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Reactions of Pulsed-Laser Evaporated Boron Atoms with Hydrogen. Infrared Spectra of Boron Hydride Intermediate Species in Solid Argon

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Abstract: Pulsed-laser ablated B atoms react with H_2 upon condensation with excess argon to give BH, a $(H_2)(BH)$ complex, and B_2H_6 as the major products. The initial reaction to form BH requires activation energy, and BH reacts with H_2 to give additional products. Sharp new bands at 2587.3 and 1129.2 cm^{-1} exhibit natural isotopic 1:4 doublets for vibrations involving a single boron atom and disappear on annealing to 25 K. Substitution of ^{10}B and D gives shifts that are matched by MBPT(2) calculations of vibrational spectra for planar BH_3. Broader bands at 2475.2 and 1134.3 cm^{-1} exhibit similar isotopic shifts for vibrations of a BH_3 submolecule and decrease on annealing to 25 K. The displacements from isolated BH_3 frequencies suggest a $(H_2)(BH_3)$ complex and are in general agreement with recent quantum chemical calculations for BH_5. A sharp 2679.9-cm^{-1} band gives the ^{10}B shift predicted by MBPT(2) calculations for linear HBBH. A weak 2212.8-cm^{-1} band exhibits the ^{10}B shift and frequency calculated for the strongest band of BH_4^-. Additional broad absorptions that remain on annealing are attributed to higher boranes.

Introduction

Boron hydrides are fundamentally important compounds in synthetic and theoretical chemistry. The smallest stable boron hydride, B_2H_6, is the textbook example of electron-deficient three-center bonding, and B_2H_6 has been thoroughly studied.[1,2] However, the simplest intermediate species BH, BH_2, and BH_3 have received relatively little study owing to their high reactivity. The ^{11}BH diatomic has been examined by high-resolution electronic spectroscopy and electronic structure calculations.[3–5] The BH_2 radical has been characterized in like manner and by matrix ESR spectroscopy.[4,6,7] Assignments to BH_3 from the matrix infrared spectrum of BH_3CO pyrolysis products reported over 20 years ago[8] have been challenged by recent diode laser spectroscopy[9,10] and electronic structure calculations.[4,11–15]

Atomic boron is very reactive particularly when generated by pulsed laser evaporation. Reactions of boron atoms and small molecules including O_2, H_2O, CO, CO_2, N_2, C_2H_2, and CH_4 have taken advantage of the hyperthermal nature of laser ablated boron atoms.[16–24] Metal atoms reacting with molecular hydrogen require activation energy,[25,26] and pulsed-laser evaporated Al, Be, and Mg atoms react directly with H_2 to give a variety of small metal hydride molecular species including the monohydrides and dihydrides.[27–29] Accordingly, pulsed-laser evaporated B atoms have been reacted with H_2 in excess argon in order to trap small reactive boron hydride intermediate species in solid argon.

Experimental Section

The experimental apparatus and technique for pulsed-laser evaporation of boron for matrix infrared studies of reaction products has been described previously.[17,20] In particular 50–80 mJ/pulse of 1064-nm radiation was focussed (10 cm focal length) onto a rotating boron target; a medium pink plume was observed. Natural isotopic boron ^{n}B (Aldrich, 80.4% ^{11}B, 19.6% ^{10}B) and enriched ^{10}B (Eagle-Pitcher, 93.8% ^{10}B, 6.2% ^{11}B) samples were employed. Hydrogen gas (H_2, D_2 Matheson, lecture bottle and HD Cambridge Isotope Laboratories) was diluted to 2% or 4% with argon and deposited at 2 to 4 mmol/h onto a 10 K cesium iodide window.

FTIR spectra were recorded on a Nicolet Model 750 spectrometer at 0.5-cm^{-1} resolution using a MCT detector; frequency accuracy is ± 0.1 cm^{-1}. Samples were irradiated by the full light of a 175-W medium-pressure mercury arc and more spectra were obtained. Samples were annealed into the 13–16 K range to allow H_2 to evaporate and into the 20–27 K range to allow diffusion and reaction of trapped species, and more spectra were recorded.

