron-deficient hydrogen in a reaction subject to frontier orbital control.

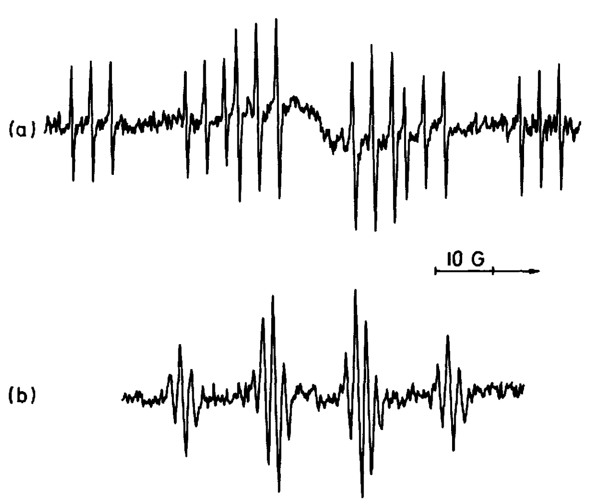

**Figure 6.** (a) E.s.r. spectra in oxirane at 216 K of (a) the radical (**10**) obtained from $(NCCH_2CH_2)_2O$ (1M) in the presence of $Me_2N{\rightarrow}BH_2(CMe_2CHMe_2)$ (0.1M) and (b) the radical (**11**) obtained from $(NCCH_2CH_2)_2O$ (2M) in the absence of catalyst

The high rate of reaction (11) at low temperatures implies that it is at least thermoneutral, if not exothermic, and sets a lower limit of 389 kJ mol$^{-1}$ for $DH^{\circ}$(B–H) in $Me_3N{\rightarrow}BH_2R$. We have previously calculated the B–H bond dissociation energy in $H_3N{\rightarrow}BH_3$ to be 416 kJ mol$^{-1}$,[8,*] and if alkylation at boron has an effect on $DH^{\circ}$(B–H) similar[†] to that which alkylation at carbon has on $DH^{\circ}$(C–H) in the isoelectronic alkanes,[31] $DH^{\circ}$(B–H) for $Me_3N{\rightarrow}BH_2R$ could be up to 17 kJ mol$^{-1}$ less than for $H_3N{\rightarrow}BH_3$.

None of the phosphine–alkylboryl radicals reacted with acetonitrile (1.0M) at a detectable rate up to 250 K, and only the e.s.r. spectrum of $X_3P{\rightarrow}\dot{B}HR$ was observed. The lower nucleophilicity of the phosphine–alkylboryl radicals and their stabilisation relative to the amine analogues are probably responsible for this lower reactivity.

The ability of (**3**; R = $Me_2CHCMe_2$) to act as a polarity-reversal catalyst for the abstraction of electron-deficient hydrogen by t-butoxyl radicals is further illustrated by the following examples. In each the change in reaction pathway is brought about by only 0.1M-amine–alkylborane. In cyclopropane with ethyl or t-butyl acetate (1.0M) and DTBP (15% v/v) between 189 and 232 K, the catalysed reaction afforded solutions showing the strong, clean e.s.r. spectra of the corresponding alkoxycarbonylmethyl radicals[32] [equation (13)]. In the absence of catalyst the cyclopropyl radical was

$$Bu^tO^{\bullet} + CH_3CO_2R \xrightarrow[\text{catalyst}]{(3;\ R\ =\ Me_2CHCMe_2)} {}^{\bullet}CH_2CO_2R + Bu^tOH \quad (13)$$

detected with t-butyl acetate, while ethyl acetate yielded overlapping spectra of cyclopropyl radicals and

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[*] We have refined our estimates[8] of the B–H and N–H bond dissociation energies in $H_3N{\rightarrow}BH_3$. *Ab initio* molecular orbital calculations were carried out using the GAUSSIAN 82 package[29] and total energies of fully optimised structures[5,8] were obtained at the (U)MP3(full)/6-31G**//(U)HF/6-31G** level.[30] At this level $H_3N{\rightarrow}\dot{B}H_2$ is found to be 2.9 kJ mol$^{-1}$ more stable than $H_2\dot{N}{\rightarrow}BH_3$, but when zero-point vibrational energies (scaled[30] by a factor of 0.9) are included the latter becomes the more stable by 10.5 kJ mol$^{-1}$. Including zero-point energies, the energy change associated with the isodesmic reaction (A) is +11.3 kJ mol$^{-1}$. If $DH^{\circ}(CH_3CH_2\text{–}H)$ is taken[31] to be

$$CH_3\text{–}\dot{C}H_2 + H_3N{\rightarrow}BH_3 \longrightarrow CH_3\text{–}CH_3 + H_3N{\rightarrow}\dot{B}H_2 \quad (A)$$

419.7 kJ mol$^{-1}$ and differences between $\Delta H^{\circ}_{298}$ and $\Delta E_0$ for reaction (A) are neglected, we estimate the B–H and N–H bond dissociation energies for $H_3N{\rightarrow}BH_3$ to be 431 and 421 kJ mol$^{-1}$, respectively. These values, which are a little higher than our previous estimates,[8] refer to the gas phase and it should be borne in mind that ammonia–borane and the derived radicals are very polar species.

