Homolytic Reactions of Ligated Boranes. Part 13.[1] An Electron Spin Resonance Study of Radical Addition to Aminoboranes

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The reactions of silyl radicals $R_3Si^\cdot$ (R = Me, CD_3, Et, MeO, Bu^tO, or Me_3SiO) with aminoboranes $R^1R^2N{\Longrightarrow}BH_2$ in solution have been studied using e.s.r. spectroscopy. The silyl radicals add rapidly at low temperatures to 2,2,6,6-tetramethylpiperidinoborane and to *N*-t-butyl-*N*-methylaminoborane to give aminyl–borane radicals of the type $R^1R^2\dot{N}{\to}BH_2SiR_3$. Di-adducts of the type $R^1R^2\dot{N}{\to}BH(SiR_3)_2$ are formed as secondary reaction products. Addition of $R_3Si^\cdot$ to $Bu^t(Me)N{\Longrightarrow}BH_2$ is much faster than the corresponding addition to the isoelectronic alkene $Bu^t(Me)C{=}CH_2$, probably because the NB π-bond is weaker than its CC counterpart. The aminyl–boranes $R^1R^2\dot{N}{\to}BH_2SiR_3$ are only weakly bound with respect to aminoborane and the silyl radical, and the extent of binding depends on the nature of R and, because of steric effects, on the bulk of the *N*-alkyl groups. The radicals $R^1R^2\dot{N}{\to}BH_3$ are more tightly bound with respect to aminoborane and $H^\cdot$. Related to this, the extent of hyperconjugative delocalisation of the unpaired electron onto the BH_2M group in $R^1R^2\dot{N}{\to}BH_2M$ is greater when M = R_3Si than when M = H and also varies with the nature of R^1 and R^2. t-Butoxyl radicals abstract hydrogen from $Me_3SiNMe_2{\to}BH_3$ to give initially $Me_3SiNMe_2{\to}\dot{B}H_2$ which rapidly rearranges, probably by a dissociative mechanism, to the aminyl–borane $Me_2\dot{N}{\to}BH_2SiMe_3$. The results are interpreted with the aid of semi-empirical molecular orbital calculations at the MNDO and INDO levels.

Addition of silicon-centred radicals to alkenes is generally exothermic and takes place rapidly at low temperatures.[2–4] The β-silylalkyl adduct radicals so formed have been studied extensively in fluid solution using e.s.r. spectroscopy and an electronic preference for the β-Si–C bond to eclipse the semi-occupied C_α-$2p_\pi$ orbital has been established.[4–7]

Homolytic addition to aminoboranes, which are isoelectronic counterparts of alkenes, has not been reported previously. In principle, addition could take place at either end of the $N{\Longrightarrow}B$ double bond to give an aminyl–borane radical (1) or an amine–boryl radical (2). However, both these modes of addition would be much less favourable thermodynamically than comparable addition to an alkene, because the difference in strengths of the $N{\Longrightarrow}B$ and $N{\to}B$ bonds is much greater than that between the C=C and C–C bonds.[8–10] For example, *ab initio* molecular-orbital calculations[10] predict that reactions (2) and (3) are endothermic by 22 and 33 kJ mol⁻¹, respectively, in the gas phase. Addition of hydrogen atoms to enthene [equation (4)] is

$$X^\cdot + {>}N{\Longrightarrow}B{<} \longrightarrow {>}\dot{N}{\to}B{-}X \text{ or } X{-}N{\to}\dot{B}{<} \quad (1)$$
$$\text{(1)} \qquad \text{(2)}$$

$$H^\cdot + H_2N{\Longrightarrow}BH_2 \left[\begin{array}{l} \longrightarrow H_2\dot{N}{\to}BH_3 \quad (2) \\ \longrightarrow H_3N{\to}\dot{B}H_2 \quad (3) \end{array} \right.$$

$$H^\cdot + H_2C{=}CH_2 \longrightarrow H_3C{-}\dot{C}H_2 \quad (4)$$

calculated[10] to be exothermic by 155 kJ mol⁻¹ at the same level of theory, while the value of ΔH_4° obtained from the experimental enthalpies of formation[11,12] is −153 kJ mol⁻¹.

In accord with their relative thermodynamic instability, we have shown previously that both of the isomeric radicals (3)[13] and (4)[8,14] undergo very rapid β-scission at low temperatures

$$\begin{array}{l} Me_2\dot{N}{\to}BH_2R \quad \text{(3)} \\ \\ RNMe_2{\to}\dot{B}H_2 \quad \text{(4)} \end{array} \Bigg] \longrightarrow R^\cdot + Me_2N{\Longrightarrow}BH_2 \quad (5)$$

when R is a tertiary alkyl group. In the present paper we describe e.s.r. spectroscopic studies of the addition of silicon-centred radicals to aminoboranes and related investigations of the radicals derived from the silylamine–borane complex[15] $Me_3SiNMe_2{\to}BH_3$.

Results and Discussion
The π component of the $N{\Longrightarrow}B$ bond in an aminoborane is weaker than the π component of the C=C bond in an alkene and barriers to rotation about $N{\Longrightarrow}B$ bonds are much smaller than C=C rotational barriers in similarly substituted alkenes.[16] Aminoboranes also show a much greater tendency to form dimers, trimers, and larger oligomers than do alkenes. The simplest aminoborane $H_2N{\Longrightarrow}BH_2$ is usually encountered as a polymer, but a cyclic trimer (*cf.* cyclohexane) is known[17] as are higher oligomers.[18] The reactive monomer can be obtained in the gas phase and a planar ethene-like structure (5) has been

(5)

established by microwave spectroscopy (the B–H and N–H bond lengths were assumed.)[19] The dipole moment of (5) is relatively small[19] (1.84 D), because π electron donation from

nitrogen to boron is offset by the closer association of the N–B σ electrons with the more electronegative nitrogen atom (the Pauling electronegativities of nitrogen and boron are 3.0 and 2.0, respectively). Alkylation at nitrogen and/or boron leads to steric stabilisation of the monomeric aminoborane, with alkylation at boron being more effective in this respect.[20] N,N-Dimethylaminoborane dimerises to give a cyclobutane analogue (6) in the condensed phase, but this dissociates back to

$$2 R_2N{\Rightarrow}BH_2 \rightleftharpoons \begin{matrix} R_2N{\rightarrow}BH_2 \\ | \quad | \\ H_2B{\leftarrow}NR_2 \end{matrix} \qquad (6)$$

(6)
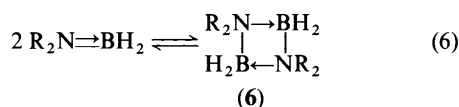
monomer when heated in vacuo [equation (6; R = Me)].[20,21] When R is a secondary alkyl group, steric effects dictate that the equilibrium (6) lies far to the left.[22,23] For example,[23] the [11]B n.m.r. spectrum of N,N-di-s-butylaminoborane indicates that only the monomer [δ_B 36.3, $^1J_{BH}$ 120 Hz] is present in the neat liquid at room temperature.

In this work we have studied the reactions of trialkylsilyl and trialkoxysilyl radicals with the aminoboranes (7) and (8), which were prepared as shown in equations (7) and (8). At room

(7)

$$Bu^tMeNH{\rightarrow}BH_3 \xrightarrow[\text{Pd catalyst}]{\text{heat}} Bu^tMeN{\Rightarrow}BH_2 + H_2 \quad (8)$$

(8)
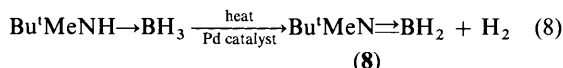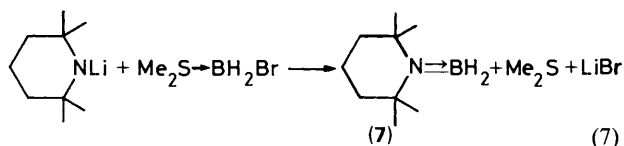
temperature (7) exists as a monomeric liquid [δ_B 36.9, $^1J_{BH}$ 127 Hz] with no tendency to dimerise. Freshly prepared, monomeric (8) is a volatile liquid [δ_B 36.4, $^1J_{BH}$ 128 Hz], which rapidly solidifies on standing at room temperature to give a mixture of two isomeric dimers [δ_B −0.9, $^1J_{BH}$ 110 Hz].* However, monomeric (8) could be regenerated by heating the dimer under reduced pressure; it could be handled easily using a vacuum line and distilled into the e.s.r. sample tubes. The silyl radicals were produced by hydrogen-atom abstraction from the corresponding silanes, using photochemically generated t-butoxyl radicals [equations (9) and (10)];[7,24–26] the solvent was cyclopropane unless noted otherwise.

