formal analogy here to the situation that prevails for the nonrigid pyramidal molecules that exhibit a wide range of barriers to pyramidal inversion:[57] the barriers are generally very sensitive to the pyramidal XMX angles.

Acknowledgment. We are indebted to Mr. L. Lardear who constructed the precision molecular models.

(57) See review by A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9**, 400 (1970).

Negative Ion Mass Spectra of Nido Carboranes

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Abstract: The negative ion mass spectra of 2,3-dicarbahexaborane(8), 2-methyl-*nido*-2,3-dicarbahexaborane(8), and 2,3-dimethyl-*nido*-2,3-dicarbahexaborane(8) have been investigated. Evidence has been found to show that formation of negative ions in these nido carboranes occurs predominantly *via* resonance capture and dissociative resonance capture mechanisms. With the aid of deuterium labeling experiments, a diagnostic fragmentation giving a $P - 1$ anion which is specific for loss of a bridge hydrogen has been found. Discrete and narrow electron energy ranges for electron capture have been determined and the electron energy dependence on ion intensities and fragmentations in the lower voltage regions have been studied.

In organoboron chemistry where a wide variety of stable anions and anionic intermediates have been known for years, it is remarkable that so few of these negative ions have been studied in the gas phase. The few reported studies have been mainly on boron hydrides.[2–6] In contrast, there have been numerous positive ion gas mass spectral studies of organoboron compounds, including carboranes.[5] Yet, the postulation of stable cations and cationic intermediates in organoboron chemistry, especially carborane chemistry, is extremely rare. For this reason, there are severe limitations on the potential for direct correlation between the positive ions produced in a mass spectrometer and the chemistry of carboranes or any other type of compounds where anions and anionic intermediates predominate. The study of these gas-phase anions with a mass spectrometer and the application of this technique hopefully will provide additional information on the well-known anionic intermediates in the chemistry of carboranes.

Experimental Section

All mass spectra were run on a Hitachi RMU-6E mass spectrometer in the negative mode at source temperatures ranging between 80 and 100°. The low voltage spectra were run with a repeller voltage of zero, filament emission range between 10 and 25 μA, and a trap current of approximately zero. The accelerating voltage used was either 1.8 or 3.6 kV and the electron multiplier voltage was 1.5 kV. Sample pressures ranged between 1 and 5×10^{-6} Torr, in the ion source. The electron energy was calibrated using literature values for the *m/e* 16 peak (O^-) maxima from CO_2 (4.4; 8.2 eV), CO (10.1 eV), N_2O (2.2 eV), and NO (8.15 eV).[7] No peaks are reported whose calculated relative monoisotopic intensity is $<0.1\%$ of the base peak. For each reported spectrum, a check was made for peaks higher than the parent ion. There were no other indications of ion-molecule reactions, such as nonlinear ion intensity variations with sample pressures.

The syntheses of **1**, **2**, **3** and the deuterium-labeled derivatives of **1** have all been reported.[8] The purity of all compounds was checked by infrared analysis on either a Beckman IR-5 or a Perkin-Elmer 137 spectrophotometer and by positive ion mass spectrometry. The highest mass checked for impurities was usually twice the mass of the parent ion. When needed, purification was effected by one of two methods: gas chromatography (a 30% Kel-F on firebrick column operating at about 60° was used) or a cold column distillation. Handling of chemicals was carried out using conventional high-vacuum apparatus.

Results and Discussion

$C_2B_4H_8$ (1). In a previous communication[9] we reported a portion of the mass spectra of 2,3-dicarbahexaborane (8) (1) at 70 and 8 eV. The major gas-phase anions produced in these spectra were shown to be *m/e* 75 ($C_2B_4H_7^-$), *m/e* 73 ($C_2B_4H_5^-$), and *m/e* 61 ($C_2B_3H_4^-$). The latter two ions have been correlated with the photochemical and thermal reaction products of $C_2B_4H_8$.[9] We have continued our study of $C_2B_4H_8$ by investigating the relationship of the energy of the bombarding electrons and intensities of these three major fragment ions. This type of information is particularly important in this case for three main reasons. (1) In contrast to positive ion mass spectrometry, there is a tremendous variation in ion intensity with electron energy in the low-voltage region (<15 eV). (2) The major ions are all characterized by narrow and intense low-voltage ion current maxima over narrow energy ranges. These low-voltage maxima rep-

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(1) Partial support for C. L. B. came from the Cal Tech President's Fund and NASA Contract No. NAS. 7-100.

