Reaction of Pentaborane(9) with Charged and Neutral Ligand Species. A New Synthesis of the Tetradecahydrononaborate(1–) ion, $B_9H_{14}^-$

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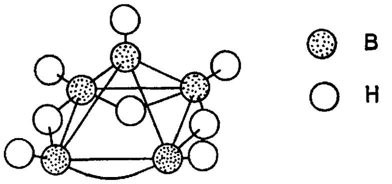
The hydride and octahydrotriborate(1–) ions react with pentaborane(9) to yield ultimately the tetradecahydrononaborate(1–) ion, $B_9H_{14}^-$. While a high conversion yield occurs with the H^- ion the yield with the $B_3H_8^-$ ion is rather less, due to an increase in other boron hydride species in the reaction mixture. The reactions of pentaborane(9) with triphenyl- and trimethyl-phosphine to yield the discrete adducts $B_5H_9,2PR_3$ (R = Me or Ph) are also reported. The latter species may also be prepared by the displacement of trimethylamine from $B_5H_9,2NMe_3$ by trimethylphosphine.

THE Bronsted acidity of several boron hydride compounds is a well established property, and a series of borane anions may be prepared from the neutral hydrides by the action of various nucleophiles such as H^-, LiR, NR_3, *etc.*[1-4] In particular for pentaborane(9) interaction with nucleophilic reagents yields a series of derivatives which may be either anionic or neutral. For example, the octahydropentaborate (1–) ion, $B_5H_8^-$ (I), has been characterised from the deprotonation of B_5H_9 with H^- in ether solvents at low temperature.



(I)

$$B_5H_9 + MX \longrightarrow MB_5H_8 + HX$$

where MX = $LiCH_3$, NaH, or KH.[3,5,6] It has been pointed out that decomposition of this ion occurs fairly rapidly at room temperature,[7] with the rate of decomposition being dependent upon both the solvent and cation present.[6] However no suggestions as to the nature of the products of this decomposition have yet been made.

In contrast to the above, pentaborane(9) reacts with a variety of ligands (*e.g.* alkyl and aryl amines, ammonia, acetonitrile, *etc.*) at low temperatures to form adducts

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of variable stoicheiometry, although reports of the properties of such systems are often conflicting. The adducts invariably decompose when the temperature is raised above room temperature, and cleavage products are often obtained.[8]

Pentaborane(9) and trimethylamine react at 195 K to yield $B_5H_9,2NMe_3$,[9-11] which on warming to ambient temperature *in vacuo* partly dissociates into the original components, and is partly converted to trimethylamine–borane, and a (B–H) polymer. Diborane has been found to displace the pentaborane(9) from this 1 : 2 adduct.[12] A 1 : 1 adduct (B_5H_9,TMED) has been obtained from the reaction of pentaborane(9) with the bidentate ligand *N,N,N′,N′*-tetramethylethylenediamine (TMED) at 298 K.[13] The suggested structure of this complex involves both nitrogen atoms of the ligand attached to one of the basal boron atoms. The attachment of two ligands to a single basal boron atom has also been proposed in the compound $B_5H_9,2NH_3$, primarily because the isolated product was formulated as $H_2B(NH_3)_2^+ B_4H_7^-$.[14]

The reaction of pentaborane(9) with phosphines, however, is not so clear, although the existence of species of the formula B_5H_9,xPR_3 [$x \not> 2$, R = alkyl or aryl] has been suggested.[15] A recent preliminary report has indicated that trimethylphosphine reacts with pentaborane(9) in ether solvents to yield the species $B_5H_9,2PMe_3$,[16] while an earlier study in the absence of solvent produced only trimethylphosphine–borane.[17]

We have investigated in some detail the overall reactions of pentaborane(9) with the hydride and octahydrotriborate(1−), $B_3H_8^-$, ions. Further, in view of the recent report that the interaction of the tetrahydroborate ion with pentaborane(9) at room temperature yields predominantly the ions $B_3H_8^-$ and $B_9H_{14}^-$, together with small quantities of unidentified products,[18,19] we have also studied the reaction with the neutral species triethylamine–borane for comparative purposes.

We have attempted to determine the nature of the adducts of pentaborane(9) with triphenylphosphine and with trimethyl-amine and -phosphine, and the relative stabilities of the last two complexes have been determined by means of displacement reactions.

