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Borane Cations of Bases with Amide and Cyanide Substitution[1]

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A new series of borane cations derived from a variety of amides, some bearing important functioning groups, is characterized. New bis-borane and tris-borane cations bridged by cyanide groups are found to be stable species with definite linkage sequences. No evidence for equilibrium mixtures of isomeric cyanide structures is found.

Earlier work has shown that amides with disubstituted nitrogen can form air- and water-stable borane cations of the type $(CH_3)_3NBH_2(amide)^+$.[3a] The preparation of cations with functional substitution like this is of interest in exploring the substitution chemistry of the cations and the effects of various substituents on the BH_2(base) moiety. Investigation of the range of amides which give borane cations and a study of cations with cyanide substitution were made therefore to extend the knowledge of substituted cations.

Discussion

Cations derived from a range of amides were prepared by iodide displacement from trimethylamine–iodoborane and characterized by physical and spectral properties. Table I, which summarizes the analytical results, shows that the variety of amides employed covers aliphatic primary amide (cation of **1**), aromatic primary amide (cation of **3**), secondary aromatic amides (cations of **2**, **4**, **5**, **9**), and lactams (cations of **6**–**8**). The cations **12** and **13** are included to show that the second base may also be chosen from among the class of strong Lewis bases toward borane, and water-stable ions result.

The hexafluorophosphate salts were white and crystalline when pure—but some had a tendency to color on standing. Good aqueous stability was observed for all but the cation with acetamide (only 20% recovered on recrystallization from 65° water). It is remarkable that the secondary amide cations were so resistant to basic hydrolysis (Table II) since borane cations of primary and secondary amines are known to be sensitive to basic hydrolysis.[4] In one quantitative experiment 70% of the hexafluorophosphate of the benzamide cation, **3**, was recovered from 0.5 *M* sodium hydroxide solution after 20 min, and only 10% of the available hydrogen had been evolved. Therefore, while the detection of gas evolution (Table II) is an admittedly crude index of hydrolysis, there are reasons to believe it is reliable. Any fragmentation of the amide from the boron is expected to produce Me_3NBH_2OH and this species is known to hydrolyze rapidly in base to produce hydrogen.[5]

Linkage of the amide to boron is believed to be B—O—C=N—R as indicated in Table I, because of their analogy to the tertiary amides whose nmr spectra are most reasonably understood by such linkage.[3] The infrared bands in the 1600–1675-cm^{-1} region (presumably C=N stretching modes) of the cations are at lower frequency than the "carbonyl" bands in the uncomplexed amides. A shift of the "carbonyl" absorption to lower frequency on complexation is normally taken as an index of lessened carbonyl π-electron density which occurs when the oxygen atom of the carbonyl is ligated.[6]

The possibility of incorporating an acyl-like halogen into borane cations encouraged an attempt to extend the amide cations using carbamyl chloride, $(CH_3)_2NCOCl$. The product so obtained appears to be the acyl-like derivative in which chloride has been replaced by iodide, namely, $(CH_3)_3NBH_2OCIN(CH_3)_2{}^+PF_6{}^-$, **11**

$$(CH_3)_3NBH_2I + (CH_3)_2NCOCl \longrightarrow$$
$$[(CH_3)_3NBH_2OCClN(CH_3)_2{}^+] \xrightarrow{I^-} (CH_3)_3NBH_2OCIN(CH_3)_2{}^+ + Cl^-$$

It is sufficiently water stable to permit isolation as the hexafluorophosphate salt followed by recrystallization from methylene chloride–hexane. A BH_2-doublet infrared absorption at 2450 cm^{-1}, a "C=N" stretching at 1620 cm^{-1}, and a PF stretch at 850 cm^{-1} support the assigned structure. The proton nmr resonance in methylene chloride, while not good because of low solubility, showed a singlet (2.74 ppm) downfield from tetramethylsilane and a doublet (3.45 and 3.52 ppm) assignable to $(CH_3)_3N$ and nonequivalent $(CH_3)_2NCO$ methyl protons. The ratio of integrated peak intensities (3.2:2) was close to that expected (3:2). The resonance in D_3CCN in which the salt is more soluble had to be taken quickly because of decomposition. Again, the same symmetry for the cation was inferred with the B–O linkage to the carbamyl iodide. Elemental analyses conform well to theory (see Table I), and considerable iodine was found to be present by qualitative analysis. Rather poor stability was observed, in that a sample stored under vacuum in a vial at room temperature with only limited light exposure had decomposed in 4 weeks, and iodine was identified as one of the products by its color in carbon tetrachloride.

