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Preparation of Substituted Derivatives of the Octahydrotriborate(1−) Ion

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The reactions between the octahydrotriborate(1−) ion, $B_3H_8^-$, and mercury(I) halides have produced the substituted anions $B_3H_7Cl^-$, $B_3H_6Cl_2^-$ and $B_3H_7Br^-$. Further treatment of $B_3H_7Cl^-$ with CN^-, SCN^- and BH_3CN^- salts yielded the anions $B_3H_7CN^-$, $B_3H_7NCS^-$ and $BH_3CNB_3H_7^-$, respectively, as the $Bu^n_4N^+$ or $[Ph_3P]_2N^+$ salts. Evidence is also presented for the existence of $B_3H_7F^-$ formed by the reaction between $B_3H_8^-$ and Hg_2F_2.

Introduction

In contrast to neutral ligand triborane adducts of which many examples are known [1], relatively little work has been reported on the preparation of substituted octahydrotriborate ions or their chemistry. The halogenated derivatives $B_3H_7X^-$ (X = Cl, Br, I) have been prepared [2] by reaction of the tetra-n-butylammonium salt of $B_3H_8^-$ with the appropriate hydrogen halide in methylene chloride; however, only i.r. spectra were reported for these species. Cleavage of tetraborane(10) with NaCN was thought [3] to yield NaB_3H_7CN as one product, although no spectroscopic evidence was reported. Anionic derivatives of the tetrahydroborate(1−) ion, BH_4^-, such as BH_3CN^-, BH_3NCS^- and $BH_3CNBH_3^-$, have been prepared and are well characterised [3, 4]. We now report a convenient method for the preparation of some substituted octahydrotriborate anions and discuss some of their chemical behaviour.

Results and Discussion

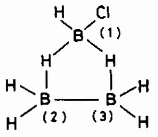
It has previously been shown [5] that treatment of tetrahydrofuran (THF) solutions of $Me_4NB_3H_8$ with mercury(I) or mercury(II) chloride yielded the adduct $B_3H_7 \cdot THF$ as the major product. However, we have found that by employing $Bu^n_4N^+$ or $[Ph_3P]_2N^+$ salts of $B_3H_8^-$ and a non-coordinating solvent such as CH_2Cl_2, oxidation and chlorination occurred, with Hg_2Cl_2 yielding the anion $B_3H_7Cl^-$ as the major product. The reaction mixture also contained a second species, $B_3H_6Cl_2^-$, present as a small impurity. This latter ion was produced exclusively by the reaction between $B_3H_8^-$ and two equivalents of Hg_2Cl_2. The reaction can be summarised as:

$$B_3H_8^- + 1/2Hg_2Cl_2 \longrightarrow B_3H_7Cl^- + 1/2H_2 + Hg^0$$

$$B_3H_7Cl^- + 1/2Hg_2Cl_2 \longrightarrow B_3H_6Cl_2^- + 1/2H_2 + Hg^0$$

We have found that the reaction between $Bu^n_4N \cdot B_3H_8$ and HCl in CH_2Cl_2 [2] also yields a mixture of $B_3H_7Cl^-$ and $B_3H_6Cl_2^-$ the latter, however, being present in about 25%.

The ^{11}B n.m.r. spectrum of $B_3H_7Cl^-$ at 32.08 MHz consisted of two multiplets where fine structure due to ^{11}B–^1H and ^{11}B–^{11}B couplings were unresolved. The low field resonance of relative area two corresponded to the two unsubstituted boron atoms (B(2) and B(3)), and the highfield resonance of area one, to the substituted boron atom B(1). This is similar to the ^{11}B n.m.r. spectra previously reported [1, 6] for neutral B_3H_7L adducts (relevant n.m.r. data are presented in Table I).