RESULTS AND DISCUSSION

We confirmed initially that pentaborane(9) and sodium hydride react rapidly in ethereal solvents (*e.g.* diglyme) at ambient temperatures liberating hydrogen, with the volume varying slightly in each experiment but always lying between 0·97 and 1·02 mol per mol of pentaborane(9) used.[5,6] On standing the colourless solutions became yellow-green, and slowly evolved further hydrogen. After being allowed to stand for about one week the addition of tetramethylammonium hydroxide caused some effervescence, and precipitated immediately a white solid which could be recrystallised unchanged from water. The ^{11}B n.m.r. spectrum of this solid (in DMSO) showed only three doublets centred at $\delta = 8{\cdot}25$, 20·40, and 23·4 p.p.m. (relative to $BF_3,Et_2O = 0$) with J_{B-H} — 140, 130, and 140 Hz respectively, which is in excellent agreement with the values reported for the $B_9H_{14}^-$ ion.[20] This result, together with the analysis and i.r. spectrum, identifies the solid as $Me_4NB_9H_{14}$. Alternatively the $B_9H_{14}^-$ ion may be recovered from the original solution by the addition of dioxan which precipitates a white solid. The ^{11}B n.m.r. spectrum of this solid (in diglyme) is similar to that for the $B_9H_{14}^-$ ion but also shows the presence of trace quantities (never more than 10% of the total boron content from the relative integrated intensities) of the $B_3H_8^-$ ion and other unidentified products which give a doublet at $\delta = 9{\cdot}8$ p.p.m. (J_{B-H} 132 Hz), a singlet *ca.* 14 p.p.m., and a triplet (or two doublets) at 39·5 p.p.m. (J_{B-H} 150 and 165 Hz).

We have attempted to follow the course of the reaction from the variation in the ^{11}B n.m.r. spectrum. When equimolar quantities of NaH and B_5H_9 in monoglyme are placed in a sealed-off n.m.r. tube, the only observable signals at 195 K coincide with those of B_5H_9. As the temperature is slowly raised from 195 to 273 K over 30 min these signals are replaced by a complicated series of overlapping peaks. After 1 h at 308 K signals from $B_9H_{14}^-$ could be observed together with small quantities of $B_3H_8^-$ and BH_4^- ions, identified by comparison with the published spectra.[21,22] The spectrum changes steadily over 7 days when it consists almost entirely of signals from $B_9H_{14}^-$ ($\gtrsim 90\%$ of relative integrated intensities), and two doublets centred at $\delta = 2{\cdot}6$ p.p.m. (J_{B-H} 130 Hz) and 39·5 p.p.m. (J_{B-H} 130 Hz). However, we found that, using our method for separating the $B_9H_{14}^-$ ion, we were never able to achieve yields of $\gtrsim 60\%$ (based on the boron content of the B_5H_9 used initially). There was no indication that any boron-containing species were lost during the reaction as insoluble (polymeric) material since the final reaction

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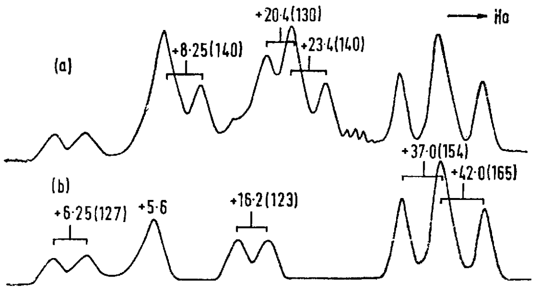
solution remained clear. Since no signals which could be assigned unambiguously to the $B_5H_8^-$ ion were observed at any time during the reaction it appears that little initial reaction occurs at 195 K. At higher temperatures (*e.g.* 273 K) the $B_5H_8^-$ ion is known to be unstable in glyme,[6,7] and, in addition, probably reacts with other species in solution, as discussed below. The appearance of small quantities of the BH_4^- and $B_3H_8^-$ ions early in the reaction suggests that the former, and possibly the latter, are reaction intermediates, but the significant difference from the reaction of pentaborane(9) with the hydroborate ion is that no appreciable proportion of the $B_3H_8^-$ ion remains at the end of the reaction. Since the $B_3H_8^-$ ion reacts only slowly with pentaborane(9) (see below) it now appears that, in the reaction using the BH_4^- ion, the $B_9H_{14}^-$ ion might arise from a hydride ion reaction as in the present case, with the BH_3 portion of the BH_4^- ion contributing to the formation of the $B_3H_8^-$ ion. This rationale is consistent with our failure in attempts to prepare derivatives of the type $B_9H_{13}L$ ($L = NEt_3$) from reaction of the uncharged H_3B,NEt_3 with pentaborane(9) at low temperatures (298—323 K). At higher temperatures (373 K) the $B_{12}H_{12}^{2-}$ ion, identified from its ^{11}B n.m.r. and i.r. spectra,[23,24] was obtained, substantiating an earlier study of this reaction.[25]