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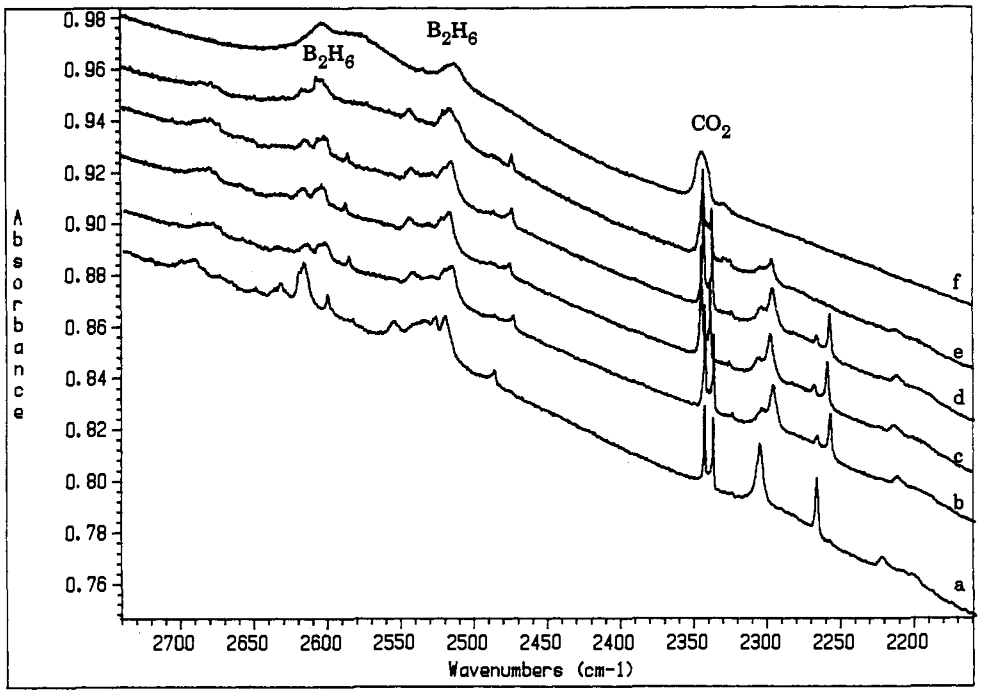

Figure 1. Infrared spectra in the 2740–2160-cm^{-1} region of pulsed-laser evaporated boron atom + H_2 reaction products in solid argon at 10 K: (a) ^{10}B codeposited with 4% H_2 in argon for 4 h, (b) ^{n}B codeposited with 4% H_2 in argon for 4.5 h, (c) after broadband photolysis for 30 min, (d) after annealing to 16 K, (e) after annealing to 25 K, and (f) after annealing to 27 K.

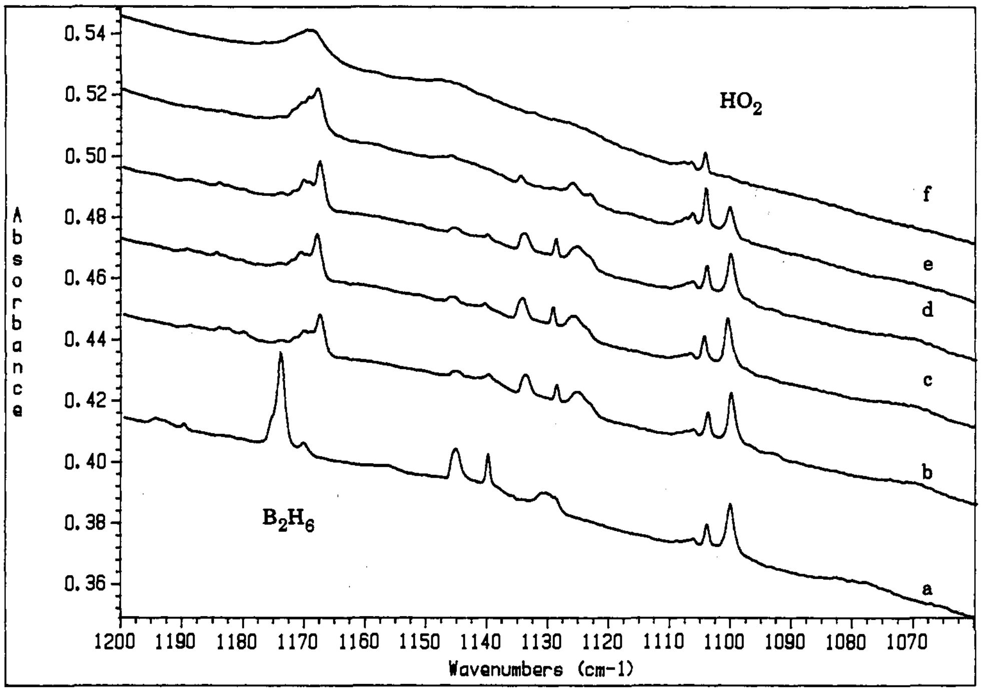

Figure 2. Infrared spectra in the 1200–1060-cm^{-1} region for samples in Figure 1.

Results

Matrix infrared spectra of boron atom reaction products with hydrogen and electronic structure calculations for small boron hydride species will be presented.