(2) D. F. Munro, J. E. Ahnell, and W. S. Koski, *J. Phys. Chem.*, **72**, 2682 (1968).

(3) R. E. Enrione and R. Rosen, *Inorg. Chim. Acta*, **1**, 1169 (1967).

(4) R. M. Reese, V. H. Dibeler, and F. L. Mohler, *J. Res. Nat. Bur. Stand.*, **57**, 367 (1956).

(5) For a review and primary references, see J. F. Ditter, F. J. Gerlart, and R. E. Williams, *Advan. in Chem. Ser.*, No. **72**, 191 (1969).

(6) R. C. Dunbar, *J. Amer. Chem. Soc.*, **93**, 4167 (1971).

(7) L. G. Christophorou and R. N. Compton, *Health Phys.*, **13**, 1277 (1967).

(8) (a) T. P. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964); (b) T. Onak and G. B. Dunks, *ibid.*, **5**, 439 (1966); (c) J. R. Spielman, R. Warren, G. B. Dunks, J. E. Scott, Jr., and T. Onak, *ibid.*, **7**, 216 (1968).

(9) C. L. Brown, K. P. Gross, and T. P. Onak, *Chem. Commun.*, 78 (1972).

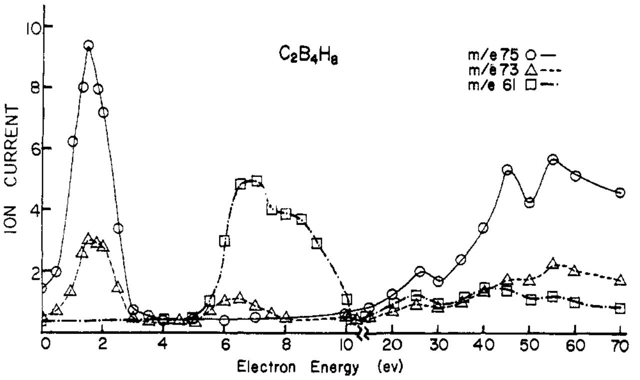
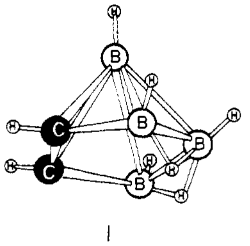


Figure 1. The ionization efficiency curves for the major fragment ions in $C_2B_4H_8$.



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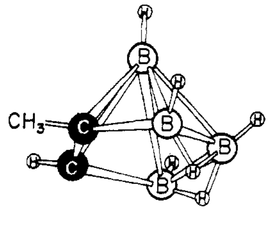

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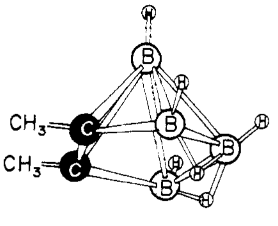

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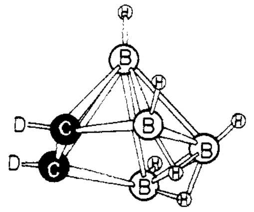

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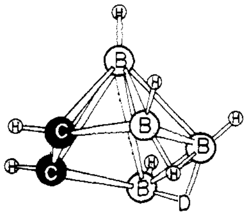

5

resent much more intense ion currents than those which are observed at the conventional operating voltage for positive ions (70 eV). (3) The specific mechanism[10] of formation of the anion can often be inferred from this type of study.