[†] The effect of alkylation will probably be smaller for the amine–boranes than for the alkanes, because the radical centre in an amine–boryl radical is more strongly pyramidal than that in the isoelectronic alkyl radical.

$MeCO_2\dot{C}HMe$.[33] Similar experiments with bis-(2-cyanoethyl) ether at 216 K afforded spectra of (**10**) [$a(H_\alpha)$ 20.1, $a(2H_\beta)$ 29.2, $a$(N) 3.4 G, $g$ 2.0030] from the catalysed reaction and of (**11**) [$a(H_\alpha)$ 14.4, $a(2H_\beta)$ 16.2, $a(2H_\gamma)$ 1.8, $a$(N) 0.3 G, $g$ 2.0031] without catalyst. The spectra of (**10**) and (**11**) are shown in Figure 6.

$$Bu^tO^\bullet + (NCCH_2CH_2)_2O \xrightarrow{-Bu^tOH} \begin{cases} \xrightarrow{\text{catalysed}} NC\dot{C}HCH_2OCH_2CH_2CN \; \mathbf{(10)} \\ \xrightarrow{\text{uncatalysed}} NCCH_2\dot{C}HOCH_2CH_2CN \; \mathbf{(11)} \end{cases} \qquad (14)$$

As noted before for reactions of t-butoxyl radicals with nitriles, trimethylamine–borane is less useful than the t-alkylborane complexes as a polarity-reversal catalyst for reactions with esters. Thus, although u.v. irradiation of a cyclopropane solution containing $Me_3N{\rightarrow}BH_3$ (0.1M), DTBP, and ethyl acetate (1M) at 190 K did afford an e.s.r. spectrum of $^\bullet CH_2CO_2Et$, it was much weaker than that obtained with $Me_3N{\rightarrow}BH_2(CMe_2CHMe_2)$ as catalyst. At lower temperatures the spectrum[2] of $Me_3N{\rightarrow}\dot{B}H_2$ was evident alongside an even weaker spectrum of $^\bullet CH_2CO_2Et$, showing that the 'primary' amine–boryl radical abstracts the α-hydrogen atom less rapidly than the 'secondary' (**4**; R = $Me_2CHCMe_2$). This difference in reactivity is presumably wholly polar in origin, $Me_3N{\rightarrow}\dot{B}H_2$ being less nucleophilic than $Me_3N{\rightarrow}\dot{B}H(CMe_2CHMe_2)$. With methyl trifluoroacetate (1M) at 255 K, $Me_3N{\rightarrow}\dot{B}H_2$ (like[34] $Me_3Si^\bullet$) undergoes addition to give $CF_3\dot{C}(OMe)OBH_2{\leftarrow}NMe_3$ [$a$(3F) 20.6, $a(^{11}B)$ 5.8 G, $g$ 2.0033].[*] The more sterically hindered (**4**; R = $Me_2CHCMe_2$) did not react at a detectable rate with the trifluoroacetate up to 244 K.

*Complexes of Secondary Amines with Alkylboranes*.—As already mentioned t-butoxyl radicals react with secondary amine–boranes to give initially the amine–boryl radical, which often undergoes rapid intermolecular isomerisation to the more stable aminyl–borane $R_2\dot{N}{\rightarrow}BH_3$ (**2**).[5] Both *ab initio* m.o. calculations for the prototype $H_2\dot{N}{\rightarrow}BH_3$ and other considerations[5] lead to the conclusion that (**2**) should undergo ready β-scission with cleavage of a B–H bond [equation (15)],

$$\underset{\mathbf{(2)}}{R_2\dot{N}{\rightarrow}BH_3} \longrightarrow R_2N\overset{\rightharpoonup}{=}BH_2 + H^\bullet \qquad (15)$$

although this mode of unimolecular fragmentation has not yet been detected directly. However, the B–C bond in $R_2\dot{N}{\rightarrow}BH_2R$ is expected to be weaker than the B–H bond and should undergo homolytic cleavage more readily. To investigate this possibility, we have examined the secondary amine–alkylboranes (**12**; R = Me, $Bu^t$, or $Me_2CHCMe_2$) and (**13**).