$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO^\bullet \qquad (9)$$

$$Bu^tO^\bullet + R_3SiH \longrightarrow R_3Si^\bullet + Bu^tOH \qquad (10)$$
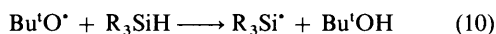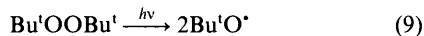
The e.s.r. spectrum shown in Figure 1 was recorded during continuous u.v. irradiation of a solution containing the aminoborane (7) (ca. 0.5 mol dm⁻³), di-t-butyl peroxide (DTBP) (ca. 15% v/v), and t-butyldimethylsilane (ca. 1.4 mol dm⁻³) at 197 K. The major features of this spectrum are assigned to the aminyl–borane adduct (9), although the central region is distorted because of the presence of the relatively persistent aminyl radical[27] (15) [a(N) 14.7, a(12 H) 0.62 G, and g 2.0048 at 197 K]. The radical (15) is presumably formed by hydrogen-atom

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* Only one [11]B resonance was detected. However, the ¹H n.m.r. spectrum indicated the presence of both the Z- and E-isomers of the dimer. The two isomers were formed in the ratio of 1 : ca. 2 and, on steric grounds, we presume that the E-dimer is the major component.

† Equal within the limits imposed by the envelope linewidth (ΔB_{p-p}) of 4.6 G.
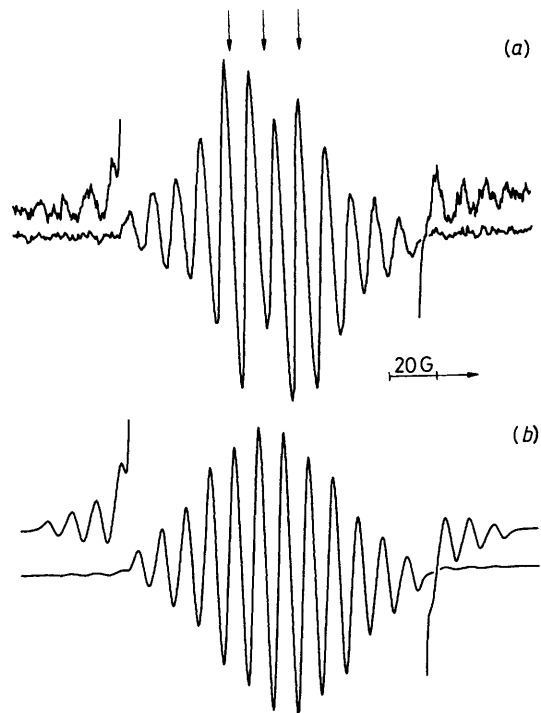
Figure 1. (a) E.s.r. spectrum of the radical (9) in cyclopropane at 197 K. The ²⁹Si satellites are shown recorded at higher gain and the arrows indicate the centres of the three multiplets arising from the aminyl radical (15). (b) Simulation of the spectrum of (9), including the contributions from radicals containing [11]B, [10]B, ²⁹Si, and the nonmagnetic isotopes of silicon in the statistical proportions, using the parameters given in Table 1.
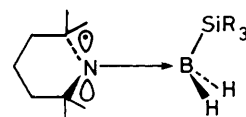
(9)	$R_3 = Bu^tMe_2$;	(10)	R = Me
(11)	R = Et;	(12)	R = MeO
(13)	R = Bu^tO;	(14)	R = Me_3SiO

abstraction from the parent amine which is present as a minor impurity in the aminoborane (7). The aminyl radical (15) was also detected when DTBP was photolysed in the presence of (7) without added silane.
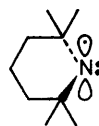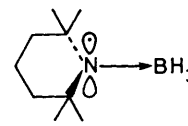
(15)   (16)

The spectrum of (9) can be computer simulated [Figure 1(b)] on the basis of equal† splittings of 10.3 G from [11]B (I = 3/2, 80.2%) and from ^{14}N, along with a splitting of 31.4 G from two equivalent protons. Satellites from the radical containing ²⁹Si (I = 1/2, 4.7%) were detected with the expected intensity [a(²⁹Si) 74.9 G], but the contribution from the radical containing [10]B [I = 3, 19.8%, γ([10]B)/γ([11]B) = 0.335] is not discernible from Figure 1. A number of other aminyl–borane radicals (10)–(14) have been generated by silyl radical addition to (7) and their e.s.r. parameters are given in Table 1. There can be little doubt that all these adducts adopt the 'eclipsed' conformation shown, if only for steric reasons.

The e.s.r parameters for (9)–(14) may be compared with those for the unsubstituted aminyl–borane[9] (16) [a(N) 16.7, a([11]B)

Table 1. E.s.r. parameters for the mono-adducts (9)–(14) of silyl radicals with the aminoborane (7) in cyclopropane.

			Hyperfine splittings/G			
Adduct	T/K	g Factor	a(N)	$a(^{11}$B)	a(2 H$_\beta$)	Others[a]
(9)	197	2.0035	10.3	10.3	31.4	74.9 (^{29}Si)[b]
(10)[c,d]	163	2.0036	11.0	9.3	31.3	1.65 (9 H)
(11)	197	2.0035	10.9	9.1	32.0	2.3 (6 H)
(12)[c,e]	197	2.0030	13.9	10.4	32.5	
(13)	181	2.0029	12.5	10.5	32.7[f]	
(14)	223	2.0029	13.2	10.6	33.3	

[a] For radicals other than (9) the spectra were insufficiently strong for the ^{29}Si satellites to be conclusively identified. [b] The sign of $a(^{29}$Si) will be negative because the magnetogyric ratio is negative. [c] When u.v. irradiation was interrupted the spectrum decayed with kinetic order between 1 and 2. The first half-life for decay from *ca.* 10^{-6} mol dm^{-3} is given. [d] $t_{\frac{1}{2}}$ *ca.* 3 s at 163 K. [e] $t_{\frac{1}{2}}$ *ca.* 4 s at 193 K. [f] The lines corresponding to $M_I(2$ H$_\beta$) $= 0$ were very broad at 181 K. This lineshape effect is attributed to the existence of restricted rotation around the Si–O bonds which renders the β-protons diastereotopic and intrinsically non-equivalent. Analogous broadening was absent for (12) and (14). Similar effects have been detected for comparable alkyl radicals (see reference 7).

(17)
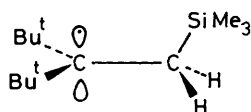
11.2, $a(3$ H$_\beta$) 46.5 G, and g 2.0043 at 268 K]. For alkyl radicals containing a H$_\beta$C$_\beta\dot{C}_\alpha$ moiety, the major mechanism by which the unpaired electron interacts with H$_\beta$ is hyperconjugation and the value of a(H$_\beta$) is given by the Heller–McConnell equation (11).[28] Here θ is the dihedral angle between the H$_\beta$CC plane and

$$a(CH_\beta) = (A_{CCH} + B_{CCH}\cos^2\theta)\rho^\pi_{C_\alpha} \qquad (11)$$

the axis of the semi-occupied C$_\alpha$-2p$_\pi$ orbital, $\rho^\pi_{C_\alpha}$ is the π unpaired electron population on C$_\alpha$, and A_{CCH} and B_{CCH} are constants, with the former negligibly small (*ca.* 1 G) in comparison to the latter. Similar relationships have been established for β-proton couplings in other types of radical and the efficiency of hyperconjugative delocalisation of the unpaired electron from the formal radical centre is reflected in the magnitude of the B term. The same value of B_{CCH} (*ca.* 56 G) appears to be applicable to a variety of types of alkyl radical, provided that the carbon centre is close to planar.[29,30]

Equation (12), in which the symbols have meanings

$$a(BH_\beta) = (A_{NBH} + B_{NBH}\cos^2\theta)\rho^\pi_{N_\alpha} \qquad (12)$$

analogous to those in equation (11), would be expected to hold for aminyl–borane radicals which contain the H$_\beta$BN moiety. Assuming that the BH$_3$ group in (16) is freely rotating ($\langle\cos^2\theta\rangle = 0.5$) and neglecting A_{NBH}, a value of *ca.* 23.3 G would be predicted for $a(2$ H$_\beta$) in (9)–(14) when θ = 60°, much smaller than the observed values, even if $\rho^\pi_{N_\alpha}$ is taken to be the same for the borane and the silylborane complexes. Clearly B_{NBH} is much larger (*i.e.* hyperconjugative spin delocalisation is much more efficient) for (9)–(14) than for (16). The total unpaired electron population on the three β-hydrogen atoms in (16) is calculated[31] to be 27% from the value of $a(3$ H$_\beta$).* Assuming that hyperconjugative delocalisation is into a ^{29}Si-sp^3 hybrid orbital in (9) with 25% ^{29}Si-3s character, the total unpaired electron population on the two β-hydrogens and the β-silicon in (9) is 37%. If the silicon coupling in (9) is assumed to

show the dependence on dihedral angle expressed by equation (13), combination of equations (12) and (13), neglecting the A

$$a(^{29}\text{Si}) = (A_{NBSi} + B_{NBSi}\cos^2\theta)\rho^\pi_{N_\alpha} \qquad (13)$$

terms, gives $(B_{NBH}/B_{NBSi}) = -1.68$. This value implies that the β-B–H and β-B–SiR$_3$ bonds are similarly effective in hyperconjugative withdrawal of the unpaired electron from nitrogen since $(508/-1213) \times 4$ is also -1.68.* The value of (B_{CCH}/B_{CCSi}), defined and calculated in an analogous way for the carbon-centred radical[6] (17) [$a(2$ H$_\beta$) 15.76, $a(^{29}$Si) 35.02 G, and g 2.0024 at 298 K], is -1.80, also fairly close to -1.68.