Substitution chemistry at the boron on the intact cations was also demonstrated by elemental chlorination of $(CH_3)_3NBH_2OCHN(CH_3)_2{}^+$ in methylene chloride at room temperature to give the bis-*B*-chloro derivative, **10**, in high yield (99%). The absence of B-H stretch at 2500 cm^{-1} and the presence of B–Cl stretch at 1700 cm^{-1} in the infrared region, along with other expected infrared bands support the assignment.

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[3] (a) N. E. Miller, D. L. Reznicek, R. J. Rowatt, and K. R Lundberg, *Inorg. Chem.*, **8**, 862 (1969); (b) see references cited in ref 3a, especially G. E. Ryschkewitsch, *J. Amer. Chem. Soc.*, **89**, 3145 (1967).

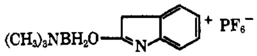
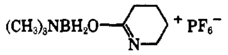
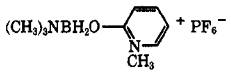
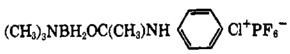
[4] T. A. Shchegoleva, V D. Sheludyakov, and B. M. Mikhailov, *Zh. Obshch. Khim.*, **35**, 1066 (1965).

[5] N. E. Miller, *J. Amer. Chem. Soc.*, **92**, 4564 (1970).

[6] R. S. Drago, "Physical Methods in Inorganic Chemistry," Reinhold, New York, N. Y., 1965, pp 230–231.

TABLE I

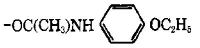
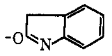
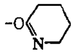
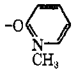
BORANE CATIONS DERIVED FROM AMIDES, AS HEXAFLUOROPHOSPHATE SALTS

No.	Compound	Mp, °C	Yield,[a] %	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
1	$(CH_3)_3NBH_2OC(CH_3)NH_2{}^+PF_6{}^-$	126–127	61	21.8	21.6	5.8	5.8	10.2	10.0
2	$(CH_3)_3NBH_2OC(CH_3)NHC_6H_5{}^+PF_6{}^-$	132–133	56	37.5	37.5	5.7	5.7	8.0	7.8
3	$(CH_3)_3NBH_2OC(C_6H_5)NH_2{}^+PF_6$	151–152	38	35.5	35.4	5.4	5.4	8.2	8.2
4	$(CH_3)_3NBH_2OC(C_6H_5)NHC_6H_5{}^+PF_6{}^-$	121–123	58	46.8	46.3	5.7	5.4	6.7	6.5
5		139–141	46	39.4	39.7	6.1	6.0	7.1	7.0
6		145–147	76	37.7	38.1	5.2	5.1	8.0	8.1
7		89–90	83	32.8	31.6	6.7	6.6	8.5	8.1
8		148–149	91	33.2	32.8	5.6	5.3	8.6	8.4
9		111–112	78	34.2	34.3	5.0	4.8	7.2	7.0
10	$(CH_3)_3NBCl_2OCHN(CH_3)_2{}^+PF_6{}^-$ [b]	126–127	99	20.0	20.5	4.5	4.5	7.2	7.8
11	$(CH_3)_3NBH_2OCIN(CH_3)_2{}^+PF_6{}^-$ [b,c]			17.4	17.9	4.1	4.1	6.7	6.9
12	$(CH_3)_3PBH_2OCHN(CH_3)_2{}^+PF_6{}^-$		68	23.5	23.3	5.9	6.0	4.6	5.1
13	$(CH_3)_3PBH_2OC(CH_3)N(CH_3)_2{}^+PF_6{}^-$		82	26.2	26.2	6.3	6.5	4.4	4.9

[a] Based upon product weight before recrystallization. [b] These cations result from substitution reactions of intact borane cations. [c] Boron analysis: calcd, 2.6; found, 2.8.

TABLE II

LABILITY OF AMIDE CATIONS IN AQUEOUS SOLUTION

Compound[a]	Gas evolution[b] in 1 *N* NaOH Cold	Hot
1, $-OC(CH_3)NH_2$	−	+
3, $-OC(C_6H_5)NH_2$	+	+
4, $-OC(C_6H_5)NHC_6H_5$	−	+
5, 	−	−
6, 	δ+	δ+
7, 	−	−
8, 	−	δ+

[a] Hexafluorophosphate salt of cation, numbered as in Table I. Amide from which cation is derived is indicated. [b] Gas observed is designated −, δ+, and + for none, slight, and significant amounts, respectively.