^{11}B N.m.r. spectrum recorded at 32·1 MHz of the products of the reaction between B_5H_9 and $Me_4NB_3H_8$; (a), the recorded spectrum; (b), the same spectrum after the signals from $B_9H_{14}^-$ have been graphically subtracted

In general the reaction of pentaborane(9) with the octahydrotriborate(1−) ion (in the form of $Me_4NB_3H_8$) is similar to those using hydride and tetrahydroborate(1−) ions, except that reaction is much slower. The ^{11}B n.m.r. spectrum of the reaction mixture shows the presence of the $B_9H_{14}^-$ ion, together with a very small quantity of the $B_3H_8^-$ ion, and other signals arising from the unidentified species previously observed in the reactions involving both the BH_4^- and H^- ions. From the integrated intensities the relative percentages of the products are $B_9H_{14}^- : \text{unknown} : B_3H_8^- = 47 : 47 : 6$. Concentration of the solution leads to the formation of a precipitate whose ^{11}B n.m.r. spectrum (in monoglyme) is essentially identical with that of the original solution. The ^{11}B n.m.r. spectrum of the final reaction mixture is shown in the Figure (a), and when the signals arising from the $B_9H_{14}^-$ ion are subtracted graphically, the spectrum shown in the Figure (b) remains. This residual spectrum could arise from one or more higher borane anions, as yet unidentified, because the species in solution is involatile. It is relevant that the reaction of diborane(6) with pentaborane(9) results in the formation of higher boron hydrides.[26] Various attempts to obtain the compound in a pure state by precipitation from solution using tetra-alkylammonium salts or dioxan have so far proved unsuccessful.

The $B_9H_{14}^-$ ion might arise from either a direct or multi-step reaction. Undoubtedly an initial reaction in any scheme would involve the formation of the $B_5H_8^-$ ion, and possibly to a lesser extent the hydroborate ion.

$$NaH + B_5H_9 \xrightarrow{-H^+} Na^+B_5H_8^- + H_2$$

and

$$NaH + B_5H_9 \xrightarrow{-BH_3} Na^+BH_4^- + [B_4H_6]$$

Subsequent reaction of the nucleophilic ion $B_5H_8^-$ with pentaborane(9) would yield the $B_9H_{14}^-$ ion directly (we have already shown that BH_4^- also yields the same ion).

$$Na^+B_5H_8^- + B_5H_9 \longrightarrow Na^+B_9H_{14}^- + [BH_3]$$

The $[B_4H_6]$ intermediate has been suggested to be involved in reactions of pentaborane(9) with nucleophiles,[27] and its high Lewis acidity has been commented upon.[28] This species could therefore react with the $B_5H_8^-$ ion again affording the $B_9H_{14}^-$ ion directly, although we regard this pathway as less important than the one given above.

$$Na^+B_5H_8^- + [B_4H_6] \longrightarrow Na^+B_9H_{14}^-$$

These direct pathways lead in turn to the second general route involving several borane anions which have been suggested[29] as intermediates in the conversion of small borane cages (*e.g.* B_2 or B_3) to the B_{12} cage in $B_{12}H_{12}^{2-}$, *e.g.*

$$B_5H_8^- \xrightarrow{BH_3} B_6H_{11}^- \xrightarrow{BH_3} \underset{+\,H_2}{B_7H_{12}^-} \xrightarrow{BH_3} \underset{+\,H_2}{B_8H_{13}^-} \xrightarrow{BH_3} \underset{+\,H_2}{B_9H_{14}^-}$$

In view of the generally slow rate of formation of the $B_9H_{14}^-$ ion, and the continuous evolution of hydrogen during the reaction it is probable that both routes occur. The results do corroborate the tentative suggestion made elsewhere that the $B_9H_{14}^-$ ion is an intermediate in the formation of the $B_{12}H_{12}^{2-}$ ion since it is known that the