In contrast, the ^{11}B n.m.r. spectrum of $B_3H_6Cl_2^-$ displayed the resonance due to B(1) to low field and that due to B(2) and B(3) to high field. This shift of the B(1) resonance to low field suggests that both chlorine atoms are substituted on the same boron, (B(1)) and is similar to the shifts observed in BH_2Cl and $BHCl_2$ adducts [7]. The solid $Bu^n_4N \cdot B_3H_6Cl_2$ salt slowly decomposed at room temperature to a $BHCl_2$ adduct [7] (δ = +3.3 ppm, J(BH) = 163 Hz) and this behaviour strongly supported this structural assignment.

A similar experiment with Hg_2Br_2 produced the anion $B_3H_7Br^-$ whose ^{11}B n.m.r. spectrum was very like that of $B_3H_7Cl^-$. Dichloromethane solutions of

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TABLE I. 32.1 MHz ^{11}B N.m.r. Spectral Data for Octahydrotriborate Derivatives.

Compound	δ (ppm) B(2), B(3)[a]	δ (ppm) B(1)[a]	$J_{^{11}B-^{1}H}$(Hz)[d]
$B_3H_7Cl^{-}$ [c]	−16.3	−22.2	42.0
$B_3H_6Cl_2^{-}$ [c]	−13.4	−5.3	35.4
$B_3H_7Br^{-}$ [b]	−12.2	−28.9	
$B_3H_7CN^{-}$ [e]	−9.6	−36.6	41.0
$B_3H_7NCS^{-}$ [c]	−13.2	−33.5	38.0
$BH_3CNB_3H_7^{-}$ [c]	−9.9	−36.1 (−43.8 quartet)	40.0
$B_3H_7F^{-}$ [c]	−17.6	−15.4	38.5

[a] Chemical shifts are expressed relative to external $BF_3O(Et)_2$. Negative shifts are to high field. [b] Solvent was CH_2Cl_2. [c] Solvent was $CDCl_3$. [d] 115.5 MHz line narrowed data. [e] Solvent was CD_3CN.

$Bu^n_4N\cdot B_3H_7Br$ quickly decomposed to give B_4H_{10}, identified by its ^{11}B n.m.r. spectrum [8]. There was no evidence for a dibrominated product.

The reaction between Hg_2I_2 and $B_3H_8^-$ in CH_2Cl_2 yielded B_4H_{10} as the major product, with no evidence for the presence of a stable $B_3H_7I^-$ salt. Thus, an increase in halogen size is paralleled by a decrease in stability of the halogen-substituted ion.

The infrared spectra of $B_3H_7Cl^-$, $B_3H_6Cl_2^-$ and $B_3H_7Br^-$ were very similar. Substitution of one halogen produced shifts of the absorptions due to BH stretching modes to higher energy relative to $B_3H_8^-$. The larger shifts were observed for bromine, which agreed with previously published results [2]. Dichlorination produced a further shift of these absorptions to higher energy (the relevant i.r. absorption frequencies are shown in Table II).

TABLE II. Infrared Absorptions of Octahydrotriborate Derivatives.

Substituent	2600–1900 cm^{-1}
H^-	2450s, 2400s, 2300sh, 2130m, 2080m.
Cl^-	2480s, 2425s, 2300sh.
Cl_2^-	2515s, 2455s.
Br^-	2490s, 2430s, 2300sh.
NCS^-	2490s, 2430s, 2300sh, 2160s.
BH_3CN^-	2505s, 2435s, 2375sh, 2345s, 2255s, 2205sh, 1990m (broad).
CN^-	2505s, 2460sh, 2440s, 2415sh, 2220s.

We have found that the chloride substituent of $B_3H_7Cl^-$ is very labile and is readily substituted by ions such as SCN^-, BH_3CN^- and CN^- offering a route to potentially more interesting species. Thus, when dichloromethane solutions of $B_3H_7Cl^-$ were treated with an equivalent quantity of AgSCN or $Bu^n_4N\cdot SCN$, the anion $B_3H_7NCS^-$ was produced in good yield. Similarly, the $[Ph_3P]_2N^+$ salt of $B_3H_7NCS^-$ was prepared by treating $[Ph_3P]_2N\cdot B_3H_7Cl$ with AgSCN in CH_2Cl_2. The ^{11}B n.m.r. spectrum of $B_3H_7NCS^-$ was similar to that already discussed for $B_3H_7Cl^-$. The i.r. spectrum showed BH stretching modes at 2490 and 2430 cm^{-1}, again similar to $B_3H_7Cl^-$. The strong band at 2160 cm^{-1} can be assigned to the NCS asymmetric stretch and is indicative of a nitrogen-coordinated isothiocyanate. It has been shown by X-ray studies that NH_3BH_2NCS [9] and $B_{10}H_{13}NCS$ [10] are both isothiocyanates and it is probable that $B_3H_7NCS^-$ is also N-coordinated.