The electron energy dependences for the intensities of the three major ions in the negative ion mass spectra of $C_2B_4H_8$ are shown in Figure 1. The ionization efficiency curve (IEC) for the P − 1 anion ($C_2B_4H_7^-$, *m/e* 75) has a very narrow and intense energy maximum at 1.5 eV. This energy maximum indicates that $C_2B_4H_7^-$ is produced *via* a dissociative resonance capture process.[10] Thus, this dissociative capture process at only 1.5 eV gives rise to a P − 1 ion current which is quite intense, relative to intensities observed at other voltages up to 70 eV. The genesis of this ion will be discussed later.

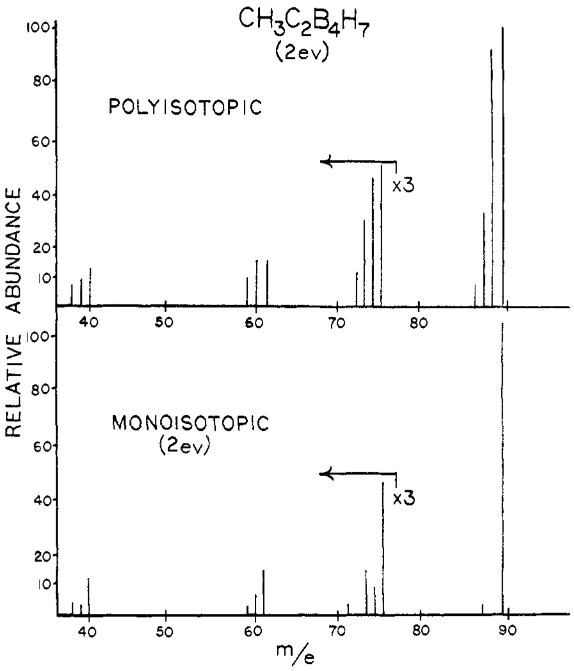

Figure 2. The 2-eV mono- and polyisotopic negative ion mass spectra of $CH_3C_2B_4H_7$. (In the calculation of the monoisotopic spectrum two boron atoms were used for the *m/e* 40 region and three for the *m/e* 61 and 75 regions.)

In the ionization curve for the *m/e* 73 ion ($C_2B_4H_5^-$) which presumably may be formed by the loss of H_2 from $C_2B_4H_7^-$, a dissociative resonance capture process is still evident by the less intense maximum at 1.5 eV (Figure 1).

The ionization efficiency curve for the *m/e* 61 ion ($C_2B_3H_4^-$), however, does not show an energy maximum at 1.5 eV (Figure 1) but rather has a maximum at 6.5 eV with a shoulder around 8 eV. In this case, the greater degree of fragmentation (loss of $BH_3 + H\cdot$ from $C_2B_4H_8$ or BH_3 from $C_2B_4H_7^-$) is a higher energy process than the previously discussed processes where H or H_2 is eliminated to form the *m/e* 75 and 73 ions. Thus, when the negative ion mass spectrum was run at any voltage in the range of 6 to 9.5 eV, the *m/e* 61 ion was found to be the base peak.

These data further show rather vividly that if the negative ion spectrum of this carborane were run only at 70 eV (as is usually the case in positive ion mass spectrometry) a great deal of information, as well as sensitivity, would have been lost.

$CH_3C_2B_4H_7$ (2). The 2-eV polyisotopic and the calculated monoisotopic spectra of $CH_3C_2B_4H_7$ (2-methyl-*nido*-2,3-dicarbahexaborane(8)) are shown in Figure 2. These spectra show clusters of ions separated by approximately 14 mass units (BH_3 unit). This general type of fragmentation pattern was found to be characteristic for the negative ion spectra of the carboranes at all voltages used to obtain spectra. From a comparison of the two spectra in Figure 2, it can be seen that the polyisotopic spectrum containing both ^{10}B and ^{11}B contributions to the relative abundance is very difficult to interpret unless the ^{10}B contributions are

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[10] There are three basic known mechanisms for the production of negative ions in the mass spectrometer: (1) resonance capture, (2) dissociative resonance capture, and (3) ion-pair formation. For a review of the criteria for these three mechanisms, see C. E. Melton, "Principles of Mass Spectrometry," Marcel Dekker, New York, N. Y., 1970.