The radical (17) was produced[6] by addition of Me$_3$Si$^\bullet$ to Bu$^t_2$C=CH$_2$ and will be more tightly bound with respect to these reactants than the analogous silyl radical adducts of (7). Hyperconjugative delocalisation onto the β-H$_2$Si triad is correspondingly more extensive for (9) than for (17). Looked at from an alternative viewpoint, because of electronegativity effects, the filled β-BH$_2$SiR$_3$ π-group orbital is more closely matched in energy to the semi-occupied N$_\alpha$-2p$_\pi$ orbital than is the β-CH$_2$SiR$_3$ π-group orbital in (17) to the C$_\alpha$-2p$_\pi$ orbital, and thus the hyperconjugative interaction will be greater for the aminyl–borane radical. In general, because of their weakly (and thus variably) bound nature, the value of B_{NBM} (M = H or SiR$_3$) for aminyl–boranes R$_2$N→BH$_2$M might be expected to vary appreciably from radical to radical, whereas for analogous alkyl radicals R$_2\dot{C}$–CH$_2$M, which are much more stable with respect to β-scission, B_{CCM} will be less dependent on the nature of the substituents. Changes in B_{NBH} are probably mainly responsible for the different values of (B_{NBH}/B_{NCH}) found previously[9,10] for Me$_2\dot{N}$→BH$_3$ (2.00) and MeNH→BH$_3$ (2.65), isoelectronic counterparts of Me$_3$C$^\bullet$ and Me$_2\dot{C}$H, respectively.

A related consequence of the greater electronegativity of nitrogen compared with boron is that the B-2p$_\pi$ orbital makes a larger contribution than the N-2p$_\pi$ orbital to the π* molecular orbital of an aminoborane.[32] If, as expected, addition of nucleophilic silyl radical to an aminoborane is dominated by the SOMO–NBπ* frontier-orbital interaction, there should be a kinetic preference for the addition to take place at boron. Of course, for reaction with (7) and (8) there will also be a thermodynamic preference for addition to boron, because of the steric and electronic effects of alkylation at nitrogen while the boron centre is unsubstituted.†

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* Unit unpaired electron population of H-1s and ^{29}Si-3s atomic orbitals would give rise to isotropic couplings of 508 and $-1\,213$ G, respectively[31] (the magnetogyric ratio of ^{29}Si is negative).

† Lifetimes must also be considered when assessing rates of radical formation from their steady-state concentrations as detected by e.s.r. spectroscopy. Adducts formed by addition to nitrogen in (7) or (8) will undoubtedly be much less persistent than those formed by addition to boron.
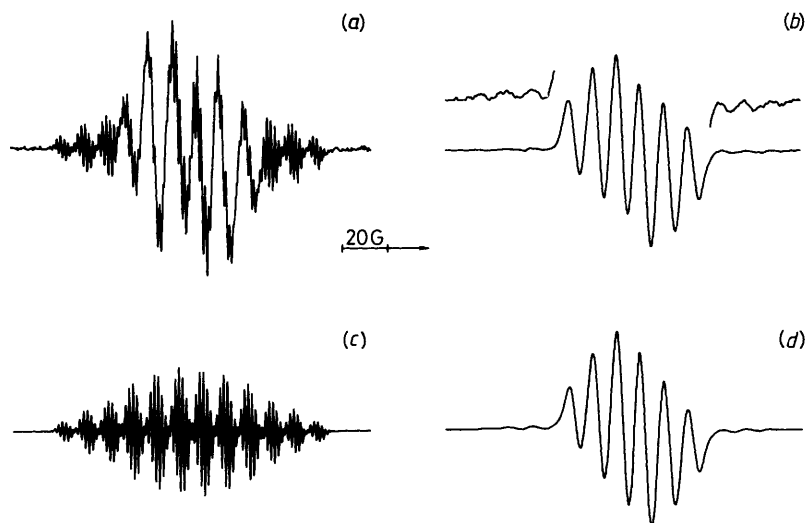
Figure 2. (a) E.s.r. spectra of the radicals (10) and (18; R = Me) in cyclopropane at 158 K recorded during u.v. irradiation of the sample. (b) E.s.r. spectrum of (18; R = Me) at 156 K recorded without u.v. irradiation. (c) and (d) Simulations of the spectra of (10) and (18; R = Me), respectively, using the parameters given in Tables 1 and 2. For (18; R = Me) the peak-to-peak linewidth (ΔB_{p-p}) is 4.5 G for the main spectrum and 7.6 G for the ^{29}Si satellites.
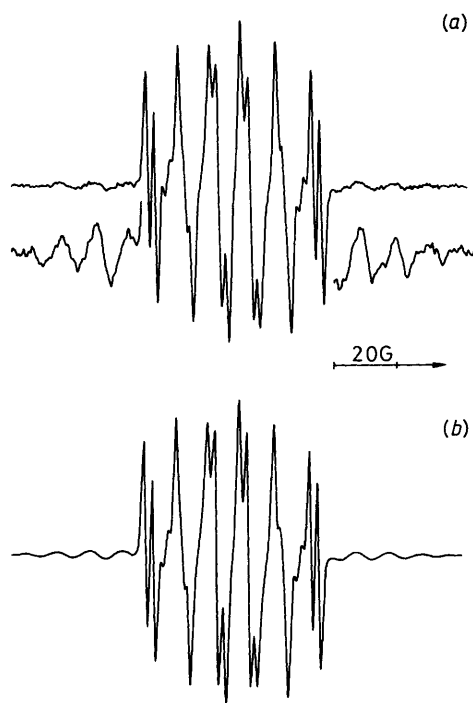

Figure 3. (a) E.s.r. spectrum of the radical (18; R = CD$_3$) in cyclopropane at 217 K recorded without u.v. irradiation of the sample. (b) Simulation of (a) using the parameters given in Table 2; ΔB_{p-p} for the ^{29}Si satellites is 3.2 G while for the main spectrum it is 1.6 G.

The spectrum shown in Figure 2(a) was recorded during continuous u.v. irradiation of a solution containing (7), DTBP, and trimethylsilane at 158 K. It consists of overlapping signals from two radicals; a wider, more highly resolved spectrum from the short-lived primary adduct (10) and a narrower spectrum which increases in relative intensity with the duration of photolysis and derives from a much more persistent secondary-product radical [see Figure 2(b)]. The comparatively large splitting from the nine protons of the Me$_3$Si group in (10) accords with the proposed 'silyl radical' character of the adduct. Thus, in free Me$_3$Si$^\cdot$ the values[25] of a(^{29}Si) and a(9 H) are

181.14 and 6.28 G, respectively, at 153 K. When this proton splitting is scaled by the ratio of the ^{29}Si splittings for (9) and for Me$_3$Si$^\cdot$, we obtain a value of 2.6 G, which is similar in magnitude to a(9 H) for the adduct (9). Only the secondary spectrum is detected without photolysis [Figure 2(b)] and ^{29}Si satellites were readily observed with a relative integrated intensity of ca. 9.5%, indicating the presence of two silyl groups in the radical, although the linewidth for the satellites is greater than for the main spectrum.

We ascribe the secondary spectrum to the bis(trimethylsilyl) adduct (18; R = Me) and this assignment is supported by deuterium labelling studies. For (18; R = CD$_3$) the splitting from the single β-proton was clearly resolved, as was the difference between a(N) and a(^{11}B) (see Figure 3). This β-proton splitting was absent in the spectrum of (19) derived from the

(18)   (19)

(20)
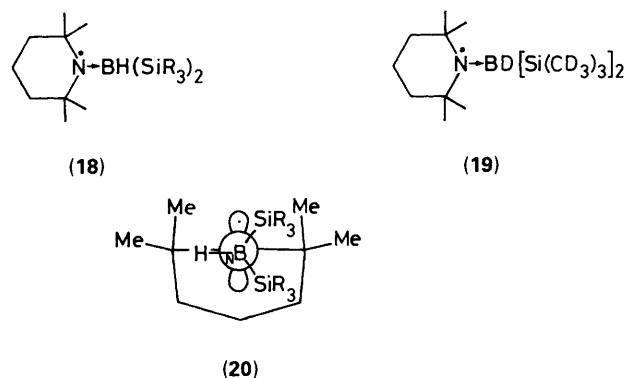
B,B-dideuteriated analogue of (7), although after prolonged photolysis (especially if this was carried out at higher temperatures), the spectrum of the B-protiated radical (18; R = CD$_3$) became evident. Probably decay of (19) and of the B,B-dideuteriated mono-adduct take place, at least in part, by hydrogen abstraction from the silane to give amine–silylborane complexes and several plausible mechanisms for radical induced H/D exchange can be envisaged in such a system.[10] The very small value of a(H$_\beta$) for (18; R = CD$_3$) (2.5 G) compared with a(2 H$_\beta$) for the monoadducts (9)–(14) (ca. 31 G) indicates that