TABLE III

ÇYANIDE-BRIDGED BORANE SPECIES

No.	Compound	Mp, °C	Analyses, % Calcd C	H	N	Found C	H	N
14	$(CH_3)_3NBH_2CNCH_3{}^+PF_6{}^-$	113–115	23.3	5.5	10.8	24.0	5.6	11.0
15	$(CH_3)_3NBH_2CNBH_2N(CH_3)_3{}^+PF_6{}^-$	143–144	27.2	6.8	12.7 (B, 6.7)	26.6	7.0	13.3 (B, 6.8)
16	$(CH_3)_3NBH_2NCBH_2P(CH_3)_3{}^+PF_6{}^-$	88–89	25.4	6.7	8.5	25.5	6.8	8.3
17	$[(CH_3)_3NBH_2NC]_2BH_2{}^+PF_6{}^-$	112–113	27.2	6.8	15.8	27.4	6.7	15.9
18	$(CH_3)_3NBH_2NCBH_3$	126–128	43.0	12.6	25.0	42.6	12.1	24.3

Cyanide-Bridged Cations.—The second class of functionally substituted cations studied was that with cyanide bases. Table III shows the scope of the cations characterized.

Linkage of the cyanide bridges between dissimilar groups was $NBC{\equiv}NCH_3$, $NBN{\equiv}CBH_2$, and $NBN{\equiv}CBH_2$ as determined from infrared and nmr evidence (*vide infra*). It does appear that binding several nitrogen atoms to one boron is a favored linkage. Work by Aftandilian, Miller, and Muetterties[7] showed that amine–BH_2NCBH_3 adducts are linked as designated, and since these adducts result from prolonged action of diborane on amine hydrocyanide salts, there is the possibility that the product is the thermodynamically favored one.

Initially the methyl isocyanide cation $(CH_3)_3NBH_2CNCH_3{}^+$ was sought from reaction of methyl isocyanide and trimethylamine–iodoborane. This cation was isolated along with another cation shown to be $(CH_3)_3NBH_2CNBH_2N(CH_3)_3{}^+$, whose presence was suspected because the crude product had two cyanide infrared absorptions. Separation was effected by recrystallization of the hexafluorophosphate salts. From methylene chloride, the isocyanide cation salt is recovered as least soluble. From hot water, the cyano-bridged bis-borane cation salt is recovered as the only sparingly soluble salt. (The isocyanide cation is hydrolyzed under these conditions.) Possibly the bis-borane cation arises by methyl transfer from the isocyanide cation and subsequent reaction with trimethylamine–iodoborane. Isolation of the tetramethylammonium ion is suggestive that methyl abstraction has occurred. Subsequent independent synthesis of the

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[7] V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **83**, 2471 (1961).

bis-borane cation following the scheme

$$CN^- + B_2H_6 \longrightarrow H_3BCNBH_3^- + I_2 \longrightarrow (IH_2BCNBH_2I)^- + 2N(CH_3)_3 \longrightarrow (CH_3)_3NBH_2CNBH_2N(CH_3)_3^+$$

gave the bis-borane cation, however, in only 7% yield. A water-insoluble by-product (10%) of the reaction was $(CH_3)_3NBH_2NCBH_3$, whose structure was assigned from the boron nmr.

The better hydrolytic stability of this bis-borane cation as compared to the isocyanide cation may result from electron-releasing property of the $BH_2N(CH_3)_3$ group as compared to CH_3. Enhanced electron density at the cyanide carbon in the bis-borane cation would hinder hydroxyl or water attack at this site and could possibly account for its greater stability. This is speculative, however, and more mechanistic data are needed to understand the causes for lability.

A tris-borane cation, $[(CH_3)_3NBH_2NC]_2BH_2^+$, with two cyanide bridges was isolated unexpectedly in attempts to make mixed-base cations of the type $(CH_3)_3NBH_2NCBH_2O(\text{base})^+$. The product after iodination of $(CH_3)_3NBH_2NCBH_3$ and treatment with pyridine *N*-oxide or *N,N*-dimethylformamide yielded this cation on work-up with water. Presence of $(CH_3)_3NBH_2NC$ and $(CH_3)_3NBH_2NCBH_2I$ in the mixture could account for the cation. The synthesis method did result in one mixed-base cation, $(CH_3)_3NBH_2NCBH_2P(CH_3)_3^+$, when trimethylphosphine was used as the second base. Taken together, these observations suggest that the pyridine oxide and DMF cations were prepared but are hydrolytically unstable, producing $(CH_3)_3NBH_2NC$ that could react with $(CH_3)_3NBH_2NCBH_2I$.