$^{n}B + H_2$. Matrix infrared experiments were done for pulsed-laser evaporated boron atoms and hydrogen using different laser powers and hydrogen flow rates; the best spectrum in terms of boron hydride product yield is illustrated in Figures 1 and 2 and the product absorptions are listed in Table 1. The spectrum contains weak boron oxide bands,[17] which are minimized after the surface of the target is cleaned by laser ablation and kept under vacuum (BO_2 absorbance at 1274.0 cm^{-1} is 0.02). Even weaker bands are detected for HBO and HOBO, which verifies reaction with hydrogen, and for B_2N and BBNN from reaction with trace nitrogen impurity.[18,20,21,30] In addition, HO_2 is always observed (absorbance at 1388 cm^{-1} is 0.04) and the $(H_2)(HO_2)$ complex increases markedly on annealing.[31,32]

One major product of the B/H_2 reaction is diborane based on agreement of the five strongest infrared bands at 2603, 2516.8, 1592.1, 1167.9, and 974.3 cm^{-1} for $^{11}B_2H_6$ with gas-phase values[33,34] of 2612, 2525, 1601, 1174, and 973 cm^{-1} and with the

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Table 1. Absorption (cm^{-1}) for B Atom–Hydrogen Reaction Products in Solid Argon

$^{n}B + H_2$	$^{10}B + H_2$	$^{n}B + D_2$	$^{10}B + D_2$	identity
2679.9	2691.3			HBBH
2616	2633	1987		higher B_xH_y
2603	2618	1972	1993	$\nu_8(B_2H_6)$
2587.3	2601.5	1953.4	1973.6	$\nu_3(BH_3)$
2544	2556		1936	higher B_xH_y
2516.8	2521.5	1842.6	1854.0	$\nu_{16}(B_2H_6)$
2475.2	2487.9	1866.2	1884.7	$(H_2)(BH_3)$
2298.3	2306.9	1708.5	1721.1	$(H_2)(BH)$
2259.4	2268.3	1682.6	1695.2	BH
2212.8	2223.5			BH_4^-
2047.6	2116.7	2047.6	2116.7	OBOB
2023	2107		2100	HOBO
1930.7	1996.6	1930.7	1996.6	BO_2^-
1912.4	1913.5	1912.4	1913.5	BBNN
1898.5	1953.0	1898.5	1953.0	$(BO)_2$
1854.4	1907.6	1854.4	1907.6	BO
1821.9	1861.0	1648.7	1663.0	HBO
1592.1	1597.0	1190.8	1197.5	$\nu_{17}(B_2H_6)$
1538.5	1545.1	1160.8	1166.6	B_xH_y
1420.2	1449.1	1420.2	1449.1	BOB
1404.5	1404.5	1030.8	1030.8	$(H_2)(HO_2)$
1388.3	1388.3	1019.8	1019.8	HO_2
1298.6	1347.0	1298.6	1347.0	BO_2 site
1274.0	1321.5	1274.0	1321.5	BO_2
1167.9	1174.4	870.9	876.8	$\nu_{18}(B_2H_6)$
1134.3	1145.6	883.0	901.4	$(H_2)(BH_3)$
1129.2	1140.5	878.5	897.6	$\nu_2(BH_3)$
1125	1131	851.1	858.8	higher B_xH_y
1104.5	1104.5			$(H_2)(HO_2)$
1100.6	1100.6			HO_2
903.4	903.4	643.4	643.4	Ar_nH^+
974.3	976.8	721.8	727.6	$\nu_{14}(B_2H_6)$
882.3	901.4	882.3	901.4	B_2N
756.6	765.4	607.3	618.6	HBO
587.1	608.6	587.1	608.6	BO_2^-

spectrum of a B_2H_6 sample in solid argon.[35] Another major product is ^{11}BH at 2259.4 cm^{-1} in solid argon, which falls just below the 2268.1-cm^{-1} gas-phase fundamental.[3] The 2259.4-cm^{-1} band exhibits a 2268.4-cm^{-1} ^{10}BH counterpart in a 1:4 relative intensity natural isotopic doublet.

Seven new absorptions are observed in the B–H stretching region: a broad band with a sharp peak at 2679.9 cm^{-1}, sharp absorptions at 2587.3 and 2475.2 cm^{-1}, and medium-width bands at 2616, 2544, 2298.3, and 2212.8 cm^{-1} (Figure 1b). Three new bands appear in the B–H bending region at 1134.3, 1129.2, and 1125 cm^{-1} (Figure 2b). Finally, sharp weak new bands are observed at 1602.0, 1599.4, and 1538.5 cm^{-1} in the bridged B–H stretching region; no absorption was observed at 1604 cm^{-1}.

Broadband photolysis in four experiments (compare Figures 1 and 2, scans b and c) increased the 2259.4-cm^{-1} BH band by 10%, decreased the 2475.2-cm^{-1} band by 10%, substantially diminished the 903.4-cm^{-1} Ar_nH^+ band,[36] and had little effect on the other absorptions.