Table I. Calculated Monoisotopic ^{11}B Negative Ion Mass Spectra of $CH_3C_2B_4H_7$[a]

m/e	Formula (neg ion)	70 eV	10 eV	2 eV	m/e	Formula (neg ion)	70 eV	10 eV	2 eV
90	$C_3B_4H_{10}$	1.1	0.4		49	C_3BH_2	1.8	24.9	
89	$C_3B_4H_9$	*100*	4.7	*100*		$C_2B_2H_3$	0.9	24.8	
88	$C_3B_4H_8$		1.1			CB_3H_4	0.1	23.5	
87	$C_3B_4H_7$		2.7	2.6	48	C_3BH		10.7	
86	$C_3B_4H_6$	3.2	0.2			$C_2B_2H_2$		4.6	
85	$C_3B_4H_5$		0.8			CB_3H_3			
83	$C_3B_4H_3$		0.3		47	C_3B		3.9	
75	$C_3B_3H_6$	16.4	88.9	16.3		C_2B_2H		2.7	
	$C_2B_4H_7$	16.4	—	16.3		CB_3H_2		2.2	
74	$C_3B_3H_5$	5.9		3.4	46	C_2B_2		2.7	
	$C_2B_4H_6$	1.9	—			CB_3H		2.3	
73	$C_3B_3H_4$	0.6	20.2	4.4	40	C_3H_4			4.3
	$C_2B_4H_5$	0.1	—	4.0		C_2BH_5			4.3
72	$C_3B_3H_3$	2.9				CB_2H_6			4.3
	$C_2B_4H_4$	2.9	—		39	C_3H_3		13.2	3.2
71	$C_3B_3H_2$		2.2	0.6		C_2BH_4		13.2	2.1
	$C_2B_4H_3$		—			CB_2H_5		13.2	1.0
64	$C_3B_2H_6$		0.7		38	C_3H_2	4.3	7.1	2.0
	$C_2B_3H_7$		0.7			C_2BH_3	4.3	3.7	1.4
	CB_4H_8		—			CB_2H_4	4.3	0.4	1.1
63	$C_3B_2H_5$	2.7	11.6		37	C_3H	2.2	20.9	
	$C_2B_3H_6$	2.7	11.5			C_2BH_2	1.1	20.0	
	CB_4H_7	—	—			CB_2H_3		19.9	
62	$C_3B_2H_4$	0.8	6.3		36	C_3	6.8	15.5	
	$C_2B_3H_5$	0.1	3.5			C_2BH	6.5	10.5	
	CB_4H_6	—	—			CB_2H_2	6.5	5.5	
61	$C_3B_2H_3$	14.3	*100*	4.7	35	C_2B	0.5	2.5	
	$C_2B_3H_4$	13.6	*100*	4.7		CB_2H		1.0	
	CB_4H_5	—	—	4.7	34	CB_2	0.9	0.5	
60	$C_3B_2H_2$	3.4	24.9	3.0	28	C_2H_4	3.8		
	$C_2B_3H_3$	0.4		1.8		CBH_5	3.8		
	CB_4H_4	—	—	0.6		B_2H_6	3.8		
59	C_3B_2H	2.9	21.2	0.9	27	C_2H_3	2.2	6.6	
	$C_2B_3H_2$	2.8	21.2	0.5		CBH_4	1.3	6.6	
	CB_4H_3	—	—	0.4		B_2H_5	0.3	—	
58	C_3B_2	2.4	4.0		26	C_2H_2	10.5	4.8	
	C_2B_3H	1.7				CBH_3	10.2	3.1	
	CB_4H_2	—	—			B_2H_4	10.1	—	
57	C_2B_3		0.1		25	C_2H	4.5	9.4	
	CB_4H		—			CBH_2	1.9	8.5	
53	C_3BH_6		2.2			B_2H_3			
	$C_2B_2H_7$		2.2		24	C_2	1.5	1.9	
	CB_3H_8		2.2			CBH	0.5		
52	C_3BH_5	1.5	0.8			B_2H_2	0.8	—	
	$C_2B_2H_6$	1.5	0.2		15	CH_3		2.9	
	CB_3H_7	1.5				BH_4		2.9	
51	C_3BH_4	0.9	10.8		14	CH_2		1.0	
	$C_2B_2H_5$	0.6	10.8			BH_3		0.3	
	CB_3H_6	0.2	10.6						
50	C_3BH_3	3.8	2.6						
	$C_2B_2H_4$	3.5							
	CB_3H_5	3.4							