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latter is obtained from the reaction of pentaborane(9) with the tetrahydroborate ion at 393 K.[25] Previously reported synthetic methods for the $B_9H_{14}^-$ ion have involved the degradation of decaborane(14),[30] and the above reactions, especially those using the hydride ion, provide a feasible alternative route to this ion which appears to have considerable potential as a ligand system.[31,32]

With the neutral ligands, the formation of a species $B_5H_9,2PMe_3$ from the reaction of B_5H_9 with PMe_3 in hydrocarbon solvents, was established tensiometrically. Removal of the solvent and an excess of PMe_3 yielded a white powder ($B_5H_9,2PMe_3$) which seems to be stable indefinitely at 298 K, unlike its amine counterpart which decomposes at 298 K.[9] We have found the latter species to be stable at 77 K, *in vacuo*, over several days.

Treatment of a solution of $B_5H_9,2NMe_3$ with PMe_3 resulted in the evolution of an almost stoicheiometric amount of trimethylamine, and removal of the solvent afforded the bis-phosphine adduct, together with traces of trimethylamine–borane, presumably from the decomposition of the bis-amine adduct.

$$B_5H_9,2NMe_3 + 2PMe_3 \longrightarrow B_5H_9,2PMe_3 + 2NMe_3 + \text{trace } Me_3NBH_3$$

Attempts to replace trimethylphosphine by trimethylamine in the bis-phosphine adduct were not successful, showing that the phosphine is the preferred ligand. Similar trends have been observed when borane, BH_3, is used as the acceptor moiety.[33,34]

The existence of the previously unreported bis-triphenylphosphine complex $B_5H_9,2PPh_3$, was also established tensiometrically. The white solid product decomposed fairly rapidly at ambient temperatures in that after 2 h a definite yellow colouration had appeared, and traces of triphenylphosphine–borane could be detected. Attempts to sublime the product also liberated triphenylphosphine–borane as the sublimate, identified from its i.r. spectrum.[35] When pentaborane(9) was treated with triphenylarsine under similar conditions no stable adduct was obtained since on evacuating the reaction flask the pentaborane(9) was removed, and only pure ligand remained.

Our attempts to determine the structures of these complexes using i.r. and n.m.r. spectroscopy have met with only limited success. The i.r. spectra of the 1 : 2 adducts with trimethyl-amine and -phosphine show some interesting differences from the composite spectra of the two reactants. In general, the absorptions associated with the ligand are slightly shifted from those observed in the free ligand itself, and are weak in comparison with those arising from the pentaborane(9) fragment. Significant changes also occur in the absorptions arising from pentaborane(9) in the complex compared with those in the free hydride. For example in the bis-amine compound the B–H terminal stretching region shows a sharp singlet at 2470 cm^{-1}, a sharp doublet at 2410 and 2380 cm^{-1}, and a shoulder at 2300 cm^{-1} (observed from a Nujol mull), whereas pentaborane(9) shows a sharp absorption at 2610 cm^{-1} (from a liquid film) which is resolved into two absorptions at 2610 and 2598 cm^{-1} in the gas-phase. The bis-trimethylphosphine compound shows a similar pattern (from a Nujol mull), but less well resolved, with a shoulder at 2450 cm^{-1}, a doublet at 2400 and 2370 cm^{-1}, and a shoulder at 2305 cm^{-1}. These spectra suggest the possibility of the presence of terminal BH_2 groups in the two adducts in addition to the normal BH terminal group. Such BH_2 groups would be expected to be formed from a transfer of a bridging hydrogen atom to a terminal position, and indeed the absorptions from the bridging hydrogens (*ca.* 1875 and 1400 cm^{-1}) in the adducts are relatively much weaker than those in pentaborane(9) at 1840 and 1500 cm^{-1}.[36] A further indication of the possibility of BH_2 groups in the adducts arises from relatively strong absorptions at 1136 and 1158 cm^{-1} (from deformation modes) in the trimethyl-amine and -phosphine compounds respectively. The strong absorption centred at *ca.* 900 cm^{-1} in pentaborane(9) appears to be retained in the adducts although it is shifted by *ca.* 50 cm^{-1}. No absorptions associated with vibrations of any $B \leftarrow N$ or $B \leftarrow P$ bands could be assigned with any confidence in the spectra of the two adducts.