$Me_2NH{\rightarrow}BH_2R$

**(12)**

**(13)**

As predicted, when an oxirane solution containing (**12**; R = $Me_2CHCMe_2$) (1.0M) and DTBP (15% v/v) was u.v.-irradiated only the e.s.r. spectrum of the 1,1,2-trimethylpropyl (thexyl) radical[35] (Figure 7) was observed between 161 and 226 K [$a$(6H) 23.1, $a$(1H) 10.2 G, $g$ 2.0026 at 184 K]. Under these experimental conditions abstraction of the electron-rich hydrogen from boron presumably takes place initially, to give the nucleophilic ligated boryl radical (**14**), which then abstracts the electron-deficient hydrogen from nitrogen in (**12**) to give the more stable dimethylaminyl–(1,1,2-trimethylpropyl)borane radical (**15**). The amine–alkylborane (**12**) is here acting as a polarity-reversal catalyst for the formation from itself of (**15**) by reaction with t-butoxyl radicals. Attempts to observe e.s.r. spectra of (**14**) and/or (**15**) at lower temperatures were inconclusive, although some very weak lines other than those of $^\bullet CMe_2CHMe_2$ were present.

In the presence of n-propyl bromide (1.0M) at 184 K, only the spectrum of $Pr^{n\bullet}$ was observed and $^\bullet CMe_2CHMe_2$ was not detected. The same result was obtained when the concentrations of $Pr^nBr$ and (**12**; R = $Me_2CHCMe_2$) were 0.50M and 2.0M, respectively, indicating that reaction (17) is slow as compared with bromine abstraction by (**14**). Conversely, with $Pr^nCl$ and (**12**; R = $Me_2CHCMe_2$) (each 1.0M) only $^\bullet CMe_2CHMe_2$ was detected between 184 and 235 K. However, with the more reactive t-butyl chloride (2.0M) and (**12**; R = $Me_2CHCMe_2$) (0.50M) in oxirane it was possible to detect both $Bu^{t\bullet}$ and $^\bullet CMe_2CHMe_2$ and thus[2,8] to measure $k_{17}$ relative to $k_{19}$. Between 163 and 187 K, the value of $(k_{17}/k_{19})$ was 40 ± 4.

$$Me_2NH{\rightarrow}\dot{B}H(CMe_2CHMe_2) + Bu^tCl \xrightarrow{k_{19}} Bu^{t\bullet} + Me_2NH{\rightarrow}BH(CMe_2CHMe_2)Cl \qquad (19)$$

U.v. irradiation of an oxirane solution containing (**12**; R = $Me_2CHCMe_2$) (1.0M), DTBP, and MeCN (1.0M) at 182 K afforded mainly $H_2\dot{C}CN$ along with a minor amount of $^\bullet CMe_2CHMe_2$, but with EtCN under the same conditions only $Me\dot{C}HCN$ was detected. When $Pr^nBr$ (1.0M) was also present in the latter system, only $Pr^{n\bullet}$ was detected, showing that reaction (20) is the source of the cyanoalkyl radical.

$$Bu^tO^\bullet + Me_2NH{\rightarrow}BH_2(CMe_2CHMe_2) \longrightarrow \underset{\mathbf{(14)}}{Me_2NH{\rightarrow}\dot{B}H(CMe_2CHMe_2)} + Bu^tOH \qquad (16)$$

$$Me_2NH{\rightarrow}\dot{B}H(CMe_2CHMe_2) + Me_2NH{\rightarrow}BH_2(CMe_2CHMe_2) \xrightarrow{k_{17}} Me_2NH{\rightarrow}BH_2(CMe_2CHMe_2) + \underset{\mathbf{(15)}}{Me_2\dot{N}{\rightarrow}BH_2(CMe_2CHMe_2)} \qquad (17)$$

$$Me_2\dot{N}{\rightarrow}BH_2(CMe_2CHMe_2) \longrightarrow Me_2N\overset{\rightharpoonup}{=}BH_2 + {}^\bullet CMe_2CHMe_2 \qquad (18)$$

$$Me_2NH{\rightarrow}\dot{B}H(CMe_2CHMe_2) + EtCN \longrightarrow Me\dot{C}HCN + Me_2NH{\rightarrow}BH_2(CMe_2CHMe_2) \qquad (20)$$

Compound (**12**; R = $Bu^t$) behaved in an analogous manner to its *B*-(1,1,2-trimethylpropyl) counterpart. U.v. photolysis of

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[*] These e.s.r. parameters refer to the isotopically labelled radical $CF_3\dot{C}(OMe)O^{11}BD_2{\leftarrow}NMe_3$; further fine structure (line spacing 1.0 G) was resolvable and this could not be explained on the basis of coupling with the methoxy protons alone. Selective line broadening was evident at lower temperatures.