[a] No peaks are reported whose calculated monoisotopic relative intensity is <0.1% of the base peak.

removed. However, to do so, a particular formula (*i.e.*, carbon:boron ratio) must be assumed for each cluster of ions and there are several possibilities for some of the clusters.

Therefore the monoisotopic ^{11}B spectra have been calculated from the polyisotopic $^{10}B:^{11}B$ spectra using all possible isomers for each mass and an abundance ratio of $^{11}B:^{10}B = 80:20$.[5] These data are given in Table I. The dash marks (—) in Table I represent those formulas giving negative residues in the ^{10}B stripping calculation and may be disregarded. An alternative to the stripping procedure would be to use only monoisotopically labeled compounds.

Analogous to the previously discussed spectra of $C_2B_4H_8$, the data in Table I further demonstrate the large variation in relative ion abundance with the electron energy. For example, the P − 1 anion (*m/e* 89) is the base peak in both the 20- and 2-eV spectra; however, it represents only about 5% of the base peak at 10 eV. The predominating mechanism at 70 eV for negative ion formation is "ion-pair" formation.[10] This is illustrated by eq 1. A resonance capture process

$$CH_3C_2B_4H_7 + e^- \longrightarrow [CH_3C_2B_4H_6]^- + H^+ + e^- \tag{1}$$

(eq 2) predominates at 2 eV. Interestingly, at either

$$CH_3C_2B_4H_7 + e^- \longrightarrow [CH_3C_2B_4H_7]^- \longrightarrow [CH_3C_2B_4H_6]^- + H\cdot \tag{2}$$

voltage, the P − 1 anion ($CH_3C_2B_4H_6^-$) is the base peak. However, the preferred mechanism for production of this ion is by dissociative resonance capture at 1.2 eV. This is clearly seen in the IEC where at the

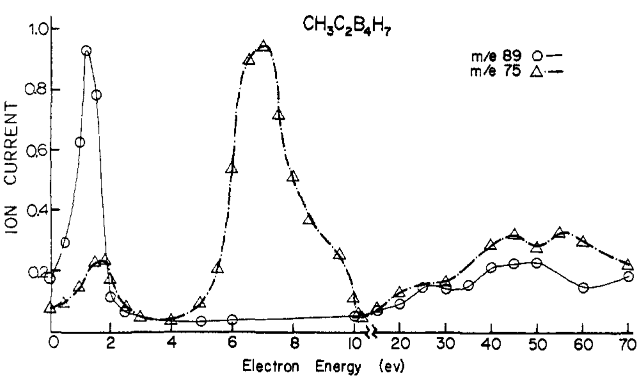

Figure 3. The ionization efficiency curves for the major fragment ions of $CH_3C_2B_4H_7$.