Table 2. E.s.r. parameters for the di-adducts (18) and (19) derived from the aminoborane (7) in cyclopropane.

| Adduct | T/K | g Factor | Hyperfine splittings/G | | | |
			a(N)	a(^{11}B)	a(1 H$_B$)	a(^{29}Si)^a
(18; R = Me)	155	2.0036	11.4^{b,c}	10.1^{b,c}	d	74.8
	219	2.0036	11.4^{b,c}	10.1^{b,c}	d	75.0
(18; R = CD$_3$)	217	2.0036	11.4	10.1	2.5	75.2
(19)	217	2.0036	11.4^{b,c}	10.1^{b,c}	d	75.2
(18; R = Et)	209	2.0036	10.7^c	10.7^c	4.5	69.0
(18; R = MeO)^e	212	2.0031	14.7	10.3	d	f
	269		14.6	10.4	1.0	
(18; R = Me$_3$SiO)	211	2.0030	14.5	10.6	d	f

^{a} The two silicon atoms are instantaneously non-equivalent (see text). The sign of a(^{29}Si) will be negative. ^{b} Assumed to be the same as the values for (18; R = CD$_3$). ^{c} The difference between a(N) and a(^{11}B) was not resolved, although [2a(N) + 3a(B)]/5 can be measured to within ±0.2 G. ^{d} Not resolved. ^{e} Decay was approximately first order at 257 K with $t_{\frac{1}{2}}$ ca. 1 min; at lower temperatures this radical was very persistent. ^{f} ^{29}Si satellites not detected, presumably because the lines are very broad.
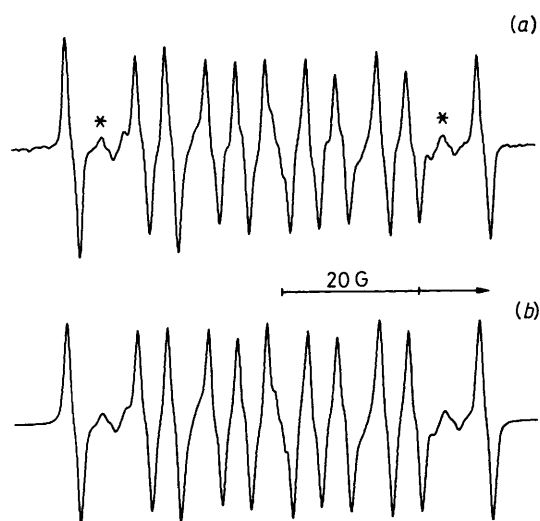
Figure 4. (a) E.s.r. spectrum of the radical (18; R = MeO) in cyclopropane at 269 K; the contribution from the radical containing ^{10}B is clearly observable at the points marked with an asterisk. (b) Simulation of (a) using a(N) 14.61, a(^{11}B) 10.38 [a(^{10}B) 3.48], and a(1 H) 1.00 G; ΔB_{p-p} is 1.10 G.

the preferred conformation about the B–N bond is that shown in (20) in which the B–H bond lies close to the nodal plane of the N-2p$_\pi$ orbital [see equation (12)], as would be expected on steric grounds. Because of the non-planar (presumably chair-like) geometry of the six-membered ring, the two silyl groups will be instantaneously non-equivalent, accounting for the greater linewidth of the ^{29}Si satellites, since the ring is probably not inverting rapidly on the e.s.r. timescale under the experimental conditions.

Similarly long-lived secondary product radicals of the type (18) were detected from (7) and the other silanes and their e.s.r. parameters are collected in Table 2. The relative intensities of the spectra from mono- and di-adducts varied with the nature of the ligands attached to silicon. With Me$_3$SiH the spectrum of (18) grew in very rapidly, while with Bu^{t}Me$_2$SiH it appeared only after very prolonged u.v. irradiation and even then the spectrum was weak; an intermediate situation was provided by the adducts derived from Et$_3$SiH. With (MeO)$_3$SiH the very persistent di-adduct (18; R = MeO) was detected soon after beginning photolysis and its spectrum often became very intense, while with (Bu^{t}O)$_3$SiH no di-adduct was evident. Steric effects are clearly important here, the di-adduct being formed more readily and more stable towards β-scission when less bulky R$_3$Si groups are involved.
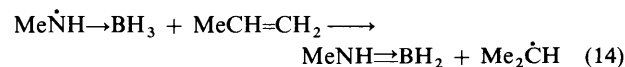
The magnitudes of a(N) and a(^{11}B) differ more for both mono- and di-adducts of trialkoxysilyl radicals (see Figure 4) than for the adducts of the corresponding trialkylsilyl radicals, and a(N) for the former adducts is generally larger and closer to that for the unsubstituted aminyl–borane (16). We take this as evidence that the Si–B bonds in the trialkoxysilyl adducts are stronger than those in the trialkylsilyl adducts, which would accord with the greater Si-3s character of an Si–Y bond in X$_3$SiY as the electronegativity of the ligand X increases.[7,33]

Analogous di-adducts are formed as secondary products when silyl radicals are generated in the presence of Bu$^t_2$C=CH$_2$. For example,[34] although (17) is produced initially during u.v. irradiation of a solution containing the alkene, DTBP, and Me$_3$SiH, the spectrum of (21) [a(H$_B$) < 2.0, a(^{29}Si) 30.74 G, and g 2.0024 at 298 K] appears after more prolonged photolysis.

(21)　　　　　　　　　　　　　(22)
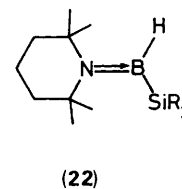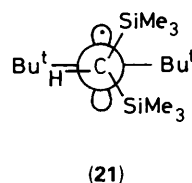
On the basis of equation (13), if $\rho^\pi_{N\alpha}$ and B_{NBSi} are the same for the di-adduct (18; R = Me) as for the mono-adduct (9), a smaller value of a(^{29}Si) would be expected for the former radical. In fact, a(^{29}Si) is the same for both adducts. It is likely that $\rho^\pi_{N\alpha}$ and, especially B_{NBSi} differ for mono- and di-adducts and also, for steric reasons, the dihedral angles subtended by the BSi bonds could be appreciably smaller than 30° in the di-adducts.

The weakly bound β-hydrogen atoms in monoalkylaminyl–borane radicals are readily transferred to alkenes [e.g. equation (14)].[10,35] We suggest that analogous β-H-atom transfer from

$$\text{Me}\dot{\text{N}}\text{H}{\longrightarrow}\text{BH}_3 + \text{MeCH=CH}_2 \longrightarrow$$
$$\text{MeNH}{\Longrightarrow}\text{BH}_2 + \text{Me}_2\dot{\text{C}}\text{H} \quad (14)$$

(9)–(14) to the parent aminoborane (7) takes place to produce the B-silylaminoboranes (22), subsequent addition of silyl radicals to which would give the di-adducts (18). Formation of (22) must occur at a rate sufficient to give rise to detectable concentrations of the persistent radicals (18), but insufficiently rapidly for the spectrum of the transient hydrogen-atom adduct (16) to be observed.

Table 3. E.s.r. parameters for mono- and di-adducts formed by reaction of trimethylsilyl radicals with the aminoborane (**8**).

Adduct	T/K	g Factor	a(N)	a(^{11}B)	a(BH_n)	a(3 H$_\beta$)	a(Me_3Si)
(**23**; R = Me)^a	160	2.0035	10.4	9.5	25.0 (2 H)^b	11.4	1.95 (9 H)
(**23**; R = CD$_3$)^c	156	2.0035	10.4	9.4	27.1 (2 H)^b	11.0	
(**24**; R = Me)^c	154	2.0034	11.2	9.3	1.9 (1 H)	11.2	1.0 (18 H)
(**24**; R = CD$_3$)^c	156	2.0034	11.3	9.4	1.9 (1 H)	11.3	

^{a} The spectrum was well-resolved, but also extremely complex and the central region was invariably corrupted because of the presence of the di-adduct radical. ^{b} Central lines of the triplet were not observed because of selective broadening (see text); the average value of a(2 H) is reported. ^{c} Obtained by computer simulation, the individual splitting constants are not directly measurable.
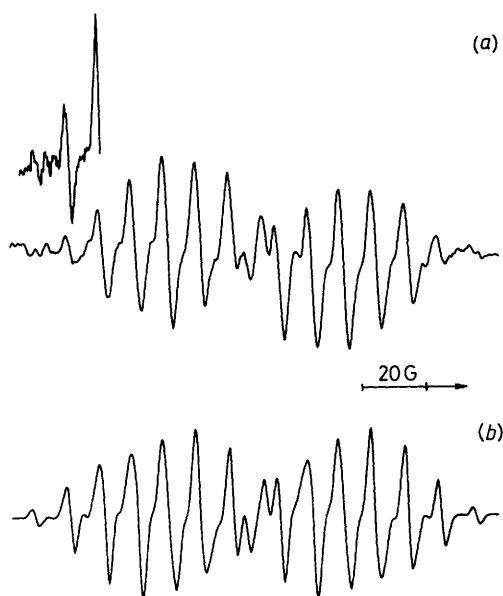
Figure 5. (*a*) E.s.r. spectrum of the radical (**23**; R = CD$_3$), containing ^{11}B and ^{10}B in natural abundance, in cyclopropane at 155 K. The wing region of the radical containing 97.5 atom% ^{11}B is shown at higher gain. (*b*) Simulation of (*a*) using the parameters given in Table 3; only the wing lines of the BH_2 triplet are included in the simulation (see text).
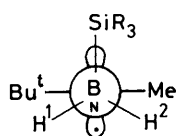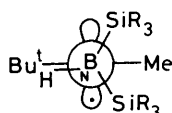
(**23**)   (**24**)