This tris-borane cation is only the second such cation known, the other being methylthio bridged.[8] It is formally a borane cation of the isocyanide base $(CH_3)_3NBH_2NC$, which is apparently not as stable as the cyanide isomer $(CH_3)_3NBH_2CN$ preparable from HCN and $(CH_3)_3NBH_3$.[9]

The ^{11}B nmr data, Table IV, are the bases for linkage assignment in $(CH_3)_3NBH_2NCBH_3$ and $(CH_3)_3NBH_2NCBH_2P(CH_3)_3^+$. In both species there is a 1:3:3:1 (approximately) quartet measurably sharper than a downfield 1:2:1 triplet (peak widths at half-height of the quartets were nearly one-third those of the triplets). If the broadness is associated with greater quadrupolar relaxation for boron bonded to nitrogen, linkages with both nitrogen atoms bonded to a single boron may be inferred. A similar argument has been used by Aftandilian, *et al.*,[7] to establish linkage in amine–BH_2NCBH_3 adducts. The chemical shift of the quartet in $(CH_3)_3NBH_2NCBH_3$, 62.6 ppm from external methyl borate, is close to that reported[10] for similarly linked carbon bonded boron in $H_3BCNBH_3^-$, namely, 62.3 ppm. The triplets have essentially the same chemical shift. The quartet-splitting pattern for the phosphorus-bonded boron in $(CH_3)_3NBH_2NCBH_2P(CH_3)_3^+$ no doubt arises because the BH coupling constant is essentially the same as the PB coupling constant. Two boron nmr environments of the tris-borane cation populated 2:1 (with the larger peak downfield where CNB-bonded boron is found) concur with the structure assignment for this ion.

TABLE IV
^{11}B RESONANCES

Compound	Resonance, shift,[a] coupling constant
$(CH_3)_3NBH_2NCBH_2P(CH_3)_3^+PF_6^-$ [b]	1:3:3:1 (approx) q, 57.0 ppm, 100 Hz 1:2:1 (approx) t, 25.6 ppm, 113 Hz
$(CH_3)_3NBH_2NCBH_3$ [b]	1:3:3:1 (approx) q, 62.6 ppm, 95 Hz 1:2:1 (approx) t, 25.8 ppm, 117 Hz
$[(CH_3)_3NBH_2NC]_2BH_2^+PF_6^-$ [c]	Two broad, unresolved peaks, probably triplets, 2:1 ratio, 24.4 and 58.9 ppm, respectively
$(CH_3)_3NBH_2NCBH_2N(CH_3)_3^+PF_6^-$ [c]	Unsymmetrical, unresolved triplet, 25.9, 32.9, and 40.0 ppm

[a] Upfield from external trimethyl borate. [b] Spectra run at 32 MHz. [c] Spectra run at 19.2 MHz.

Proton magnetic resonance data, Table V, support the structure assignments of the cyanide cations even though these data cannot be used to determine linkage sequences. Two methyl resonances, for example, were found for $(CH_3)_3NBH_2NCBH_2N(CH_3)_3^+PF_6^-$ so the difference in magnetic environment arising from linkage to C or N of the cyanide is detectable four atoms away.

TABLE V
PROTON MAGNETIC RESONANCE[a]

Compd[b]	Chem shift, ppm[c]		Peak intens	Coupling constant
1	$(CH_3)_3N$	2.78	3.1	
	$(CH_3)CO$	2.45	1	
2	$(CH_3)_3N$	2.56	12	
	CH_3CO	2.61	5.2	
	C_6H_5	7.56		
3	$(CH_3)_3N$	2.48	9	
	C_6H_5	7.75–8.1	5	
4	$(CH_3)_3N$	2.48		
	C_6H_5	7.5–8.0		
5	$(CH_3)_3N$	2.50	11.3	
	C_2H_5	1.39 t, 4.04 q	2.3/3.3	J_{HCCH} = 7 Hz
	C_6H_4	6.8–7.3	4.3	
	CH_3CO	2.50		
6	$(CH_3)_3N$	2.75	9	
	CH_2CO	4.06	2	
	C_6H_4	7.43	4.1	
7	$(CH_3)_3N$	2.67		
	CH_3N	3.18		
8	$(CH_3)_3N$	2.73	9	
	CH_3N	3.98	3.2	
	C_5H_4N	7.23–8.04	4.1	
9	$(CH_3)_3N$; CH_3CO	2.56	12	
	C_6H_4	7.55	3.9	
11	$(CH_3)_3N$	2.68	2.9	
	$(CH_3)_2NCO$	3.32, 3.43	1/1	
12	$(CH_3)_3P$	1.45[d]	9	J_{PCH} = 11 Hz
	$(CH_3)_2NCO$	3.12, 3.27	2.9/2.9	
	CHO	7.88	1	
13	$(CH_3)_3P$	1.45[d]	3	J_{PCH} = 11 Hz
	$(CH_3)_2NCO$	3.13, 3.27	1/1	
	CH_3CO	2.38	1	
14	$(CH_3)_3N$	2.89	2.9	
	CH_3	2.79	1	
15	$(CH_3)_3NBC$	2.80	1	
	$(CH_3)_3NBN$	2.87	1	
16	$(CH_3)_3N$	2.67	1	
	$(CH_3)_3P$	1.56 d	1	J_{PCH} = 12 Hz
17	$(CH_3)_3N$	2.70		
18	$(CH_3)_3N$	2.67		