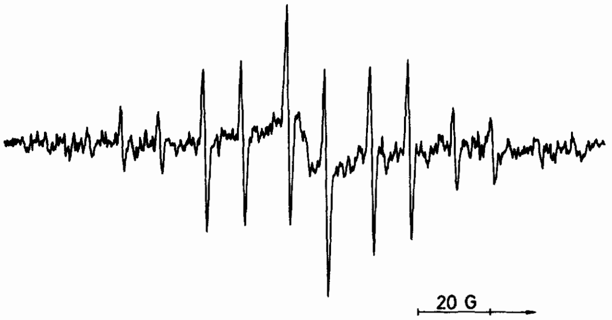


**Figure 7**. E.s.r. spectrum of the 1,1,2-trimethylpropyl radical obtained during u.v. irradiation of an oxirane solution containing DTBP and $Me_2NH\rightarrow BH_2(CMe_2CHMe_2)$ at 199 K

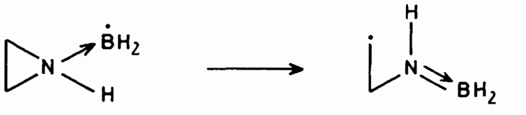
DTBP in the presence of (**12**; R = $Bu^t$) (1.0M) in oxirane solvent between 163 and 238 K afforded only the spectrum of the t-butyl radical [*cf.* equations (16)—(18)]. When the DTBP was replaced by bis(cyclopropylformyl) peroxide (BCFP), which acts as a photochemical source of cyclopropyl radicals,[5,36] $Bu^{t\bullet}$ was again the only radical detected at 238 K. When these experiments were repeated in the presence of n-propyl bromide (1.0M) at 238 K under otherwise identical conditions, both $Bu^{t\bullet}$ and $Pr^{n\bullet}$ were detected with either peroxide but the values of $[Pr^{n\bullet}]/[Bu^{t\bullet}]$ were very different, being *ca.* 20 (DTBP) and 0.5 (BCFP). Photolysis of BCFP in the presence of $Pr^nBr$ (1.0M) in oxirane solvent did not afford a detectable concentration of $Pr^{n\bullet}$. These results indicate that, under our experimental conditions, $Bu^tO^\bullet$ abstracts hydrogen almost exclusively from boron whilst the cyclopropyl radical abstracts hydrogen from nitrogen about twice as readily as from boron. Polar effects are presumably mainly responsible for these regioselectivities; the highly electrophilic alkoxyl radical reacts much more rapidly at the more strongly bound (but electron rich) hydrogen attached to boron, whilst the less electrophilic cyclopropyl radical prefers to abstract the more weakly bound electron-deficient hydrogen attached to nitrogen.

Photolysis of DTBP in the presence of (**12**; R = Me) (1.0M) in oxirane between 161 and 263 K afforded a very complex (and consequently relatively weak) e.s.r. spectrum, but the methyl radical was not detected. In the presence of methyl bromide (1M), only the spectrum of $Me^\bullet$ was observed. We conclude that the complex multi-line spectrum detected in the absence of halide is most probably due to the aminyl–alkylborane radical $Me_2\dot{N}\rightarrow BH_2Me$, which does not undergo β-scission to form $Me^\bullet$ at a detectable rate up to 263 K. The general form of the complex spectrum was certainly in accord with expectation,[5] but a complete analysis has not been possible so far.

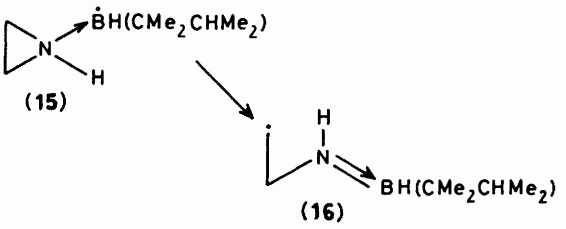
The foregoing results leave little doubt that the previously established $S_H2$ reaction (21) between dimethylaminyl radicals and a trialkylborane[37] must proceed in a stepwise manner[38] *via* the short-lived aminyl–trialkylborane radical $Me_2\dot{N}\rightarrow BR_3$.