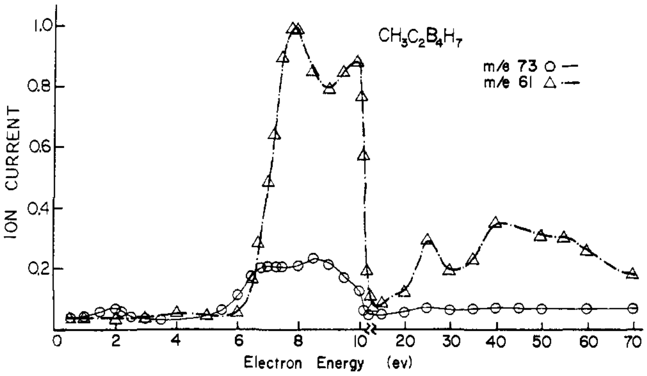

Figure 4. The ionization efficiency curves for the *m/e* 73 and 61 ions in $CH_3C_2B_4H_7$.

1.2-eV maximum the ion current is much greater (~ a a factor of 5) than at 70 eV (see Figure 3).

The *m/e* 75 and 61 ions are both major ions in the negative ion mass spectra of $CH_3C_2B_4H_7$ and could possibly originate *via* a sequential elimination of two BH_3 molecules to give $C_3B_3H_6^-$ and $C_3B_2H_3^-$, respectively, as shown below. Without high resolution data it is not possible to rule out the alternate formulas, $C_2B_4H_7^-$ and $C_2B_3H_4^-$, for the *m/e* 75 and 61 ions, respectively. The formation of these two ions does not, however, seem as probable as the proposed elimination of BH_3 shown below.[11]

The loss of BH_3 has been shown to be a major mode of fragmentation in some positive ion mass spectra studies of carboranes.[5] The IE curves for the *m/e* 75 ion (Figure 3) and the *m/e* 61 ion (Figure 4) both show large energy maxima in the 6–9 eV range. This also would seem to rule out the probability of an ion-pair mechanism being important in the formation of these two ions and again indicates dissociative resonance capture processes as the dominant mechanisms.[10] Indeed, the similar energy ranges of the two maxima may lend further support for the *m/e* 89 ion as the likely precursor to both of these ions (*m/e* 75, 61) as proposed in eq 3. The IEC for the much less abundant *m/e* 73 ion (Figure 4) shows a small maximum in the same energy range as the *m/e* 75 and 61 ions. This ion (*m/e* 73) could likely be formed by the loss of H_2 from the *m/e* 75 ion (see eq 3). No metastable peaks were observed for any of the proposed fragmentation processes discussed above.

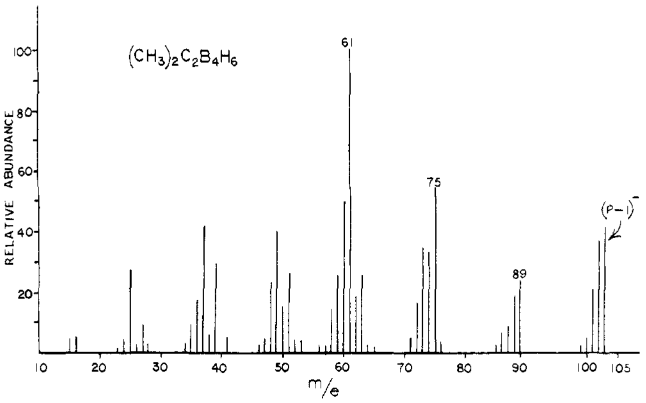

Figure 5. The polyisotopic 10-eV spectrum of $(CH_3)_2C_2B_4H_6$.

$$\begin{tikzcd}
CH_3C_2B_4H_7 \arrow[d, "+e^-"] & & \\
{[CH_3C_2B_4H_7]^-} \arrow[r, "-{[BH_3 + H\cdot]}"] \arrow[d, "-H\cdot"] & \begin{array}{c} C_3B_3H_6^- \\ m/e\ 75 \end{array} \arrow[r, "-H_2"] \arrow[d, "-BH_3"] & \begin{array}{c} C_3B_3H_4^- \\ m/e\ 73 \end{array} \quad (3) \\
\begin{array}{c} CH_3C_2B_4H_6^- \\ m/e\ 89 \end{array} \arrow[ur, "-BH_3"] & \begin{array}{c} C_3B_2H_3^- \\ m/e\ 61 \end{array} &
\end{tikzcd}$$

There are also relatively abundant ions (>20% of base) at *m/e* 60, 59, 49, and 37 in the 10-eV spectrum of $CH_3C_2B_4H_7$ (Table I). In contrast to the ions mentioned above, none of these anions corresponds to the conjugate base of any known carborane systems or previously known relatively stable anions.