Addition to N-*t-Butyl*-N-*methylaminoborane* (**8**).—Trialkyl-silyl radicals also undergo ready addition to the aminoborane (**8**) at low temperatures and both mono- and di-adducts have been detected; in some experiments aminoborane containing 97.5 atom% ^{11}B was used. The mono-adducts evidently prefer the eclipsed conformation (**23**) (drawn idealised), while the staggered conformation (**24**) is adopted by the di-adducts. The e.s.r. spectrum of (**23**; R = Me) was difficult to analyse on account of the large number of lines, but that of the deuteriated adduct (**23**; R = CD$_3$) was more readily interpretable (see Figure 5). The β-BH protons in (**23**; R = CD$_3$) are non-equivalent and, at the low temperatures necessary for its

detection ($< ca.$ 220 K), the lines corresponding to M_l(2 H$_\beta$) = 0 are broadened beyond detectability. The e.s.r. parameters for (**23**) and (**24**) are collected in Table 3. Trimethoxy- and tri-t-butoxy-silyl radicals also add to the aminoborane (**8**), although the spectra were weak and difficult to analyse completely.

Using the average value of a(2 H$_\beta$) in (**23**; R = Me) and taking $\langle \cos^2 \theta \rangle$ to be 0.25 for both β-B–H bonds, we calculate (B_{NBH}/B_{NCH}) to be 4.4, much larger than for the unsubstituted complexes[9] Me(R)N→BH$_3$ (2.0 when R = Me or Bu^t). Again the difference is attributed mainly to a change in B_{NBH}.

2,3,3-Trimethylbut-1-ene [Bu^t(Me)C=CH$_2$] is the carbon counterpart of the aminoborane (**8**) and trimethylsilyl radicals add to this alkene to give (**25**), the alkyl analogue of (**23**; R = Me). The e.s.r. parameters for (**25**) [a(3 H$_\beta$) 21.6, $\bar{a}$(2 H$_\beta$) 16.6 G,

$$Me_3SiCH_2\dot{C}(Me)Bu^t$$
(**25**)
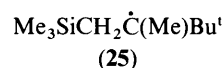
and g 2.0025 at 158 K]* confirm that an eclipsed conformation is again preferred, although the ratio a(3 H$_\beta$):a(2 H$_\beta$) is greater than the value (2.0) appropriate to idealised perfect eclipsing as shown for (**23**) [see equation (11)]. Line-broadening effects similar to those observed for the aminyl-boranes (**23**) were also evident in the spectrum of (**25**). When trimethylsilyl radicals were generated at 158 K in the presence of a mixture of (**8**) (0.6 mol dm^{-3}) and Bu^t(Me)C=CH$_2$ (3.0 mol dm^{-3}), only the aminyl-borane adduct was detected and [(**23**; R = Me)]/[(**25**)] must be $> ca.$ 3. Since (**23**; R = Me) and (**25**) appear to be similarly transient and their spectra decay completely within the fall time of the spectrometer (0.5 s), this result implies that addition of Me$_3$Si· to the aminoborane is appreciably faster than its addition to the alkene, despite the probability that addition to the alkene is much the more exothermic process. It seems likely that the activation energy for addition to the aminoborane will be relatively small because the π component of the N⇒B bond is weak compared to that of the C=C bond in the alkene.

Radicals Derived from Me$_3$SiNMe$_2$→BH$_3$ (**26**).—N,N-Dimethyl-N-trimethylsilylamine–borane[15] (**26**) was prepared

Me$_3$SiNMe$_2$ + Me$_2$S→BH$_3$ ⟶
        Me$_3$SiNMe$_2$→BH$_3$ + Me$_2$S   (15)
                    (**26**)
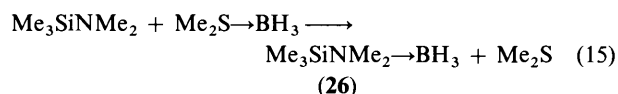
by the reaction of the silylamine with dimethyl sulphide–borane in diethyl ether. Material containing 97.5 atom% ^{11}B was used to simplify and strengthen e.s.r. spectra when resolved splitting from boron was anticipated.

U.v. irradiation of a solution containing DTBP (15% v/v) and (**26**) (0.5 mol dm^{-3}) in cyclopropane–dimethyl ether (1:1 v/v) at 203 K afforded the e.s.r. spectrum shown in Figure 6. This spectrum is not as expected for the amine–boryl radical (**27**),

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* The lines are broad and further fine structure, presumably arising from coupling to protons of the Bu^t and Me$_3$Si groups, is poorly resolved.
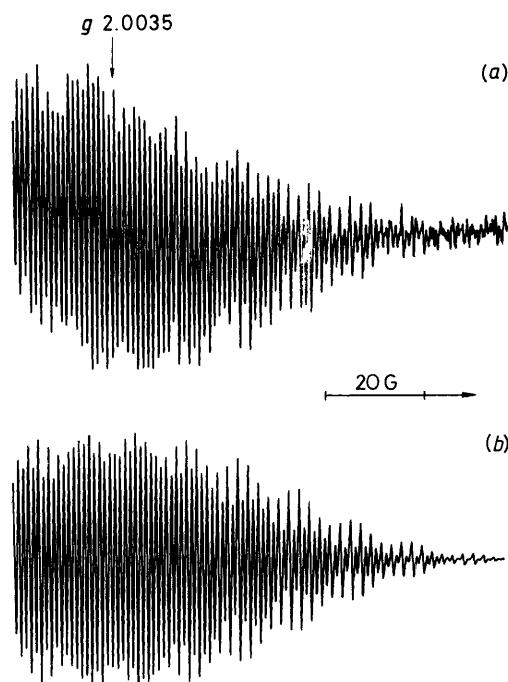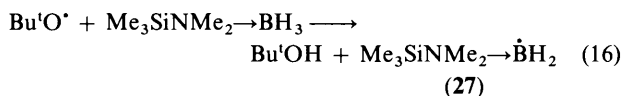
g 2.0035

(a)

|← 20 G →|

(b)

Figure 6. (a) High-field part spectrum of the radical (28) in cyclopropane-dimethyl ether at 203 K. (b) Simulation of (a) using the parameters given in the text.

which should be the initial product of reaction between (26) and Bu^{t}O$^•$ [equation (16)]. The spectra of amine–boryl radicals are
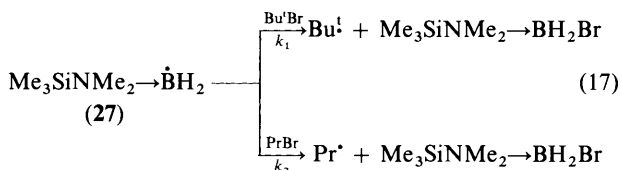
$$Bu^tO^• + Me_3SiNMe_2{\rightarrow}BH_3 \longrightarrow$$
$$Bu^tOH + Me_3SiNMe_2{\rightarrow}\dot{B}H_2 \quad (16)$$
$$(27)$$

dominated by a large quartet splitting of *ca.* 50 G due to coupling with the ^{11}B nucleus; the α-proton splitting is normally *ca.* 10 G and the nitrogen and γ-proton couplings are very small [*e.g.* Me$_3$N→$\dot{B}$H$_2$ shows[8] $a(^{11}$B) 51.3, a(2 H$_α$) 9.6, a(N) 1.4, a(9 H$_γ$) 1.4 G, and g 2.0022 at 180 K]. The spectrum shown in Figure 6 is strongly reminiscent of that obtained from the aminyl–borane radical (23; R = Me) and it can be simulated using $a(^{11}$B) 9.4, a(N) 10.5, a(2 H$_β$) 23.0, a(6 H$_β$) 12.5, and a(9 H$_δ$) 2.1 G, (g 2.0035). This analysis leaves little doubt that the spectrum should be assigned to the dimethylaminyl-silylborane radical Me$_2$Ṅ→BH$_2$SiMe$_3$, which could be formed from (27) by either an intramolecular rearrangement or a dissociation–addition pathway. Assuming that the eclipsed conformation (28) is adopted by the aminyl–borane, the calculated value of (B_{NBH}/B_{NCH}) would be 3.7, provided that the dihedral angles subtended by the B–H bonds are close to 60°.
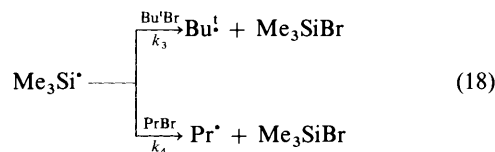
SiMe$_3$

Me—B—Me
H   N   H

(28)
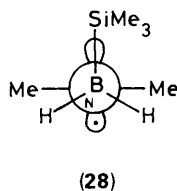
The spectrum of (28) became less intense as the temperature was reduced below 200 K, partly because of small changes in the coupling constants which resulted in less exact reinforcing line overlap, but also because of a decrease in the steady-state radical concentration. However, even at the lowest accessible

temperature (150 K), no spectrum which could be conclusively ascribed to the initially formed amine–boryl radical (27) was observed. This is not too surprising since spectra of similar radicals[8] are difficult to detect on account of the large number of relatively broad lines.