[a] Run at machine temperature; A-60A Varian spectrometer; in CH_2Cl_2 solution except **5** and **11** which were run in CD_3CN. [b] Compounds as numbered in Tables I and III. [c] Downfield from internal tetramethylsilane; t = triplet, q = quartet. [d] Multiplet.

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(8) R. J. Rowatt and N. E. Miller, *J. Amer. Chem. Soc.*, **89**, 5509 (1967).

(9) S. S. Uppal and H. C. Kelly, *Chem. Commun.*, 1619 (1970).

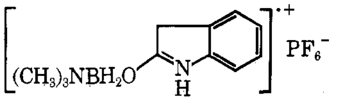
(10) R. C. Wade, E. A. Sullivan, J. R. Berschied, Jr., and K. F. Purcell, *Inorg. Chem.*, **9**, 2146 (1970).

The singlet resonance for $[(CH_3)_3NBH_2NC]_2BH_2{}^+PF_6{}^-$ and $(CH_3)_3NBH_2NCBH_3$ supports the notion of distinct species as opposed to mixtures with isomeric cyanide linkage.

Experimental Section

Solvents used were reagent grade and some were dried before use: chloroform and DMF over phosphorus pentoxide and pentane over sulfuric acid. Amides were commercial grade, used without further purification. Melting points were taken in a Thomas-Hoover capillary apparatus and are uncorrected for emergent stem. Diborane was commercial grade (Callery) stored in a stainless steel cylinder at −78° and used in a vacuum line equipped with Delmar-Urry greaseless valves. The most useful characterization data for the new species were the infrared spectra, and these are summarized in Table VI.

Amide Cations.—For the most part the syntheses of the amide-derived cations were similar. A typical preparation, that for *O*-oxindoletrimethylaminedihydroboron(1+), **6**, is described. A 3.344-g (16.8-mmol) sample of trimethylamine–iodoborane in 10 ml of chloroform was added to a solution of 2.243 g (16.8 mmol) of oxindole in 17 ml of chloroform under nitrogen. The mixture was allowed to stand 1.5 days, and then the solvent was removed under vacuum. The residue was washed twice with 20-ml portions of benzene to yield 5.543 g of dry solid. A 1.823-g portion was dissolved in water, and saturated ammonium hexafluorophosphate was added, whereupon a white $PF_6{}^-$ salt precipitated; the yield was 1.474 g, 76%, after collection and drying. Recrystallization of 1.296 g of this $PF_6{}^-$ salt from 120 ml of 65° water, followed by recrystallization from CH_2Cl_2–hexane, gave 0.426 g of large white crystals, mp 89–90°, of



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Reaction of $(CH_3)_3NBH_2I$ and $ClCON(CH_3)_2$.—To a solution of 14.6 mmol of trimethylamine–iodoborane in 60 ml of chloroform in a 100-ml flask was added 0.94 ml (14.6 mmol) of dimethylcarbamyl chloride *via* a syringe. The mixture was stirred under nitrogen at room temperature for 3 days during which time the color changed from yellow to gold. Removal of solvent under vacuum left a golden yellow solid which changed to a pale yellow color on washing with small quantities of chloroform. The $PF_6{}^-$ salt was prepared by repeated extraction of the product with water at room temperature followed by addition of ammonium hexafluorophosphate to the extract. Recrystallization of the $PF_6{}^-$ salt obtained from 944 mg of iodide salt gave 168 mg of recrystallized $PF_6{}^-$ salt **11** as a fluffy solid. The infrared spectrum showed BH, CO, and PF absorptions at 2450, 1620, and 850 cm^{-1}.