$(CH_3)_2C_2B_4H_6$ (3). The polyisotopic negative ion mass spectrum of $(CH_3)_2C_2B_4H_6$ at 10 eV is shown in Figure 5. In contrast to the parent compound ($C_2B_4H_8$) there are many more alternative formulas for most of the fragment ions in the spectrum of $(CH_3)_2C_2B_4H_6$. Since the calculated monoisotopic relative percentages will vary depending on the particular fragment formula used (*i.e.*, the number of boron atoms present), only the polyisotopic spectrum is given (see Figure 5). From this spectrum it is possible to calculate the monoisotopic relative intensities of the fragment ions in a given cluster assuming any number of boron atoms. We have calculated the monoisotopic ^{11}B ion relative intensities using almost all of the possible isomers of each mass; however, for brevity, only those discussed will be presented.

The 10-eV negative ion spectrum $(CH_3)_2C_2B_4H_6$ is quite similar in appearance to the spectra of the previously discussed parent and monomethyl derivative. There are major ions in each cluster at roughly 14 mass unit intervals in the higher mass region of the spectrum (103 → 89 → 75 → 61). Without high resolution data, it is not possible to determine whether these fragmentations represent the successive elimination of BH_3 units as previously mentioned for $CH_3C_2B_4H_7$ or whether these intervals are due in some cases to methyl group eliminations. Similar to $C_2B_4H_8$ and $CH_3C_2B_4H_7$, the base peak in the 10-eV spectrum is at *m/e* 61. Further analogies are found in the 70-eV spectrum (Table II). The base peak in the 70-eV spectrum is the P − 1 ion (*m/e* 103), and there is a relatively abundant P − 2 ion at *m/e* 102 (see Table II).

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(11) A large negative residue was obtained when $C_2B_4H_7$ was used in the ^{10}B stripping calculation in the 10-eV spectrum thus shedding some doubt on the possibility that $C_2B_4H_7^-$ is the ion composition for the *m/e* 75 ion.

Table II. Major Ions in the Calculated Monoisotopic ^{11}B Negative Ion Spectrum of $(CH_3)_2C_2B_4H_6$ at 70 eV[a]

m/e	Formula	Rel intensities
104	$(CH_3)_2C_2B_4H_6^-$	7.6%
103	$(CH_3)_2C_2B_4H_5^-$	100
102	$(CH_3)_2C_2B_4H_4^-$	16
78[b]	$C_4B_2H_8^-$	17
64[b]	$C_2B_3H_7^-$	71
63	$C_2B_3H_6^-$	15

[a] Only fragment ions >10% of base peak are shown. [b] The formulas shown were used in the calculation of the monoisotopic relative intensities. Alternative possible formulas fo the *m/e* 78 and 64 ions are $C_3B_9H_9$, $C_2B_4H_{10}$, and C_4BH_5, respectively.

The ionization efficiency curve for the P − 1 ion (*m/e* 103) and *m/e* 61 are shown in Figure 6. Analogous to $CH_3C_2B_4H_7$, the intense energy maximum for the P − 1 anion is at 1.2 eV. This indicates that the highly favorable low-energy P − 1 ionization does not represent the loss of a hydrogen atom from a carbon atom.

The ionization efficiency curve for the *m/e* 61 ion (Figure 6) is almost identical with those for the *m/e* 61 ions in $C_2B_4H_8$ and $CH_3C_2B_4H_7$. However, the *m/e* 61 ion maximum in $(CH_3)_2C_2B_4H_6$ is much less intense relative to the P − 1 ion than in $C_2B_4H_8$ and $CH_3C_2B_4H_7$. Whether or not the *m/e* 61 ion has the same composition in all three compounds is open to speculation. If so, then the stronger carbon–carbon bonds are being broken and the methyl groups are being eliminated. If not, the IE curves show that the energy requirements and mechanisms of formation for the three different ions at *m/e* 61 from the three compounds are basically the same.