In contrast to the halogen-substituted salts, which are thermally and hydrolytically rather unstable, $B_3H_7NCS^-$ is very stable and the $Bu^n_4N^+$ or $[Ph_3P]_2N^+$ salts show negligible decomposition when stored in air, at room temperature, over a period of months.

Reaction of CH_2Cl_2 solutions of $B_3H_7Cl^-$ with $Bu^n_4N\cdot BH_3CN$ yielded the bridged cyanide ion $BH_3CNB_3H_7^-$ as the major product, along with small amounts of $BH_3CNBH_3^-$ and $BH_3CNBH_2CN^-$ which were identified by their ^{11}B n.m.r. spectra [3, 11]. The formation of $BH_3CNBH_2CN^-$, which is an oxidation product of BH_3CN^-, probably arises from the presence of small amounts of dissolved mercury salts in the solution of $B_3H_7Cl^-$. The presence of $BH_3CNBH_3^-$ can be rationalised by the fact that some LB_3H_7 adducts undergo cleavage [12–14] by excess ligand to yield LBH_3 and $L_2B_2H_4$ as decomposition products. The presence of the dianion, $(BH_3CN)_2B_2H_4^{2-}$ was not observed. A similar reaction using $[Ph_3P]_2N\cdot B_3H_7Cl$ and $[Ph_3P]_2N\cdot BH_3CN$ yielded the $[Ph_3P]_2N^+$ salt of $BH_3CNB_3H_7^-$.

The ^{11}B n.m.r. spectrum of $BH_3CNB_3H_7^-$ consisted of the usual low field resonance due to B(2) and B(3) and a high field resonance due to B(1), along with a well defined 1:3:3:1 quartet at δ = −43.8 ppm [J(B–H) = 93 Hz] consistent with the BH_3CN moiety. This compares with a chemical shift of −41.8 ppm [J(B–H) = 90 Hz] in free BH_3CN^-

[4]. The i.r. spectrum of $BH_3CNB_3H_7^-$ showed BH stretching modes due to the B_3H_7 moiety along with bands at 2375 and 2345 cm^{-1} due to BH stretching modes of the BH_3 moiety. The strong sharp band at 2255 cm^{-1} is characteristic of a bridging cyanide and is similar to that reported for $BH_3CNBH_3^-$ [4]. The $BH_3CNB_3H_7^-$ salts had a comparable stability to those of $B_3H_7NCS^-$.

It was of interest to examine the hydrolytic stabilities of $B_3H_7NCS^-$ and $BH_3CNB_3H_7^-$. $[Ph_3P]_2N\cdot B_3H_7NCS$ was found to be stable to pH4, at which point free SCN^- could be detected by i.r. spectroscopy. In contrast, $[Ph_3P]_2N\cdot BH_3CNB_3H_7$ was found to be stable to pH 1 but hydrolysis occurred when solutions of the salt in CH_3CN were treated with 12 *M* HCl.

Reactions of $[Ph_3P]_2N\cdot B_3H_7Cl$ with AgCN produced the anion $B_3H_7CN^-$, the ^{11}B n.m.r. spectrum of which consisted of a low field resonance of area two due to B(2) and B(3) and a high field resonance of area one due to B(1). The i.r. spectrum of $B_3H_7CN^-$ showed BH stretching modes due to the B_3H_7 moiety, along with a sharp band at 2220 cm^{-1} which can be assigned to the CN stretching mode.