Synthesis of $(CH_3)_3BH_2CNCH_3{}^+$ and $(CH_3)_3NBH_2CNBH_2N(CH_3)_3{}^+$.—A mixture of 1.930 g (9.7 mmol) of trimethylamine-iodoborane in 10 ml of chloroform and 10 mmol of methyl isocyanide (measured as a gas) was prepared by condensation of the latter at −78° into a reaction flask under vacuum. After standing 8 hr at room temperature, the small amount of precipitate which was present was filtered and identified by infrared analysis as the tetramethylammonium salt after metathesis to $PF_6{}^-$. The filtrate was concentrated under vacuum to give 1.874 g of cream-colored solid. A 1.24-g portion of this was metathesized to the $PF_6{}^-$ salt in water; yield 0.884 g. Two cyanide absorptions in the infrared spectrum were evident: a strong band at 2340 cm^{-1} and a weak band at 2280 cm^{-1}. Recrystallization from 50 ml of 80° water gave only 60 mg of solid. After two recrystallization from methylene chloride–hexane, this was identified by analysis, infrared spectra, and nmr to be $(CH_3)_3NBH_2NCNCH_3{}^+PF_6{}^-$. Only the 2280-$cm^{-1}$ band was now present in the CN region.

The remainder, 630 mg, of the cream-colored iodide salt was converted to the $PF_6{}^-$ salt in water; yield 445 mg. Recrystallization from methylene chloride–pentane gave 322 mg of white solid, mp 113–115°, identified as $(CH_3)_3NBH_2NCBH_2N(CH_3)_3{}^+PF_6{}^-$ by analytical and spectral data. Thus the crude iodide product from the reaction is roughly three-fourths the bis-borane cation and one-fourth isocyanide cation.

TABLE VI
INFRARED SPECTRA[a]

Compd[b]	Absorption,[c] cm^{-1}
1	3460 m, 3375 m, 3315 w, 2425 m, 2390 w, 2325 w, 1675 s, 1575 m, 1490 m, 1415 w, 1255 w, 1205 w, 1175 s, 1130 w, 1035 w, 990 m, 850 s, b
2	3365 s, 3025 w, 2470 s, d, 2380 w, 2340 w, 1625 s, b, 1600 m, 1575 s, 1480 m, 1350 w, 1315 w, 1255 m, 1200 m, 1175 s, 1135 w, 1115 w, 1080 w, 1035 m, d, 890 m, 930 w, 850 s, b, 785 m, 765 m, 700 w
3	3450 m, 3375 m, 3305 w, 3270 w, 3040 w, 2435 m, 2380 w, 2325 w, 1665 s, 1605 m, 1545 s, 1480 m, 1415 w, 1310 w, 1270 w, 1190 w, 1170 s, b, 1115 w, 995 m, 850 s, b, 690 m
4	3330 m, 2475 m, d, 2380 w, 2340 w, 1610 m, 1585 m, 1570 s, 1550 s, 1485 m, 1350 w, 1315 w, 1250 w, 1200 w, 1175 s, 1140 m, 1115 w, 1085 w, 1040 w, 1015 w, 995 w, 930 w, 850 s, b, 780 m
5	3340 s, 3290 w, 3015 w, 2450 m, d, 2390 w, 2340 w, 1625 s, b, 1585 s, 1570 w, 1510 s, 1485 m, 1425 w, 1350 w, 1310 w, 1280 m, 1250 s, 1225 w, 1200 w, 1175 s, 1125 w, 1115 w, 1040 s, 1020 w, 1015 w, 990 m, 950 w, 925 w, 850 s, b, 740 m
6	3340 m, 2450 m, 2325 w, 1655 s, b, 1480 s, 1260 w, 1200 w, 1165 s, 1120 w, 1110 w, 1000 m, 850 s, b, 770 s
7	2425 m, 2390 w, 2330 w, 1650 s, d, 1485 s, 1415 m, 1345 w, 1325 w, 1290 w, 1255 m, 1200 m, 1175 s, 1130 w, 1115 w, 990 m, 960 m, 850 s, b, 750 w
8	2440 m, 2400 w, 2340 w, 1645 s, 1585 s, 1530 s, 1485 m, 1420 w, 1320 m, 1290 w, 1255 w, 1210 m, 1165 s, d, 1120 m, 1075 w, 1040 w, 1020 w, 990 m, 950 m, 850 s, b, 760 m
9	3350 m, 2450 w, d, 1625 m, b, 1580 w, 1485 s, 1415 w, 1340 w, 1255 w, 1200 w, 1170 s, 1115 w, 1100 w, 1050 w, 1020 w, 990 w, 850 s, b
10	1700 s, b, 1480 m, 1415 w, 1325 s, 1250 w, 1230 w, 1125 w, 1065 m, 980 s, 950 m, 850 s, b
11	2450 m, b, 2375 w, 1620 s, 1485 w, 1425 m, 1250 m, 1200 m, 1155 s, 1120 m, 1050 w, 1015 w, 990 w, 980 w, 920 w, 850 s, b
12	2425 m, d, 2350 w, 1700 s, b, 1430 s, 1345 s, 1300 m, 1205 w, 1160 m, 1105 s, 1065 w, 1010 w, 960 m, 910 m, 850 s, b, 770 w
13	2405 m, d, 1640 s, 1490 m, 1435 m, 1405 m, 1320 w, 1300 w, 1265 w, 1180 m, 1090 m, 1020 w, 970 s, 850 s, b, 765 w
14	2480 m, 2460 w, 2340 m, 1485 m, 1420 w, 1250 w, 1140 m, 1105 m, 1020 w, 975 w, 965 w, 880 s, 850 s, b
15	2450 m, b, 2280 m, 1485 m, 1410 w, 1250 m, 1180 w, 1160 m, 1140 s, 1100 m, 1015 w, 980 m, 960 w, 885 m, 850 s, b
16	2480 m, 2445 m, 2290 s, 1490 w, 1435 w, 1420 w, 1310 m, 1255 w, 1190 w, 1160 s, 1120 m, 975 s, 850 s, b
17	2500 m, 2460 m, 2300 s, 1490 m, 1415 w, 1250 w, 1190 w, 1155 s, 1115 m, 1100 m, 1080 s, 980 m, 880 s, 850 s, b
18	2455 s, 2370 s, 2255 s, 1475 m, 1415 w, 1255 m, 1185 m, 1165 m, 1130 m, 1120 s, 1110 m, 1025 w, 985 s, 870 s, 835 m, 725 m