The ^{11}B n.m.r. spectrum of the bis-amine adduct (in dichloromethane solution) shows three broad symmetrical resonances in the ratio 2 : 2 : 1 (Table), and suggests three different boron atom environments (two basal and one apical). The general broadness of the signals in our spectra prevents any coupling from being

^{11}B N.m.r. spectral date for pentaborane and some complexes

Compound	Shift, δ (p.p.m.) [a]	Ratio	Assignment
B_5H_9	13·30(d); *J* 161 Hz	4	4 basal atoms
	52·7(d); *J* 176 Hz	1	1 apical atom
$B_5H_9,2NMe_3$ (at 30°)	−1·45	2	2 basal atoms
	21·2	2	2 basal atoms
	54·3	1	1 apical atom
$B_5H_9,2PMe_3$ (at 30°)	+22·9 +32·7	4	4 basal atoms [b]
	+54·4	1	1 apical atom
$B_5H_9,2PMe_3$ (at 60°)	+20·2 +24·3 +30·8	4	4 basal atoms [b]
	+54·8	1	1 apical atom

[a] Shifts are relative to $BF_3,Et_2O = 0{\cdot}0$. [b] Overlap prevents integration of the separate signals.

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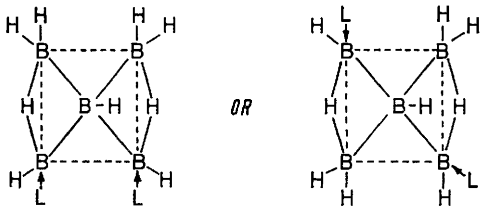
observed. An attempt to observe any inherent 'structure' within the resonances, by warming the sample in the probe, was unsuccessful; decomposition of the sample occurs and signals attributable to trimethylamine–borane are observed.[34] It is interesting that in contrast the ^{11}B n.m.r. spectrum of the bis-phosphine adduct (in monoglyme) shows only two resonances in the ratio 4 : 1, the more intense low field signal showing some asymmetry while the high field signal is again symmetrical. Warming the sample in the probe results in an increased resolution of the low-field signal (Table), but at 353 K some decomposition seems evident when signals due to trimethylphosphine–borane are observed.[34] The ^{1}H n.m.r. spectrum of the bis-phosphine adduct shows a doublet at 9·26 τ (J_{P-H} 11 Hz) and a broad resonance below this; none of the quartets seen in pentaborane(9) could be observed. Two features are of interest; first, in the ^{11}B spectra of both compounds the signal at highest field appears to be a symmetrical signal in contrast to the well defined doublet observed for pentaborane(9). Secondly, significant shifts to high field occur for the basal and apical (especially the former) boron atoms in both compounds. Thus, although the spectra do not clearly define the position of ligand substitution on the B_5 framework the two ligand molecules would appear to be co-ordinated to two of the four basal boron atoms with a concomitant rearrangement of the bridging hydrogen atoms. A structure such as that shown in (II) would be consistent with the experimental evidence presented here. It is interesting that the half-height width of the signal from the apical boron atom in each complex is less (by *ca.* 70 Hz) than the corresponding doublet signal in pentaborane(9) suggesting that it arises by coalescence of this signal rather than by a broadening of each part of the doublet. The loss of the resolution in the B–H (terminal) coupling presumably arises from a more asymmetric field gradient at this atom in the adducts with an increase in the rate of quadrupole relaxation. In the mass spectra of the trimethylamine and -phosphine compounds ions corresponding to both pentaborane(9) and the respective ligands are clearly observed. This suggests that there are no major changes in the B_5 framework in these compounds. In addition strong ions corresponding to the 1 : 1 adducts, B_5H_9,MMe_3 (where M = N or P), are present, as is a weak molecular ion from $B_5H_9,2PMe_3$ although a molecular ion for the bis-amine adduct could not be detected. The fact that the 1 : 1 but not the 1 : 2 compounds are observed in each case may be due to some thermal decomposition in the source (at *ca.* 323 K), but the evidence does suggest the possibility of the 1 : 1 compounds being intermediates in the formation of the 1 : 2 complexes. Further, the observation of the original reactants indicates some degree of reversibility in the overall process:



(II)

$$B_5H_9 \underset{-L}{\overset{+L}{\rightleftharpoons}} B_5H_9,L \underset{-L}{\overset{+L}{\rightleftharpoons}} B_5H_9,2L$$

(where L = NMe_3 or PMe_3)

However, it should be stressed that as yet there is no other evidence for the existence of 1 : 1 compounds in these systems.