When a cyclopropane–dimethyl ether solution containing DTBP, (26), and an equimolar mixture of propyl and t-butyl bromides was u.v. irradiated at temperatures between 169 and 201 K, only spectra of Pr$^•$ and Bu$^t_•$ were observed. These alkyl radicals presumably arise by halogen-atom abstraction[8] from the alkyl bromides by the amine–boryl radical (27) [equation (17)] and, making the usual assumptions,[36] the value of (k_1/k_2)

$$Me_3SiNMe_2{\rightarrow}\dot{B}H_2 \begin{cases} \xrightarrow[k_1]{Bu^tBr} Bu^t_• + Me_3SiNMe_2{\rightarrow}BH_2Br \\ \\ \xrightarrow[k_2]{PrBr} Pr^• + Me_3SiNMe_2{\rightarrow}BH_2Br \end{cases} \quad (17)$$
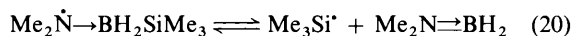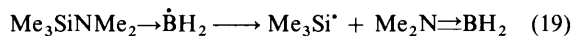(27)

was found to be 1.2 ± 0.1 at 201 K. A similarly low primary/tertiary selectivity is shown by other amine–boryl radicals[8–10] and confirmation that (27), rather than the trimethylsilyl radical is responsible for bromine abstraction was obtained by conducting experiments in which the amine–borane was replaced by trimethylsilane (2.5 mol dm^{-3}). The value of (k_3/k_4) [equation (18)] was found to be 3.0 ± 0.3 at 201
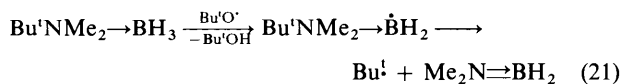
$$Me_3Si^• \begin{cases} \xrightarrow[k_3]{Bu^tBr} Bu^t_• + Me_3SiBr \\ \\ \xrightarrow[k_4]{PrBr} Pr^• + Me_3SiBr \end{cases} \quad (18)$$

K, in agreement with the previously reported[7,37] higher selectivity of Me$_3$Si$^•$. Hence, although the e.s.r. spectrum of the amine–boryl radical (27) was not detected at low temperatures, it is clear that this species is formed initially by the reaction of Bu^{t}O$^•$ with the silylamine–borane (26).

In the absence of alkyl halides at temperatures above *ca.* 240 K, the spectrum of the aminyl–borane (28) is replaced by that of the trimethylsilyl radical [a(9 H) 6.35 G and g 2.0032 at 246 K],[25] showing that (27) and/or (28) undergo rapid β-scission [equations (19) and (20)]. For such loosely bound radicals, it

$$Me_3SiNMe_2{\rightarrow}\dot{B}H_2 \longrightarrow Me_3Si^• + Me_2N{=}BH_2 \quad (19)$$

$$Me_2\dot{N}{\rightarrow}BH_2SiMe_3 \rightleftharpoons Me_3Si^• + Me_2N{=}BH_2 \quad (20)$$

would be very difficult to distinguish between a dissociative mechanism for the rearrangement of (27) to (28) and an intramolecular 1,2-migration of the trimethylsilyl group.
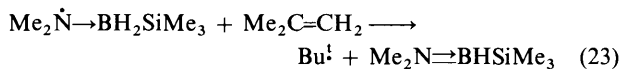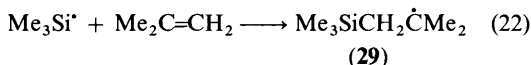
Reaction (19) is analogous to the β-scission undergone by Bu^{t}NMe$_2$→$\dot{B}$H$_2$, the carbon counterpart of (27) which we have studied previously [equation (21)],[8,14] and the latter reaction

$$Bu^tNMe_2{\rightarrow}BH_3 \xrightarrow[-Bu^tOH]{Bu^tO^•} Bu^tNMe_2{\rightarrow}\dot{B}H_2 \longrightarrow$$
$$Bu^t_• + Me_2N{=}BH_2 \quad (21)$$

was employed as a low temperature source of monomeric Me$_2$N$=$BH$_2$ in order to provide independent support for the identification of (28). When a dimethyl ether solution containing DTBP (15% v/v), Bu^{t}NMe$_2$→BH$_3$ (0.5 mol dm^{-3}), and Me$_3$SiH (5.5 mol dm^{-3}) was u.v. irradiated at 203 K, the

spectrum of the aminyl–borane (28) was observed alongside the expected strong spectrum of the t-butyl radical; the trimethylsilyl radical was not detected *ca.* 1 min after beginning photolysis. Of course, the detection of (28) in this experiment requires a fortunate balance to exist between competing reactions and monomeric $Me_2N{\Longrightarrow}BH_2$ must be sufficiently stable under the reaction conditions to allow its concentration to build up to a level at which rapid trapping of $Me_3Si^{\bullet}$ takes place.

When a cyclopropane–dimethyl ether solution containing DTBP and $Me_3SiNMe_2{\rightarrow}BH_3$ (0.5 mol dm⁻³) was u.v. irradiated at 216 K, the spectrum of (28) was still strong and that of $Me_3Si^{\bullet}$ was not obvious. When part of the cyclopropane was replaced with 2-methylpropene (2.6 mol dm⁻³), the alkene analogue of $Me_2N{\Longrightarrow}BH_2$, under otherwise identical conditions the spectrum of (28) was barely detectable initially and in its place spectra of the adduct[38] (29) and of the t-butyl radical were observed in the relative concentrations of *ca.* 4:1, respectively. We suggest that (29) is formed by trapping of $Me_3Si^{\bullet}$ by the alkene in competition with $Me_2N{\Longrightarrow}BH_2$, although a direct reaction between (27) and/or (28) and the alkene is difficult to rule out. The t-butyl radical probably arises by direct hydrogen-atom transfer from (28) to the alkene [equation (23)] in a

$$Me_3Si^{\bullet} + Me_2C{=}CH_2 \longrightarrow Me_3SiCH_2\dot{C}Me_2 \quad (22)$$
$$(29)$$

$$Me_2\dot{N}{\rightarrow}BH_2SiMe_3 + Me_2C{=}CH_2 \longrightarrow$$
$$Bu^t_{\cdot} + Me_2N{\Longrightarrow}BHSiMe_3 \quad (23)$$

reaction analogous to that known[10] to occur between $R\dot{N}H{\rightarrow}BH_3$ and 2-methylpropene (see earlier).

Molecular-orbital Calculations.—In order to support the assignments of e.s.r. spectra and the interpretations of the spectroscopic data, we have carried out semi-empirical molecular-orbital calculations at the MNDO[39] and INDO[40] levels, using the spin-unrestricted Hartree–Fock (UHF) method for radicals and the spin-restricted (RHF) method for singlet-state molecules. Geometries were optimised at the MNDO level using Bischof's program[41] modified by substituting the revised parameters for silicon as recommended by Dewar *et al.*[42] The structures (30) and (31) were located for the eclipsed conformations of (27) and (28) as shallow minima on the potential-energy surface when all geometric parameters were optimised within the constraint of C_s symmetry. Structure (31) is calculated to be more stable than (30) by 107.9 kJ mol⁻¹; both are predicted to be unstable with respect to $Me_3Si^{\bullet}$ and $Me_2N{\Longrightarrow}BH_2$, (30) by 125.3 kJ mol⁻¹ and (31) by 17.4 kJ mol⁻¹. The results are, thus, in accord with the ready rearrangement of (27) to (28). Selected computed properties are presented in Table 4. The Si–N bond in (30) is easily stretched and the radical is predicted to undergo β-scission very readily; it would not be feasible to distinguish between a dissociative mechanism for the rearrangement and an intramolecular 1,2-Me_3Si shift on the basis of calculations at this level of theory.