[a] Run as mineral oil mulls on a PE 237B grating spectrophotometer or a Beckman IR-12. [b] As numbered in Tables I and III. [c] Absorptions in common with or masked by mineral oil not tabulated. Abbreviations: s, strong; m, moderate; w, weak; b, broad; d, doublet.

Structure proof of the bis-borane cation was attempted by independent synthesis from $Na^+H_3BCNBH_3{}^-$. Dry sodium cyanide, 617 mg (12.6 mmol), in 15 ml of 1,2-dimethoxyethane was allowed to absorb 12.9 mmol of diborane at −20° and the resulting solution was kept at room temperature 1 hr. Pentane was added to cause precipitation of the $Na^+H_3BCNBH_3{}^-$. Filtration of this solid proved difficult, so all the volatile material was removed and the remaining tacky solid was put into 20 ml of chloroform and treated with 2.913 g (11.4 mmol) of iodine in 20 ml of chloroform, slowly. Hydrogen was evolved during the addition. After 8 hr at room temperature, the mixture was cooled (−190°), evacuated, and warmed to −78° and 23 mmol (measured as a gas) of trimethylamine was added. The mixture was stirred for 1 day, the solid (NaI) was separated by filtration, and the filtrate was concentrated to a pale yellow solid residue under vacuum. Extraction of this with water and metathesis of the solution with ammonium hexafluorophosphate gave 249 mg (7%) of solid whose melting point (143–144°) and spectral data matched those of material designated as $(CH_3)_3NBH_2CNBH_2N(CH_3)_3^+$ prepared from methyl isocyanide and trimethylamine–iodoborane. The water-insoluble product, 156 mg, was recrystallized from methylene chloride–pentane and identified as $(CH_3)_3NBH_2NCBH_3$ by elemental analyses and spectral data; yield 123 mg, mp 126–128°.

Syntheses of $[(CH_3)_3NBH_2NC]_2BH_2^+PF_6^-$ and $(CH_3)_3NBH_2NCBH_2P(CH_3)_3^+PF_6^-$.—Iodine, 587 mg, in 20 ml of chloroform was added to 516 mg (4.6 mmol) of $(CH_3)_3NBH_2NCBH_3$ in 5 ml of chloroform. Only a very slow discoloration was noticed. After stirring overnight a yellow solid was present in a brownish solution. To this was added 0.6 g of pyridine *N*-oxide in 3 ml of chloroform. Some lightening of the coloration was noticed, but the mixture was still cloudy yellow after 3 days of stirring. A small amount of insoluble material was filtered. The filtrate was evaporated under vacuum and the resulting residue was treated with 20 ml of water which dissolved all but a trace. Metathesis to the hexafluorophosphate salt gave 488 mg of solid later identified as the first title compound by analytical and spectral data. A similar experiment using DMF instead of pyridine oxide gave the same product. When *N*,*N*-dimethylacetamide or pyridine was employed, no PF_6^- salt was isolated. When trimethylphosphine was used as the second base, 64% of the salt $(CH_3)_3NBH_2NCBH_2P(CH_3)_3^+PF_6^-$ was obtained.