P − 1 Anion. The P − 1 anion was the base peak at 70 eV in all three of the nido carboranes studied. And as previously discussed the ionization efficiency curves for the P − 1 ion all showed intense maxima in the 1.2–1.5-eV range. Two deuterium labeled derivatives of $C_2B_4H_8$ (**4** and **5**) were prepared[8] in an effort to determine if a bridged or terminal hydrogen atom was being eliminated to form the P − 1 anion. Table III shows the normalized 70-eV monoisotopic relative intensities for the P − 1 and P − 2 ions in compounds **1**, **4**, and **5**. A comparison of the relative intensities of **1** and **4** indicated that essentially no deuterium (<5%) is being lost to form the P − D ion. However, a comparison of the labeled bridged compound (**5**) and **1** shows an approximately equal P − H and P − D fragmentation. These data in Table III strongly indicate that in the P − 1 fragmentation of $C_2B_4H_8$, the hydrogen atom being eliminated is one of the bridged hydrogen atoms and does not come from the carbon atoms. A comparison of the 1.5-eV data for compounds **1**, **4**, and **5** further substantiated this conclusion by giving the same results, within experimental error as shown in Table III. In addition, the closo carboranes we have investigated show no P − 1 maxima in the 1–2-eV range.[12] Thus, the P − 1 fragmentation having a maximum in the 1.2–1.5-eV range is a good diagnostic test for bridged hydrogen atoms in nido carboranes and may prove to be valuable in other types of compounds containing bridged hydrogen atoms.[13]

Table III. The P − 1 and P − 2 Ions in the Calculated Monoisotopic 70 eV ^{11}B Negative Ion Mass Spectra of Compounds **1**, **4**, and **5**[a]

	Relative intensity of		
	1	**4**[b]	**5**[c]
P − H	100 (*m/e* 75)	100 (*m/e* 77)	100 (*m/e* 76)
P − D + (P − 2H)	4.2	8.8	92

[a] These data represent the average of 11 determinations with a possible experimental error of approximately 15–20%. [b] Contained >95% D_2. [c] Contained 50% D_1.

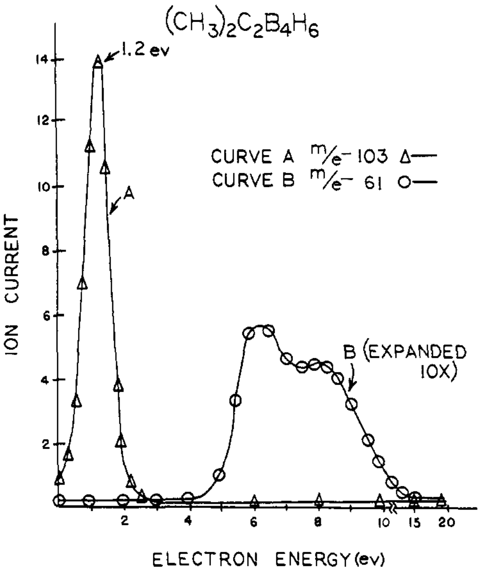

Figure 6. The ionization efficiency curves for the *m/e* 103 and 61 ions in $(CH_3)_2C_2B_4H_6$.

Acknowledgment. This work was supported in part by the Office of Naval Research. We wish to thank the Chemistry Department of the University of Southern California for the use of the mass spectrometer which was purchased in part by a grant from the National Science Foundation. We also wish to thank Dr. J. R. Spielman for providing one of the deuterium-labeled compounds.

[12] A detailed study of the negative ion mass spectra of the closo carboranes is currently underway and will be reported later.

[13] We have also observed P − 1 fragmentation having a similar energy maximum in pentaborane.