It has been suggested elsewhere that the structures of the $B_5H_9,2NMe_3$ and B_5H_9,TMED complexes are similar.[12] The present results on the other hand intimate basic differences in the two structures in view of the different n.m.r. spectra, and the fact that no major rearrangement of the B_5H_9 framework apparently occurs. Certainly ionic structures of the type $[BH_2,TMED]^+$-$[B_4H_7]^-$ which have been eliminated as possibilities for B_5H_9,TMED [13] appear equally unlikely in the present case. Further evidence, in particular on the solid-state structures, is obviously required to provide a definitive answer to this problem.

EXPERIMENTAL

Lithium and sodium hydrides were used as received (L. Light and Co. Ltd.) and estimations by hydrolysis showed *ca.* 90% active hydrogen. Trimethylamine (B.D.H.) and trimethylphosphine (Emanuel) were dried by distillation from lithium tetrahydroaluminate on the vacuum line. Pentaborane(9) was purified by distillation under vacuum, and the solvents, monoglyme and diglyme were distilled from lithium tetrahydroaluminate, and stored over molecular sieve 4A. n-Decane and n-hexane were dried by distillation from sodium. Tetramethylammonium octahydrotriborate was obtained from α-Inorganics Inc., and $B_5H_9,2NMe_3$ [9] and triethylamine–borane [37] were prepared by the literature methods.

Infra-red spectra were recorded using a Perkin-Elmer 457 Grating Infracord, and mass spectra were obtained on an A.E.I. MS9 mass spectrometer. The ^{11}B and ^{1}H n.m.r. spectra were obtained using a Varian HA 100 instrument operating at 32·1 and 100 MHz respectively.

Reaction of Sodium Hydride with Pentaborane(9).—The pentaborane(9) (0·481 g, 7·52 mmol) was distilled on to sodium hydride (0·205 g, 7·52 mmol of active hydrogen) in monoglyme (15 ml) at 77 K under vacuum. The mixture was then allowed to warm to room temperature with stirring, and after 30 min 164 ml (7·34 mmol) of hydrogen had been evolved. The solution was then light yellow, and slowly turned green over the course of several days evolving a further quantity of hydrogen (23·3 ml, 1·04 mmol). Removal under vacuum of *ca.* 5 ml of liquid from the reaction flask yielded only pure solvent with no other volatile species containing B–H bonds, as indicated from the i.r. spectra of various fractions of the liquid. Treatment of the residual solution with aqueous tetramethylammonium hydroxide (*ca.* 15 ml) yielded a white solid precipitate [0·394 g, 57% yield based on the boron content of the pentaborane(9) used] which was shown to be $Me_4NB_9H_{14}$ from the ^{11}B n.m.r.

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spectrum and analysis of the solid by combustion in oxygen at 1073 K (Found: C, 25·15; H, 13·8; N, 7·2. Calc. for $C_4H_{26}B_9N$: C, 25·95; H, 14·5; N, 7·55%). When a further aliquot of the reaction solution was treated with 1,4-dioxan a white solid precipitated whose ^{11}B n.m.r. spectrum (in diglyme) was consistent with the presence of the $B_9H_{14}^-$ ion [probably as the sodium salt, NaB_9H_{14},n-(dioxan)] with traces of the $B_3H_8^-$ ion, and at least one other species which was not identified.

The reaction using lithium hydride with monoglyme as the solvent proceeded very similarly, albeit more slowly, to those reactions using sodium hydride, and the same borane anions were identified.

Reaction of Tetramethylammonium Octahydrotriborate with Pentaborane(9).—The $Me_4NB_3H_8$ (0·454 g, 3·95 mmol) was suspended in diglyme (15 ml) and pentaborane(9) (0·236 g, 3·69 mmol) was distilled on to the mixture at 77 K under vacuum. After warming to room temperature, and stirring for 12 h no reaction was apparent, and a considerable proportion of the $Me_4NB_3H_8$ remained undissolved. Over a period of ten days the solid slowly dissolved, and both hydrogen (54 ml, 2·42 mmol) and diborane (0·069 g, 2·46 mmol) were evolved. The ^{11}B n.m.r. spectrum of the solution showed the presence of the $B_9H_{14}^-$ ion, together with a very small quantity of the $B_3H_8^-$ ion, and some signals arising from an unidentified species.