$$Me_2N^\bullet + BR_3 \longrightarrow Me_2N \rightleftharpoons BR_2 + R^\bullet \qquad (21)$$

We have shown previously[2,5] that the aziridine–boryl radical (**14**) and *N*- or *C*-methylated analogues undergo rapid ring-opening β-scission, and that this reaction is faster than the intermolecular isomerisation of (**14**) to the aziridinyl–borane radical. Photolysis of DTBP in the presence of aziridine–(1,1,2-trimethylpropyl)borane (**13**) (1.0M) in oxirane solvent afforded only a spectrum which we attribute to the radical (**16**) [$a(2H_\alpha)$ 22.1, $a(2H_\beta)$ 32.4, $a$(N) 2.5 G, $g$ 2.0025 at 182 K] between 180 and 230 K. Ring opening of the aziridine–(1,1,2-trimethylpropyl)boryl radical (**15**) is thus also rapid in comparison with its intermolecular isomerisation to the correspondoing aminyl–borane. Of course, the N–H bond in (**13**) will probably be stronger than that in (**12**), just as the tertiary C–H bond in 1-methylcyclopropane is undoubtedly stronger than that in isobutane.[5,24]



(**14**) (22)



(**15**) (**16**) (23)

## Experimental

E.s.r. spectra were recorded with a Varian E-109 instrument operating at *ca.* 9.1 GHz. Samples were sealed in evacuated Suprasil quartz tubes (2 or 3 mm i.d., depending on the dielectric constant of the contents) and irradiated with u.v. light (λ *ca.* 240—340 nm) while in the microwave cavity of the spectrometer. The light source was an Osram HBO-500W/2 high-pressure mercury-discharge lamp in an Oriel housing fitted with an Aspherab fused silica condensing lens (f/0.7). Focusing was achieved with a second fused silica lens (10 cm focal length; 7.5 cm diam.) and the beam was passed through an aqueous filter solution (path length 3 cm) containing $NiSO_4\cdot 7H_2O$ (0.38M), $CoSO_4\cdot 7H_2O$ (0.07M), and $H_2SO_4$ (0.04M) before being directed onto the sample tube.[39] *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 ($g$ 2.00271) as standard.[40] Usually 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.[13]

Computer simulations of spectra were obtained by using a modified version of ESRSPEC2,[41] extended to handle composite spectra from up to four radicals with different centres, second-order shifts for coupling to single nuclei with $I > \frac{1}{2}$, and lineshapes continuously variable between 100% Gaussian and 100% Lorentzian.

Relative radical concentrations were determined by double integration of suitable lines in each spectrum and absolute radical concentrations were measured by comparison with the spectrum obtained from a standard solution of *N,N*-diphenyl-*N'*-picrylhydrazyl in carbon tetrachloride, using the signal from a piece of synthetic ruby (fixed permanently inside the microwave cavity) as an internal standard.[39] Absolute rate coefficients for radical self-reaction were determined as described previously.[19]

*Materials.*—N.m.r. spectra ($C_6D_6$ solvent unless noted otherwise) were obtained with a Varian XL-200 instrument (200 MHz for $^1H$), using tetramethylsilane as internal standard ($^1H$) or $Et_2O\rightarrow BF_3$ or 85% aqueous $H_3PO_4$ as external standard ($^{11}B$ or $^{31}P$, respectively); all $^{31}P$ n.m.r. spectra were proton-decoupled. Preparations and manipulations of all boron-containing compounds were conducted under dry nitrogen or argon; all solvents were dried before use.