Solutions of $B_3H_7CN^-$ in chlorinated hydrocarbons quickly decomposed at room temperature, depositing a black solid, whereas solutions in CH_3CN appeared to be air-stable. Attempts to prepare pure samples of the $Bu_4^nN^+$ salt of $B_3H_7CN^-$ met with failure as it rapidly decomposed to a brown oil.

The 115.5 MHz ^{11}B spectra of the derivatives gave essentially similar spectra to those at 32.08 MHz, in the absence of data manipulation of the free induction decay prior to transformation. Application of the line-narrowing procedure to the FID before transformation resulted in resolution of some fine structure, from which the values of $J_{^{11}B-^{1}H}$ could be derived. This is illustrated in Fig. 1 for $B_3H_7Cl^-$ and $B_3H_6Cl_2^-$. The resonance due to boron atoms B(2) and B(3) in $B_3H_7Cl^-$, on line narrowing, showed six lines the intensities of which corresponded to the six most intense lines of an 'octet'. Similarly the resonance due to B(2) and B(3) of $B_3H_6Cl_2^-$ showed five lines the intensities of which corresponded to the five most intense lines of a 'septet'. On a simple basis this is indicative of fluxional behaviour in which all protons are equivalent on the n.m.r. time scale. Similar spectra were obtained for $B_3H_7NCS^-$, $BH_3CNB_3H_7^-$ and $B_3H_7CN^-$.

When CH_2Cl_2 solutions of $[Ph_3P]_2N\cdot B_3H_8$ were treated with Hg_2F_2, the major product formed was thought to be $B_3H_7F^-$, along with a number of uncharacterised impurities. Attempts to obtain pure samples of $B_3H_7F^-$ met with failure; however, the 115.5 MHz ^{11}B n.m.r. of the crude product gave evidence for its existence. It consisted of a low field resonance of area one due to B(1) and a high field resonance of area two due to B(2) and B(3). The