Chlorination of $(CH_3)_3NBH_2OCHN(CH_3)_2^+PF_6^-$.—A 313-mg sample of $(CH_3)_3NBH_2OCHN(CH_3)_2^+PF_6^-$ in 5 ml of methylene chloride was treated with chlorine by passing gas into solution for 0.5 hr, resulting in a slurry of a white solid suspended in a yellow liquid. Volatiles were removed under vacuum (at first with water aspirator vacuum) to leave 386 mg (99%), mp 126–127°, of white reflective crystals of $(CH_3)_3NBCl_2OCHN(CH_3)_2^+PF_6^-$ identified by spectral data and analyses.

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Carborane Formation in Alkyne–Borane Gas-Phase Systems. V.[1] Conversion of Two-Carbon to Four-Carbon Carboranes *via* Alkyne Insertion. Nuclear Magnetic Resonance Studies of Tetracarba-*nido*-hexaboranes

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The reaction of the square-pyramidal carborane 1,2-$C_2B_3H_7$ with acetylene yields one volatile product, 2,3,4,5-$C_4B_2H_6$, a carborane of pentagonal-pyramidal geometry. The process occurs as a straightforward alkyne insertion into the carborane cage, as shown by the use of deuterium- or carbon-13-labeled acetylene. The reaction of 1,2-$C_2B_3H_7$ with methylacetylene produces 3-$CH_3C_4B_2H_5$ and a lesser quantity of 2-$CH_3C_4B_2H_5$, while the reaction with dimethylacetylene generates predominantly 2,3-$(CH_3)_2C_4B_2H_4$ with a smaller amount of 3,4-$(CH_3)_2C_4B_2H_4$. The results indicate that alkyne insertion into $C_2B_3H_7$ occurs primarily at C–B bonds without C–C cleavage but that insertion into the carborane C–C bond also occurs to a significant extent. The proton and boron-11 nmr spectra of the $C_4B_2H_6$ derivatives are correlated with structural features, and the spectra of the parent compound are interpreted.

The synthesis of volatile carboranes in reactions of boranes with alkynes has been described in many previous reports.[2] Of the carboranes produced in such reactions, those having two framework carbon atoms are overwhelmingly predominant, although one- and three-carbon species have been isolated in some cases. A logical extension of these syntheses would be the insertion of acetylene into a two-carbon carborane to generate a four-carbon system, but such reactions have been unknown prior to the present work. However, the new compound 1,2-dicarbapentaborane(7), 1,2-$C_2B_3H_7$,[3] has been found to react with acetylene under mild conditions (50°) to yield 2,3,4,5-tetracarbahexaborane(6), $C_4B_2H_6$ (Figure 1).[4] This latter molecule, the only known four-carbon carborane system, was previously characterized as a peralkylated derivative by Binger[5] and has recently been isolated in parent form by Onak and Wong[6] from the 550° pyrolysis of tetramethylenediborane. Since the formation of $C_4B_2H_6$ from $C_2B_3H_7$ and C_2H_2 implied a simple alkyne–carborane insertion, our interest in the mechanism of this process has stimulated further studies involving labeled acetylenes and higher alkynes.

Results

Reaction of $C_2B_3H_7$ with $^{13}C_2H_2$ and C_2D_2.—As reported elsewhere,[4] the gas-phase reaction of $C_2B_3H_7$ with C_2H_2 at 50° yields a white nonvolatile solid and a single volatile product, $C_4B_2H_6$. The ^{11}B and ^1H nmr spectra of this material establish that only the 2,3,4,5 isomer, containing four basal carbons in a pentagonal-pyramidal cage, is present. The apparent insertion of a C_2H_2 unit has been confirmed by allowing ^{13}C-enriched acetylene to react with normal $C_2B_3H_7$. The mass spectrum of the $C_4B_2H_6$ product establishes

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[1] Part IV: D. A. Franz and R. N. Grimes, *J. Amer. Chem. Soc.*, **93**, 387 (1971).

[2] Recent reviews: R. E. Williams, *Progr. Boron Chem.*, **2**, 37 (1970); R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970.

[3] D. A. Franz and R. N. Grimes, *J. Amer. Chem. Soc.*, **92**, 1438 (1970).

[4] D. A. Franz, V. R. Miller, and R. N. Grimes, *ibid.*, **94**, 412 (1972).

[5] P. Binger, *Tetrahedron Lett.*, 2675 (1966).

[6] T. P. Onak and G. T. F. Wong, *J. Amer. Chem. Soc.*, **92**, 5226 (1970).