The computed structure (31) of the aminyl–borane (28) is close-to planar at the nitrogen radical centre. The NB bond length (1.449 Å) is intermediate between that calculated for $Me_2N{\Longrightarrow}BH_2$ (1.399 Å) and that for $Me_2\dot{N}{\rightarrow}BH_3$ (1.530 Å) [see structure (32)], reflecting the expected decrease in *r*(NB) as the strength of the B–M bond in $Me_2\dot{N}{\rightarrow}BH_2M$ (M = H or SiR_3) decreases. The computed dipole moment of (32) is also much larger than that of (31), which is relatively close to that of the amino–borane $Me_2N{\Longrightarrow}BH_2$. Apart from $a(^{29}Si)$, the isotropic hyperfine splitting constants for (31) (Table 4), calculated using

(30)

(31)

(32)

(33)
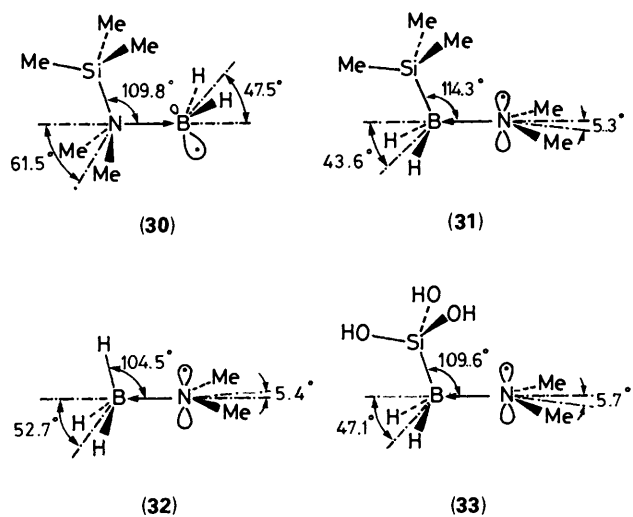
the INDO approximation in conjunction with the MNDO-optimised geometry, are in reasonable agreement with the experimental values for (28). The boron splitting constant is negative presumably because the coupling arises predominantly by spin-polarisation of the N→B bonding electrons; $a(^{29}Si)$ is negative because the magnetogyric ratio for ^{29}Si is negative.

Structure (31) is also easily deformed. In particular, if the NB bond length is fixed equal to the computed value for $Me_2\dot{N}{\rightarrow}BH_3$ and the other geometric parameters are re-optimised, the resulting structure is less stable than (31) by only 8.9 kJ mol⁻¹. However, the calculated value of $a(BH_\beta)$ decreases by 7.5 to 25.9 G and $a(CH_\beta)$ increases by 3.3 to 14.0 G (Table 4). On the basis of these calculations, the large increases in $a(BH_\beta)$ for N,N-dialkylaminyl–silylboranes of the type (34) which is

$$\begin{array}{c} R^1 \\ \diagdown \\ \dot{N}{\rightarrow}BH_2SiMe_3 \\ \diagup \\ R^2 \end{array}$$

(34)
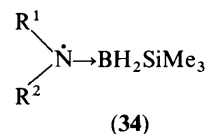
observed as the bulk of the groups R^1 and R^2 increases is attributed to a steric effect. As the size of the N-alkyl substituents increases, the adducts become more loosely bound, the N→B bond length would decrease, and B_{NBH} would increase, although $\rho^{\pi}_{N_\alpha}$ decreases. However, in terms of equation (12), while $\rho^{\pi}_{N_\alpha}$ decreases for (34) along the series $R^1 = R^2 = Me > R^1 = Me$, $R^2 = R^t > R^1 = R^2 = R^t$, the value of B_{NBH} increases more rapidly so that $a(BH_\beta)$ also increases. The value of B_{NBH} is evidently very sensitive to the N→B bond length; as *r*(NB) decreases, overlap between the N-$2p_\pi$ orbital and the BH_2M group π orbital increases rapidly.

Finally, MNDO calculations were carried out for $Me_2\dot{N}{\rightarrow}BH_2Si(OH)_3$ as a model for the aminyl–boranes formed by addition of trialkoxysilyl radicals to aminoboranes. The partially optimised structure (33) was obtained by assuming C_s symmetry for the radical excluding the hydroxyl protons and local threefold symmetry for the $Si(OH)_3$ group. The aminyl–borane (33) is now stable with respect to $Me_2N{\Longrightarrow}BH_2$ and $(HO)_3Si^{\bullet}$ by 14.3 kJ mol⁻¹, in accord with the suggestion that adducts of $(RO)_3Si^{\bullet}$ are more tightly bound than trialkysilyl adducts. As observed by experiment for the trialkoxysilyl adducts, the difference in computed magnitudes of $a(N)$ and $a(^{11}B)$ for (33) is greater than the corresponding difference for the trimethylsilyl adduct (31) and also the value of $a(N)$ is larger for (33) than for (31).

Table 4. Results of semiempirical molecular-orbital calculations.

Molecule	ΔH_f°/ kJ mol⁻¹	E_i/ eV	Dipole moment/ D	r(NB)/ Å	r(SiB)/ Å	BH dihedral angle[a]/°	Hyperfine splittings[b]/G				
							a(N)	a(¹¹B)	a(BH₂)	a(CH₃)[c]	a(²⁹Si)
Me₃SiNMe₂→ḂH₂[d] (30)	−35.5	6.85	5.44	1.597			−0.7	140.6	0.3	0.4	−2.1
Me₂Ṅ→BH₂SiMe₃[d] (31)	−143.4	8.62	2.89	1.449	2.034	65.5	13.5	−12.5	33.4	10.7	−42.7
Me₂Ṅ→BH₂SiMe₃[d,e]	−134.5	9.05	3.86	1.530	1.984	61.5	15.0	−9.6	25.9	14.0	−28.9
Me₂Ṅ→BH₂Si(OH)₃[f] (33)	−952.8	9.29	4.12	1.466	1.990	63.8	14.6	−9.7	29.3	11.4	−73.2
Me₂Ṅ→BH₃[d] (32)	+56.6	10.79	5.55	1.530		62.1[g]	15.8	−11.0	13.8[g]	17.9	
Me₃Si˙[h,i]	−77.9	7.33	0.07							23.4[i]	−68.7[i]
(HO)₃Si˙[j]	−855.6	8.61	1.02								−446.0
Me₂N⇌BH₂[k]	−82.9	10.76	1.81	1.399							

[a] Dihedral angle between the H₆BN plane and the axis of the semi-occupied orbital on nitrogen. [b] Calculated using the INDO method. The scaling factors used to convert valence shell s-orbital unpaired-electron populations into coupling constants were 720.82 G for ¹¹B and −1 213.2 G for ²⁹Si (see ref. 31). [c] Averaged splitting from the three non-equivalent protons. [d] C_s symmetry. [e] NB bond length fixed at 1.530 Å. [f] No symmetry. [g] For the two non-eclipsing BH groups; a(H) for the eclipsing β-proton is 67.0 G. [h] C_{3v} symmetry. [i] The MNDO method overestimates repulsion between non-bonded atoms and, therefore, predicts Me₃Si˙ to be too close to planar. [j] C_3 symmetry. [k] C_{2v} symmetry; the C₂NBH₂ skeleton is planar.

Experimental

E.s.r. spectra were recorded with Varian E-109 or Bruker ESP-300 spectrometers operating at 9.1–9.3 GHz. Samples were sealed in evacuated Suprasil quartz tubes (2 or 3 mm i.d., depending on the dielectric properties of the contents) and irradiated with u.v. light (λ ca. 240–340 nm) while in the microwave cavity of the spectrometer. The techniques employed have been described previously.[13]

Materials.—N.m.r. spectra (C₆D₆ solvent) were obtained with a Varian XL-200 instrument (200 MHz for ¹H), using SiMe₄ as internal standard (¹H) or Et₂O→BF₃ as external standard (¹¹B). Preparations and manipulations of all boron-containing compounds were conducted under dry nitrogen or argon.

Cyclopropane (Argo International), dimethyl ether (Fluka), 2-methylpropene (BDH), and trimethylsilane (PCR) were used as received. Di-t-butyl peroxide (Aldrich) was purified before use as described previously.[43] Trimethoxysilane (Aldrich) and tris(trimethylsiloxy)silane (Petrarch Systems) were distilled before use, the former from CaH₂. Tris(trideuteriomethyl)silane was prepared by reduction of (CD₃)₃SiCl (MSD Isotopes) with LiAlH₄ in triglyme and tri-t-butoxysilane was prepared from t-butyl alcohol and Cl₃SiH in the presence of pyridine.[44]

Dimethyl sulphide complexes of BH₃ (97.5 atom% ¹¹B) and of BD₃ were prepared as described previously[45] and the Me₂S→BD₃ was used to prepare Me₂S→BD₂Br by the method of Brown and Ravindran.[46]

2,2,6,6-Tetramethylpiperidinoborane (7).—2,2,6,6-Tetramethylpiperidine (33.9 g, 0.24 mol) in diethyl ether (50 cm³) was added dropwise during 0.5 h to a stirred solution of butyllithium in hexane (150 cm³ of 1.60 mol dm⁻³ solution, 0.24 mol) cooled in an ice–water bath. After the addition, the mixture was refluxed gently for 2 h, allowed to cool, and added dropwise during 0.5 h to a stirred solution of Me₂S→BH₂Br (37.2 g, 0.24 mol) in diethyl ether (40 cm³) maintained at ca. −5 °C. After the addition, the mixture was refluxed for 1 h, allowed to cool, the solid LiBr removed by filtration, and the solvents removed from the filtrate under reduced pressure. The residual oil was distilled twice to give the aminoborane (7), b.p. 46–48 °C at 5 Torr* which contained a small amount (ca. 4%) of tetramethyl-piperidine, as judged from the ¹H n.m.r. spectrum. δ_H 1.29 (s, 4 Me) and 1.38 (m, 3 CH₂); δ_B 36.9 (t, ¹J_BH 127 Hz). The

*1 Torr = 133.322 Pa.