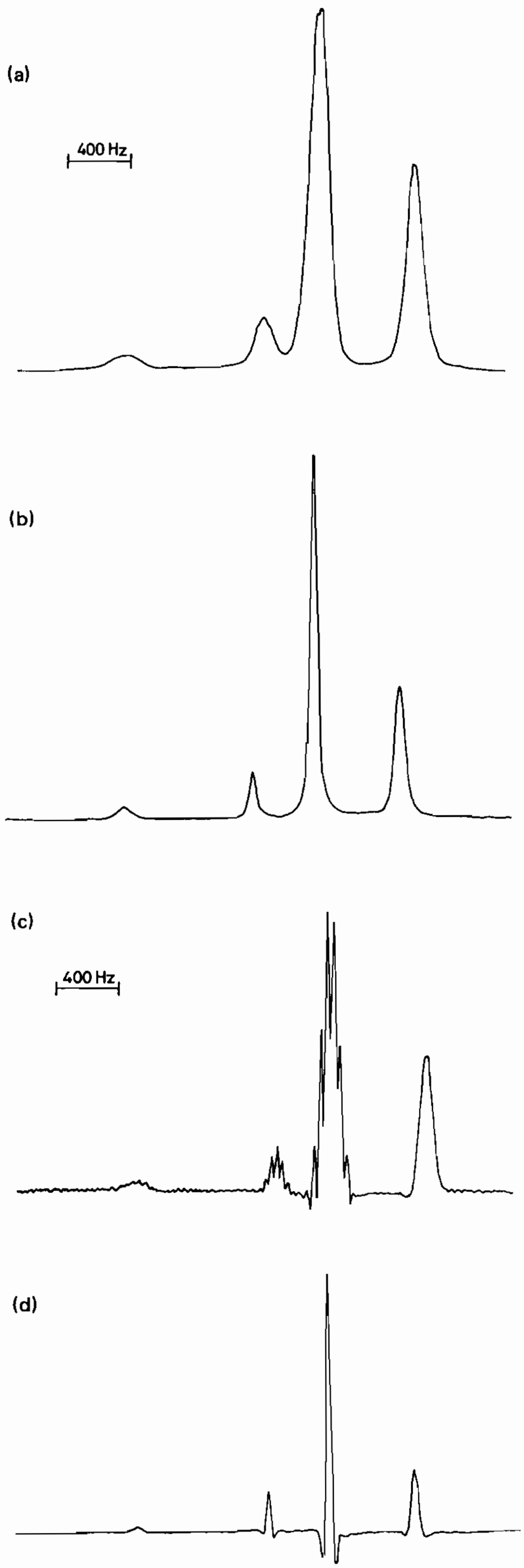

Fig. 1. 115.5 MHz ^{11}B n.m.r. spectrum of a mixture of $B_3H_7Cl^-$ and $B_3H_6Cl_2^-$. (a) normal; (b) proton decoupled; (c) line narrowed; (d) line-narrowed, proton decoupled.

presence of the substituted boron resonance at low field is in contrast to those of the monosubstituted ions already discussed and is undoubtedly due to the high electronegativity of the fluorine substituent. Fine structure could be resolved from the high field resonance, indicating a multiplet with an even number of lines, almost certainly an 'octet', giving evidence for seven equivalent protons and a $B_3H_7L^-$ species.

Experimental

All operations were carried out under nitrogen or *in vacuo* unless otherwise specified. Dichloromethane was stored over CaH_2. Chromatography solvents were reagent grade and were used without further purification. $Me_4NB_3H_8$ was purchased from Callery Chemical Company and recrystallised from acetonitrile–diethylether before use. $Bu^n_4N\cdot B_3H_8$ was prepared from $Me_4NB_3H_8$ and $Bu^n_4N\cdot OH$ in methylene chloride and was recrystallised from dichloromethane–diethylether. $[Ph_3P]_2N\cdot B_3H_8$ was prepared from $[Ph_3P]_2N\cdot Cl$ and $Me_4N\cdot B_3H_8$ in water and recrystallised from dichloromethane–diethyl ether. $NaBH_3CN$ was a gift from Dr. R. Wade, Ventron Corporation, and was recrystallised from acetonitrile. $Bu^n_4N\cdot BH_3CN$ was prepared according to the literature [15]. $[Ph_3P]_2N\cdot BH_3CN$ was prepared from $[Ph_3P]_2N\cdot Cl$ and $NaBH_3CN$ in water and recrystallised from dichloromethane–diethylether. $Bu^n_4N\cdot SCN$ and $Bu^n_4N\cdot CN$ were prepared from $Bu^n_4N\cdot I$ and the corresponding silver salt in dichloromethane. All other reagents were used as received. Kieselgel G(type 60) (Merck) was used for thin-layer chromatography. Silica gel (MFC) was used for liquid chromatography.

Spectroscopic Techniques

Infrared spectra were obtained as mulls in nujol or H.C.B.D. or as thin films between KBr plates on a Perkin-Elmer 457 grating spectrometer. 32.1 MHz ^{11}B n.m.r. spectra were recorded on a Jeol-PS-100-PFT-100 spectrometer. 115.5 MHz ^{11}B n.m.r. spectra were recorded on a Bruker WH-360 spectrometer. Chemical shifts are quoted as being negative to high field of the reference standard BF_3OEt_2. All spectra were recorded at ambient temperatures.

Preparation of $Bu^n_4N\cdot B_3H_7Cl$

Dry CH_2Cl_2 (10 cm^3) was condensed onto the solid reagents $Bu^n_4N\cdot B_3H_8$ (0.283 g; 1 mmol) and Hg_2Cl_2 (0.236 g; 0.5 mmol). The mixture was allowed to warm to room temperature and stirred until H_2 evolution was complete, *ca.* 1.5 hr. The resulting solution was filtered to remove elemental mercury and the clear filtrate evaporated to dryness, leaving a white crystalline solid. This produced samples of $Bu^n_4N\cdot B_3H_7Cl$ which were typically 90% pure by ^{11}B n.m.r. Relevant spectral data are presented and discussed in the text in all cases.