Bis(cyclopropylformyl) peroxide,[5,36,42] $Me_2S\rightarrow {}^{11}BH_3$ and

**Table 4.** Boiling points and analytical and $^{11}B$ n.m.r. data for ligated alkylboranes $L\rightarrow BH_2R$

| R | L | B.p. (°C) [Torr] | Lit. b.p. (°C) [Torr] | Elemental composition Found % (Calc. %) | | | | $\delta(^{11}B)$ (*J*/Hz) |
|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | P | |
| Me | $Me_3N$ | 61—63 [16] | 62.1 [17.6] [a] | 55.4<br>(55.2) | 15.9<br>(16.2) | 16.3<br>(16.1) | | −3.1 (t)<br>(96.6, BH) |
| | $Me_2NH$ | 35 [0.04] | | *b*<br>(49.4) | *b*<br>(16.6) | *b*<br>(19.2) | | −6.7 (t)<br>(95.0, BH) |
| | $Et_3P$ | 44 [0.03] | | 57.3<br>(57.6) | 13.7<br>(13.8) | | 21.3<br>(21.2) | −31.3 (d, t)<br>(91.9, BH; 50.7, BP) |
| | $(MeO)_3P$ | *ca.* 40 [1.5] | | *c*<br>(31.6) | *c*<br>( 9.3) | | *c*<br>(20.4) | −34.3 (q)<br>(92.3, BH; 84.6, BP) |
| Bu$^t$ | $Me_3N$ | 59 [3.5] | 60 [3.5] [d] | | | | | 2.8 (t)<br>(98.2, BH) |
| | $Me_2NH$ | 30 [0.01] [e] | | 62.4<br>(62.7) | 16.0<br>(15.8) | 12.2<br>(12.2) | | −0.3 (t)<br>(97.6, BH) |
| | $Et_3P$ | 59 [0.01] | | 63.3<br>(63.9) | 13.6<br>(13.9) | | 16.4<br>(16.5) | −22.8 (d, t)<br>(90.5, BH; 46.5, BP) |
| | $(MeO)_3P$ | 75 [3] | | 43.3<br>(43.3) | 10.1<br>(10.4) | | 15.6<br>(16.0) | −27.4 (q)<br>(92.4, BH; 82.0, BP) |
| $CMe_2CHMe_2$ | $Me_3N$ | 58—60 [0.05] | | 69.0<br>(68.8) | 15.2<br>(15.4) | 8.7<br>(8.9) | | 1.8 (t)<br>(98.8, BH) |
| | $Me_2NH$ | 62—64 [0.01] | | 66.9<br>(67.2) | 15.8<br>(15.5) | 9.8<br>(9.8) | | −1.6 (t)<br>(99.3, BH) |
| | $\overline{CH_2CH_2N}H$ | | | *f*<br>(68.1) | *f*<br>(14.3) | *f*<br>(9.9) | | −2.1 (t)<br>(97.7, BH) |
| | $Et_3P$ | 64—66 [0.03] | | 66.4<br>(66.7) | 13.7<br>(14.0) | | 14.3<br>(14.3) | −25.9 (d, t)<br>(89.2, BH; 45.2, BP) |
| | $(MeO)_3P$ | 59—61 [0.01] | | 48.8<br>(48.7) | 10.4<br>(10.7) | | 13.7<br>(13.9) | −29.9 (q)<br>(90.8, BH; 84.6, BP) |

[a] Vapour pressure data from H. I. Schlesinger, N. W. Flodin, and A. B. Burg, *J. Am. Chem. Soc.*, 1939, **61**, 1078. [b] Satisfactory microanalytical data could not be obtained, although no impurities were detected by n.m.r. spectroscopy. [c] Contained $Me_3N\rightarrow BH_2Me$ (see text). [d] Data from ref. 44. [e] Sublimation temperature; m.p. 78—79 °C. [f] Contained a small amount of an unidentified impurity (see text).

$Me_2S\rightarrow{}^{11}BD_3$ (both 97.5 atom % $^{11}B$),[8] tri-t-butylboroxine,[43] and trimethylamine-t-butylborane[44] were prepared as described previously. Syntheses of new compounds or of known compounds prepared by new routes are described below; b.p.s, microanalytical results, and $^{11}B$ n.m.r. spectroscopic data are given in Table 4.

*Trimethylamine–(1,1,2-trimethylpropyl)borane.*[45] (*a*) 2,3-Dimethylbut-2-ene (12.0 cm$^3$, 0.10 mol) was added dropwise with stirring to dimethyl sulphide–borane (10 cm$^3$ of a 10M-solution in an excess of dimethyl sulphide) maintained at *ca.* −10 °C. After the addition was complete, the mixture was stirred for a further 2 h at 0 °C before dimethyl sulphide was removed under reduced pressure and collected in a trap cooled to −78 °C to leave essentially pure (1,1,2-trimethylpropyl)-borane dimer.[46] The reaction flask was equipped with a condenser containing solid $CO_2$–$Me_2CO$ slush and an excess of trimethylamine (15 cm$^3$) was allowed to condense from a calibrated trap onto the (trimethylpropyl)borane cooled to 0 °C. After transfer was complete the mixture was stirred for a further 20 min at 0 °C before the excess of amine was removed under reduced pressure to leave analytically pure *trimethylamine–(1,1,2-trimethylpropyl)borane*; $\delta(^1H)$ 1.08 (s, $CMe_2$), 1.17 (d, *J* 6.7 Hz, $CH\mathit{Me}_2$), 1.60 (septet, *J* 6.7 Hz, $C\mathit{H}Me_2$), and 2.00 (s, MeN). Some loss of amine occurred on distillation, especially if this was conducted slowly, and a small amount of (1,1,2-trimethylpropyl)borane dimer was detected in the product [$\delta(^1H)$ 0.86 (d, *J* 7.0 Hz, $\mathit{Me}_2CH$) and 0.96 (s, $Me_2C$); $\delta(^{11}B)$ 24.2 (br d, $^1J_{BH}$ *ca.* 110 Hz)]. The $^{11}B$-enriched complex and $Me_3N\rightarrow BD_2CMe_2CMe_2D$ were prepared using the same method starting from $Me_2S\rightarrow{}^{11}BH_3$ and $Me_2S\rightarrow{}^{11}BD_3$, respectively.