B,B-dideuteriated material was prepared in the same way from Me₂S→BD₂Br.

N-t-*Butyl*-N-*methylaminoborane* (8).—Under an atmosphere of dry argon, t-butyl(methyl)amine–borane[9] (3.12 g, 0.031 mol) and 10% palladium on charcoal (0.13 g) were placed in a round bottomed flask containing a magnetic stirrer bar. (**WARNING** The palladium catalyst must be mixed with the amine–borane under an inert gas with rigorous exclusion of air. In the presence of oxygen the mixture of catalyst and amine–borane is pyrophoric.) The flask was then connected to a vacuum line via a trap cooled in a solid CO₂-acetone bath; the trap could be isolated by taps on both sides. The pressure of argon in the apparatus was reduced to ca. 200 Torr and the mixture was stirred while being slowly heated in an oil bath to a maximum temperature of 120 °C. After 1 h, the pressure had increased to 380 Torr because of hydrogen production; the pressure was then reduced to 200 Torr and heating continued for a total of 2.5 h, after which time hydrogen evolution had ceased. The liquid which collected in the trap was distilled at atmospheric pressure to yield the aminoborane (8), b.p. 86–89 °C. The aminoborane dimerised quite rapidly at room temperature, but could readily be separated from dimer by bulb-to-bulb distillation on the vacuum line. The monomer showed δ_H 1.07 (s, 9 H) and 2.76 (s, 3 H) and δ_B 36.4 (t, ¹J_BH 128 Hz).

The monomer dimerised completely on being left to stand at 10 °C overnight. Although the solid, dimeric material exhibited only a single triplet in the ¹¹B n.m.r. spectrum (δ_B −0.9, ¹J_BH 110 Hz), the ¹H n.m.r. spectrum showed the presence of two isomers: δ_H 1.19 (s, 18 H) and 2.48 (s, 6 H) assigned to the E-dimer, and δ_H 1.15 (s, 18 H) and 2.61 (s, 6 H) assigned to the Z-dimer (E:Z = ca. 2:1). When the dimer was heated at ca. 60 °C under reduced pressure it dissociated back to the monomeric aminoborane.

Under the same conditions, in the absence of the palladium catalyst there was no evolution of hydrogen and no apparent change appeared to occur to the amine–borane, which re-solidified after the reaction flask was cooled.

N,N-*Dimethyl*-N-*trimethylsilylamine–borane* (**26**).—Dimethyl sulphide–borane (0.87 cm³ of 10 mol dm⁻³ solution in excess Me₂S, 8.7 mmol) was added dropwise by syringe to a stirred solution of Me₃SiNMe₂ (1.02 g, 8.7 mmol) in diethyl ether (20 cm³) at a bath temperature of ca. −30 °C. The mixture was allowed to warm to room temperature and was then stirred for a further 0.5 h. Removal of the ether under reduced pressure left a white solid which was purified by rapid chromatography

on silica (light petroleum b.p. 40–60 °C–ethyl acetate, 3:1 v/v eluant). In a sealed capillary, (26) showed signs of melting at *ca.* 40 °C, which probably corresponds to the onset of decomposition; it finally fell to liquid at 102–103 °C (lit.,[15] m.p. 102–105 °C decomp.). δ_H 0.02 (s, 9 H), 1.98 (s, 6 H), and 2.24 (q, $^1J_{BH}$ 100 Hz, 3 H); δ_B −11.9 (q, $^1J_{BH}$ 100 Hz). The silylamine–borane was stored in a freezer at −20 °C.

References

1 Part 12, V. Paul, B. P. Roberts, and C. R. Willis, *J. Chem. Soc., Perkin Trans. 2*, 1989, preceding paper.

2 R. A. Jackson, *J. Chem. Soc., Chem. Commun.*, 1974, 573.

3 C. Chatgilialoglu, K. U. Ingold, and J. C. Scaiano, *J. Am. Chem. Soc.*, 1983, **105**, 3292.

4 A. Alberti and G. F. Pedulli, *Rev. Chem. Intermed.*, 1987, **8**, 207.

5 P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1969, **91**, 6161; 1971, **93**, 846.

6 D. Griller and K. U. Ingold, *J. Am. Chem. Soc.*, 1973, **95**, 6459.

7 K. M. Johnson and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1111.

8 J. A. Baban, V. P. J. Marti, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1723.

9 I. G. Green and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1597.

10 J. N. Kirwan and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1989, 539.

11 D. Griller, J. M. Kanabus-Kaminska, and A. Maccoll, *J. Mol. Struc. (Theochem)*, 1988, **163**, 125.

12 J. B. Pedley, R. D. Naylor, and S. P. Kirby, 'Thermochemical Data of Organic Compounds,' Chapman and Hall, London, 2nd edn., 1986.

13 V. Paul and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1183.

14 J. A. Baban, J. P. Goddard, and B. P. Roberts, *J. Chem. Res. (S)*, 1986, 30.

15 H. Nöth, *Z. Naturforsch., Teil B*, 1961, **16**, 618.

16 M. J. S. Dewar and P. Rona, *J. Am. Chem. Soc.*, 1969, **91**, 2259; H. Nöth and B. Wrackmeyer, *Chem. Ber.*, 1973, **106**, 1145; B. Wrackmeyer, *J. Organometal. Chem.*, 1980, **45**, 2115.

17 G. H. Dayl and R. Schaeffer, *J. Am. Chem. Soc.*, 1961, **83**, 3032.

18 K. W. Böddeker, S. G. Shore, and R. U. Bunting, *J. Am. Chem. Soc.*, 1966, **88**, 4396.

19 M. Sugie, H. Takeo, and C. Matsumura, *Chem. Phys. Lett.*, 1979, **64**, 573.

20 H. Nöth and H. Vahrenkamp, *Chem. Ber.*, 1967, **100**, 3353.

21 O. T. Beachley, *Inorg. Chem.*, 1967, **6**, 870; A. B. Burg and C. C. Randolph, jr., *J. Am. Chem. Soc.*, 1951, **73**, 953; G. A. Hahn and R. Schaeffer, *ibid.*, 1964, **86**, 1503; E. Wiberg, A. Bolz, and P. Buckheit, *Z. Anorg. Chem.*, 1948, **256**, 285.

22 R. Köster, H. Bellut, and S. Hattori, *Justus Liebigs Ann. Chem.*, 1968, **720**, 1.

23 W. R. Nutt and R. L. Wells, *Inorg. Chem.*, 1982, **21**, 2473.

24 A. Hudson and R. A. Jackson, *Chem. Commun.*, 1969, 1323.

25 P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1969, **91**, 3938.

26 A. Hudson, R. A. Jackson, C. J. Rhodes, and A. L. DelVecchio, *J. Organomet. Chem.*, 1985, **280**, 173.

27 J. R. Roberts and K. U. Ingold, *J. Am. Chem. Soc.*, 1973, **95**, 3228.

28 C. Heller and H. M. McConnell, *J. Chem. Phys.*, 1960, **32**, 1535.

29 H. Fischer, *Z. Naturforsch., Teil A*, 1965, **20**, 428.

30 J. K. Kochi, *Adv. Free Radical Chem.*, 1975, **5**, 189.

31 M. C. R. Symons, 'Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy,' Van Nostrand Reinhold, Wokingham, 1978.

32 H. Bock and W. Fuss, *Chem. Ber.*, 1971, **104**, 1687.

33 E. A. Williams and J. D. Cargioli, *Ann. Rep. N.M.R. Spectrosc.*, 1979, **9**, 221 and references cited therein.

34 D. Griller and K. U. Ingold, *J. Am. Chem. Soc.*, 1974, **96**, 6203.

35 J. N. Kirwan and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1988, 480.

36 A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc. B*, 1971, 1823.

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

38 V. P. J. Marti, V. Paul, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1986, 481.

39 M. J. S. Dewar, H. S. Rzepa, and M. L. McKee, *J. Am. Chem. Soc.*, 1978, **100**, 3607.

40 J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970; A. R. Gregory, *J. Chem. Phys.*, 1974, **60**, 3713.

41 P. Bischof and G. Friedrich, *J. Comput. Chem.*, 1982, **3**, 486.

42 M. J. S. Dewar, J. Friedheim, G. Grady, E. F. Healy, and J. J. P. Stewart, *Organometallics*, 1986, **5**, 375.

43 I. G. Green, R. L. Hudson, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1773.

44 W. E. Newton and E. G. Rochow, *Inorg. Chim. Acta*, 1970, **4**, 133; *J. Chem. Soc. A*, 1970, 2664.

45 J. A. Baban and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1987, 497.

46 H. C. Brown and N. Ravindran, *Inorg. Chem.*, 1977, **16**, 2938.