Preparation of $[Ph_3P]_2N\cdot B_3H_7Cl$

When $[Ph_3P]_2N\cdot B_3H_8$ was used in place of $Bu^n_4N\cdot B_3H_8$, the results were similar.

Preparation of $Bu^n_4N\cdot B_3H_6Cl_2$

The procedure was identical to that for the preparation of $Bu^n_4N\cdot B_3H_7Cl$, except that two equivalents of Hg_2Cl_2 were used. The white crystalline $Bu^n_4N\cdot B_3H_6Cl_2$ was isolated in the same manner. (Found: C, 53.60; H, 12.15; B, 10.30; N, 4.65; Cl, 20.00; Calc. for $C_{16}H_{42}B_3NCl_2$: C, 54.60; H, 12.00; B, 9.22 N, 4.00; Cl, 20.15).

Preparation of $Bu^n_4N\cdot B_3H_7NCS$

Dry CH_2Cl_2 (25 cm^3) was condensed onto the solid reagents $Bu^n_4N\cdot B_3H_8$ (2.83 g; 10 mmol) and Hg_2Cl_2 (2.36 g; 5 mmol). The mixture was warmed to room temperature and stirred until H_2 evolution was complete (*ca.* 2 hr). The solution was filtered onto AgSCN (1.66 g; 10 mmol) and the resulting mixture stirred for 1 hr. MeOH (10 cm^3) was added resulting in some gas evolution. The solution was filtered and the solvent removed from the filtrate leaving a clear oil. This was chromatographed on silica gel using 90% CH_2Cl_2–10% CH_3CN as eluting solvent. Fractions collected were monitored by t.l.c.. Evaporation of the solvent from the first product eluted yielded $Bu^n_4N\cdot B_3H_7NCS$ as a clear oil (1.53 g, 45%). (Found: C, 59.25; H, 13.25; B, 9.60; N, 8.50. Calc. for $C_{17}H_{43}B_3N_2S$: C, 60.05; H, 12.75; B, 9.55; N, 8.25).

T.l.c. showed one component, $R_F = 0.86$ (eluting solvent as above).

A similar experiment using $Bu^n_4N\cdot SCN$ yielded the same product.

Preparation of $[Ph_3P]_2N\cdot B_3H_7NCS$

The reaction between $[Ph_3P]_2N\cdot B_3H_7Cl$ and AgSCN yielded $[Ph_3P]_2N\cdot B_3H_7NCS$ as a white crystalline solid. T.l.c. showed one component, $R_F = 0.65$ (eluting solvent was CH_2Cl_2).

Preparation of $Bu^n_4N\cdot BH_3CNB_3H_7$

A solution of $Bu^n_4N\cdot B_3H_7Cl$ (10 mmol in CH_2Cl_2) was prepared as for the preparation of $Bu^n_4N\cdot B_3H_7NCS$. To this was added a solution of $Bu^n_4N\cdot BH_3CN$ (2.82 g, 10 mmol) in CH_2Cl_2 (10 cm^3) and the resulting mixture stirred for 2 hr. Removal of the solvent left a clear oily solid which was chromatographed on silica gel using 95% CH_2Cl_2–5% CH_3CN as eluting solvent.

Evaporation of the solvent from the first component eluted yielded $Bu^n_4N\cdot BH_3CNB_3H_7$ as a white, low-melting-point solid (0.96 g, 30%). (Found: C, 62.30; H, 14.20 B, 13.60 N, 9.10. Calc. for $C_{17}H_{46}B_4N_2$: C, 63.05 H, 14.40 B, 13.45, N, 8.70).

T.l.c. showed one component, $R_F = 0.80$ (eluting solvent as above).

Preparation of $[Ph_3P]_2N{\cdot}BH_3CNB_3H_7$

The reaction between $[Ph_3P]_2N{\cdot}B_3H_7Cl$ and $[Ph_3P]_2N{\cdot}BH_3CN$ yielded $[Ph_3P]_2N{\cdot}BH_3CNB_3H_7$ as a white crystalline solid. T.l.c. showed one component, $R_F = 0.68$ (eluting solvent was CH_2Cl_2).