Preparation of $B_5H_9,2NMe_3$ *and* $B_5H_9,2PMe_3$.—Both compounds were prepared by the same method, a typical procedure being as follows: pentaborane(9) (0·0998 g, 1·56 mmol) was condensed on to n-decane (10 ml) at 77 K. The flask and contents were then allowed to warm to 273 K (melting ice) and the vapour pressure noted. Trimethylphosphine was then distilled into the solution at 77 K in 0·0462 g (0·608 mmol) aliquots, measured by pressure using a calibrated bulb. Between each addition the reactants were allowed to warm to 273 K and equilibrated at this temperature for 15 min, with stirring. The vapour pressure was then recorded and, after cooling to 77 K, the pressure was again determined. No non-condensable gas was detected during the reaction, and after the first addition of trimethylphosphine a white precipitate was formed in the reaction flask. The pressure decreased steadily until a mole ratio of 2·1 : 1 ($PMe_3 : B_5H_9$) was reached and thereafter rose steeply and linearly with successive additions of trimethylphosphine. Removal of the solvent and excess ligand afforded the product $B_5H_9,2PMe_3$; the weight of ligand recovered also indicated this composition. n-Hexane was also used as the solvent over the temperature range 213—295 K. Both the 2 : 1 compounds were analysed by hydrolysis with hydrochloric acid in a sealed bulb at 393 K for the $B_5H_9 : 2NMe_3$ compound 0·246 g, 1·35 mmol, yielded 347 ml of hydrogen at s.t.p., calculated 363 ml based on the equation $B_5H_9{\cdot}2NMe_3 + 15H_2O \longrightarrow 5B(OH)_3 + 12H_2 + 2NMe_3$, while the $B_5H_9,2PMe_3$ compound 0·203 g, 0·94 mmol, yielded 237 ml of hydrogen at s.t.p., calculated value is 253 ml.

An i.r. spectrum (Nujol mull) showed bands at: 2450sh,s, 2400vs, 2370vs, 2305sh,m, 1890m, 1405m, 1300m, 1290s, 1158vs, 1060w, 992sh,w, 965vs, 946vs, 925sh,s, 870m, 850w, 756sh,vw, 746m, 722sh,w, and 691m cm^{-1}, for $B_5H_9,2NMe_3$.

An i.r. spectrum (Nujol mull) of $B_5H_9,2PMe_3$ showed bands at 2470vs, 2410vs, 2380vs, 2300sh,m, 1840m, 1400m, 1250m, 1136vs, 1100s, 1034s, 980vs, 950s, 886w, 848vs, 762m, 700w, 656br,m, and 520br,m cm^{-1}.

Preparation of $B_5H_9,2PPh_3$.—Triphenylphosphine (0·4514 g, 1·72 mmol) was dissolved in monoglyme (10 ml), and after degassing the mixture the vapour pressure at 283 K was recorded. Pentaborane(9) was now added (0·0154 g, 0·24 mmol per addition), and the vapour pressure at 0° recorded after each addition after equilibration. The vapour pressure remained almost constant until a mole ratio of 1·98 : 1 $PPh_3 : B_5H_9$ was reached and thereafter rose slowly but linearly with successive additions of pentaborane(9). The solvent and the excess of pentaborane(9) were removed on the vacuum line to leave a white powdery solid which over a 2 h period started to turn yellow. An attempt at sublimation led only to the isolation of triphenylphosphine–borane.

Reaction of PMe_3 *with* $B_5H_9,2NMe_3$.—$B_5H_9,2NMe_3$ (0·4552 g, 2·51 mmol) was weighed under nitrogen and rapidly transferred to a 100 ml QQ flask containing 1,2-dichloroethane (5 ml) and equipped with a stopcock and magnetic stirring bar. The flask was then placed on the vacuum line, degassed, and trimethylphosphine (0·382 g, 5·02 mmol) condensed in at 77 K. The reactants were allowed to warm to room temperature and stirred over a 12 h period. No hydrogen was evolved and vacuum fractionation of the volatile components through traps at 193 and 77 K yielded trimethylamine (0·254 g, 4·31 mmol, 86% theoretical) in the latter. The 193 K trap contained only 1,2-dichloroethane and a small quantity of a white crystalline material identified as trimethylamine–borane from its i.r. spectrum. The white solid remaining in the reaction flask was identified as $B_5H_9,2PMe_3$ by its i.r. and ^{11}B n.m.r. spectra.

A similar reaction with $B_5H_9,2PMe_3$ and NMe_3 left the former unchanged over a 48 h period and NMe_3 was recovered almost quantitatively (94%).

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