(*b*) Trimethylamine–(1,1,2-trimethylpropyl)borane was also prepared starting from borane–tetrahydrofuran (THF) complex. A solution of $Me_2O\rightarrow BF_3$ (22.5 g, 0.20 mol) in 1,2-dimethoxyethane (DME) (30 cm$^3$) was added dropwise during 2 h to a stirred slurry of lithium aluminium hydride (5.0 g, 0.13 mol) in DME (60 cm$^3$) maintained at room temperature. After the addition was complete, the temperature was increased to 70 °C and held there for 1 h. During the whole reaction the diborane produced was carried in a slow stream of nitrogen through a trap cooled to −78 °C and dispersed into a stirred solution of 2,3-dimethylbut-2-ene (10.5 cm$^3$, 0.09 mol) in THF (120 cm$^3$) maintained at −10 °C. The temperature was then increased to 0 °C and stirring continued for a further 1 h. The flask was equipped with a condenser cooled to −78 °C and trimethylamine (8.0 cm$^3$) was passed in, after which the mixture was stirred for a further 20 min at 0 °C. Excess of amine and solvent were removed under reduced pressure to leave trimethylamine–(1,1,2-trimethylpropyl)borane, indistinguishable from material prepared from dimethyl sulphide–borane.

*Dimethylamine–(1,1,2-trimethylpropyl)borane* was prepared from dimethyl sulphide–borane by the method described for the trimethylamine complex; $\delta(^1H)$ 0.95 (s, $CMe_2$), 1.14 (d, *J* 6.6 Hz, $CH\mathit{Me}_2$), 1.53 (septet, *J* 6.6 Hz, $C\mathit{H}Me_2$), and 1.80 (d, *J* 5.8 Hz, MeN).

Aziridine–(1,1,2-trimethylpropyl)borane was prepared from THF–borane by the method described for the trimethylamine complex; it 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; $\delta(^1H)$ 0.89 (m, CHN), 1.08 (s, $CMe_2$), 1.26 (d, *J* 6.7 Hz, $CH\mathit{Me}_2$), 1.30 (m, CH′N), and 1.68 (septet, *J* 6.7 Hz, $C\mathit{H}Me_2$). Although the $^{11}B$ n.m.r. spectrum was as expected for this compound, the $^1H$ n.m.r. spectrum indicated the presence of a small amount of unidentified impurity and it was not possible to obtain satisfactory microanalysis results.

*Triethylphosphine–(1,1,2-trimethylpropyl)borane.* (1,1,2-Trimethylpropyl)borane dimer was prepared from 2,3-dimethylbut-2-ene (4.8 cm$^3$, 0.040 mol) and dimethyl sulphide–borane and dissolved in ether (5 cm$^3$). The solution was cooled to 0 °C and stirred while triethylphosphine (5.0 g, 0.042 mol) was added dropwise from a syringe. The mixture was stirred for a further 20 min before the ether and excess of phosphine were removed under reduced pressure; the product was purified by distillation; $\delta(^1H)$ 0.74 (d, t, $J_{HH}$ 7.5, $J_{HP}$ 14.4 Hz, MeC*H*$_2$P), 1.15 (d, q, $J_{HH}$ 7.5, $J_{HP}$ 9.3 Hz, *Me*CH$_2$P), 1.16 (s, CMe$_2$), 1.31 (d, *J* 6.7 Hz, CH*Me*$_2$), and 1.65 (m, C*H*Me$_2$); $\delta(^{31}P)$ 13.9 (q, $J_{BP}$ 45.2 Hz).

*Trimethyl phosphite–*(1,1,2-*trimethylpropyl*)*borane* was prepared from the phosphite as described for the triethylphosphine complex; $\delta(^1H)$ 1.30 (d, *J* 6.7 Hz, CH*Me*$_2$), 1.31 (s, CMe$_2$), 1.78 (m, C*H*Me$_2$), and 3.22 (d, $J_{HP}$ 10.1 Hz, MeOP); $\delta(^{31}P)$ 111.1 (q, $J_{BP}$ 84.1 Hz).