Preparation of $[Ph_3P]_2N{\cdot}B_3H_7CN$

A solution of $[Ph_3P]_2N{\cdot}B_3H_7Cl$ (10 mmol in CH_2Cl_2) was prepared as above and to this was added AgCN (1.34 g, 10 mmol). The resulting mixture was stirred for 2 hr. After filtering, the filtrate was reduced to dryness and chromatographed on silica gel using 95% CH_2Cl_2–5% CH_3CN as eluting solvent. Evaporation of the solvent from the first component eluted yielded $[Ph_3P]_2N{\cdot}B_3H_7CN$ as a white crystalline solid.

T.l.c. showed one component, $R_F = 0.80$ (eluting solvent was CH_2Cl_2).

Preparation of $[Ph_3P]_2N{\cdot}B_3H_7F$

Dry CH_2Cl_2 (10 cm^3) was condensed onto $[Ph_3P]_2N{\cdot}B_3H_8$ (1.16 g; 2 mmol) and the mixture allowed to warm to 0 °C. Hg_2F_2 (0.66 g; 1.5 mmol) was added from a side arm and the resulting mixture stirred until H_2 evolution was complete (*ca.* 1 hr). After filtering to remove the grey mercury-containing slurry, the filtrate was reduced to dryness and the residue chromatographed on silica gel using 90% CH_2Cl_2–10% CH_3CN as eluting solvent. Evaporation of the solvent from the first components eluted yielded a white solid, the ^{11}B n.m.r. of which showed it to contain unreacted $B_3H_8^-$, $B_3H_7F^-$ and a number of uncharacterised minor products. A better separation could not be achieved (see text).

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References

1 (a) G. Kodama, R. W. Parry and J. C. Carter, *J. Am. Chem. Soc., 81,* 3534 (1959). (b) W. R. Deever and D. M. Ritter, *Inorg. Chem., 7,* 1036 (1968). (c) R. T. Paine and R. W. Parry, *Inorg. Chem., 11,* 268 (1972). (d) A. R. Dodds and G. Kodama, *Inorg. Chem., 15,* 741 (1976).

2 G. E. Ryschkewitsch and V. A. Miller, *J. Am. Chem. Soc., 97,* 6258 (1975).

3 V. D. Aftandilian, H. C. Miller and E. L. Muetterties, *J. Am. Chem. Soc., 83,* 2471 (1961).

4 R. C. Wade, E. A. Sullivan, J. C. Berschied and K. F. Purcell, *Inorg. Chem., 9,* 2146 (1970).

5 A. Drummond and J. H. Morris, *Inorg. Chim. Acta, 24,* 191 (1978).

6 (a) W. N. Lipscomb, *Adv. Inorg. Nucl. Chem., 1,* 117 (1959). (b) M. A. Ring, E. F. Wituki and R. C. Greenough, *Inorg. Chem., 6,* 395 (1967). (c) G. Kodama, *Inorg. Chem., 14,* 452 (1975).

7 D. J. Pasto and P. Balasubramaniyan, *J. Am. Chem. Soc., 89,* 295 (1967).

8 R. E. Williams, S. G. Gibbons and I. Shapiro, *J. Am. Chem. Soc., 81,* 6164 (1959).

9 D. S. Kendall and W. N. Lipscomb, *Inorg. Chem., 12,* 2920 (1973).

10 D. S. Kendall and W. N. Lipscomb, *Inorg. Chem., 12,* 2915 (1973).

11 J. F. Kay, J. H. Morris and D. Reed, *J. Chem. Soc. Dalton,* 1917 (1980).

12 B. M. Graybill and J. K. Ruff, *J. Am. Chem. Soc., 84,* 1062 (1962).

13 E. R. Lorry and D. M. Ritter, *Inorg. Chem., 10,* 939 (1971).

14 W. R. Deever, E. R. Lorry and D. M. Ritter, *Inorg. Chem., 8,* 1262 (1969).

15 R. O. Hutchins and D. Kandasamus, *J. Am. Chem. Soc., 95,* 6132 (1973).