*Dimethylamine–t-butylborane.* A large excess of dimethylamine (15 cm$^3$) was condensed onto trimethylamine–t-butylborane[44] (2.1 g, 0.016 mol) in a thick-walled glass flask equipped with a greaseless stopcock. The vessel was sealed and the contents stirred at room temperature for 36 h. Free amines were removed under reduced pressure to yield *dimethylamine–t-butylborane* as a white crystalline solid which was purified by sublimation; $\delta(^1H)$ 1.15 (s, Bu$^t$) and 1.70 (d, *J* 5.7 Hz, MeN).

*Triethylphosphine–t-butylborane* was prepared by stirring trimethylamine–t-butylborane (1.3 g, 0.010 mol) with an excess of triethylphosphine (3.0 g, 0.025 mol) for 18 h at 40 °C; distillation of the residue gave the phosphine complex; $\delta(^1H)$ 0.74 (d, t, $J_{HP}$ 13.9, $J_{HH}$ 7.7 Hz, *Me*CH$_2$P), 1.14 (d, q, $J_{HP}$ 8.3, $J_{HH}$ 7.7 Hz, MeC*H*$_2$P), and 1.33 (s, Bu$^t$); $\delta(^{31}P)$ 12.1 (q, $J_{BP}$ 46.0 Hz).

*Trimethyl phosphite–t-butylborane* was prepared from the phosphite as described for the triethylphosphine complex by stirring for 10 h at 30 °C; $\delta(^1H)$ 1.41 (s, Bu$^t$) and 3.22 (d, $J_{HP}$ 10.2 Hz, MeOP); $\delta(^{31}P)$ 109.6 (q, $J_{BP}$ 81.3 Hz).

*Trimethylamine–methylborane.* Lithium aluminium hydride (1.8 g, 0.047 mol) was dissolved in ether (50 cm$^3$) by stirring under reflux for 1 h. The solution was cooled to 0 °C, the reaction flask was equipped with a condenser containing solid CO$_2$–Me$_2$CO slush, and trimethylamine (6.0 cm$^3$) was allowed to evaporate into the mixture. The mixture was warmed under reflux and stirred during dropwise addition of di-isopropoxy(methyl)borane (Aldrich; 5.0 g, 0.035 mol) in ether (5 cm$^3$). Stirring under reflux was continued for a further 5 h, after which water (4.0 cm$^3$) was added cautiously at 0 °C. The mixture was filtered, the filtrate was dried (MgSO$_4$), the ether was removed under reduced pressure, and the residual *trimethylamine–methylborane* was purified by distillation; $\delta(^1H)$ 0.24 (br s, MeB), 1.91 (s, MeN), and 2.39 (q, *J* 99.5 Hz, BH$_2$).

*Dimethylamine–methylborane* was prepared from the trimethylamine complex by amine exchange[47] as described for dimethylamine–t-butylborane and was purified by rapid distillation. The $^1$H n.m.r. spectrum [$\delta$(CDCl$_3$) −0.17 (t, $J_{HH}$ 5.8 Hz, MeB), 1.78 (q, $J_{BH}$ 95.0 Hz, BH$_2$), 2.54 (d, *J* 5.8 Hz, MeN), and 3.65 (s, NH)] was essentially as reported previously,[47] apart from the sign of $\delta$(MeB).

*Triethylphosphine–methylborane* was prepared from the phosphine as described for the trimethylamine complex, except that a water-cooled condenser was used for the reflux stage and the triethylphosphine was added dropwise from a syringe; $\delta(^1H)$ 0.28 (d, $J_{HP}$ 20.2 Hz, MeB), 0.78 (d, t, $J_{HH}$ 7.6, $J_{HP}$ 14.4 Hz, *Me*CH$_2$P), and 1.12 (d, q, $J_{HH}$ 7.6, $J_{HP}$ 9.4 Hz, MeC*H*$_2$P); $\delta(^{31}P)$ 16.7 (q, $J_{BP}$ 50.5 Hz).

Trimethyl phosphite–methylborane was prepared by stirring trimethylamine–methylborane (1.5 g, 0.017 mol) with an excess of trimethyl phosphite (8.0 cm$^3$, 0.064 mol) at 40 °C for 24 h. Exchange was incomplete and after distillation the product contained *ca.* 30% of the trimethylamine complex; $\delta(^1H)$ (in CDCl$_3$) −0.17 (m, MeB) and 3.73 (d, $J_{HP}$ 10.4 Hz, MeOP).

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