Stepwise annealing was done to allow diffusion and further reaction of hydrogen. The first annealing to 16 K (Figures 1d and 2d) sharpened the 2475.2-cm^{-1} band and made evident the natural ^{10}B counterpart at 2487.9 cm^{-1}. A second annealing to 20 K (not shown) decreased the 2587.3-, 2475.2-, 1134.3-, and 1129.2-cm^{-1} bands slightly. Annealing to 25 K (Figures 1e and 2e) essentially destroyed the 2587.3-, 2259.4-, 1134.3-, and 1129.2-cm^{-1} bands, slightly decreased the remaining product bands, broadened the B_2H_6 bands and produced sharp satellite peaks at 2608.4 and 2522.2 cm^{-1}, and increased the 1404.5-cm^{-1} $(H_2)(HO_2)$ band. A final annealing to 27 K left broadened B_2H_6 bands at 2605, 2514, 1589, 1170, and 973 cm^{-1}, a broad 2580-cm^{-1} shoulder, a broad CO_2 band at 2346 cm^{-1}, broad boron oxide bands at 2020 and 1370 cm^{-1}, and a sharp 1404.5-cm^{-1} band, part of which is illustrated in Figures 1f and 2f. Similar annealing behavior was observed in other B + H_2 experiments.

$^{10}B + H_2$. The substitution of ^{10}B for natural isotopic boron shifted the product bands as is listed in Table 1. The boron isotopic shifts are indicated by comparison of the spectra in Figures 1 and 2, scans a and b. The ^{10}B components of 1:4 doublets observed with natural isotopic boron were observed as major peaks with the ^{10}B reagent. Note in Figure 2b weak ^{10}B bands at 1145.6 and 1140.5 cm^{-1} in natural abundance define a 1:4 doublet with the stronger ^{11}B bands at 1134.4 and 1129.2 cm^{-1}. Annealing had the same effect on the spectrum as found for the natural boron system. The $^{10}B_2H_6$ and 2487.9-cm^{-1} bands increased slightly on annealing to 20 K. The 2601.5-, 2268.4-, and 1140.5-cm^{-1} bands disappeared on annealing to 25 K, and sharp satellites appeared on the diborane bands at 2621.2 and 2527.6 cm^{-1}. Broad diborane bands at 2618, 2520, 1594, 1176, and 976 cm^{-1} and weak broad boron oxide bands at 2100 and 1400 cm^{-1} remained on annealing to 27 K.

B + D_2. Several matrix isolation experiments were done with ^{n}B and ^{10}B and D_2. Figures 3 and 4, scans a and b, compare the infrared spectra. Again B_2D_6 is the major product and isotopic bands are given in Table 1. The sharp 1:4 doublet at 1695.2 and 1682.6 cm^{-1} with ^{n}B gives way to a 15:1 doublet with the ^{10}B enriched target for the diatomic BD isotopic molecules. Other product bands are observed in the B–D stretching region for ^{n}B reactions at 1953.4, 1866.2, 1767, and 1708.5 cm^{-1} and for ^{10}B reactions at 1973.6, 1884.7, 1788, and 1721.1 cm^{-1}. Below the strong B_2D_6 fundamental, new bands are observed for ^{n}B at 1160.8 and for ^{10}B at 1166.6 cm^{-1}. Another strong 1:4 doublet at 858.5 and 851.1 cm^{-1} with ^{n}B gave only the upper band with ^{10}B. The sharp bands at 878.5 cm^{-1} with ^{n}B and 897.6 cm^{-1} with ^{10}B decrease on annealing with the 1953.4- and 1973.6-cm^{-1} bands while the broader 883.0- and 901.4-cm^{-1} bands are associated with the 1866.2- and 1884.7-cm^{-1} bands.

Stepwise annealing was done for all D_2 experiments, and the behavior is analogous to that reported above for H_2. In the ^{10}B + D_2 experiments, annealing to 18 K doubled the absorbance of the $^{10}B_2D_6$ bands and annealing to 25 K broadened the $^{10}B_2D_6$ bands, decreased the 858.8-cm^{-1} band, and destroyed the sharp 1973.6-, 1695.2-, and 897.6-cm^{-1} bands. Annealing to 27 K resulted in broad B_2D_6 and boron oxide absorptions, a sharp $(D_2)(DO_2)$ band[32] at 1030.8 cm^{-1}, and a broad 855-cm^{-1} band (Figures 3 and 4).

^{n}B and HD. The strongest product band at 1599.4 cm^{-1} in an experiment with HD and 2524.5- and 1195.2-cm^{-1} bands are presumably due to mixed isotopic $B_2H_xD_{6-x}$ species. The 2298.3- and 2259.4-cm^{-1} bands ($A = 0.010$) and 1708.5- and 1682.6-cm^{-1} bands ($A = 0.006$) exhibited the same annealing behavior as described above. Sharp weak bands at 2710.0, 1053.3, and 970.6 cm^{-1} decreased substantially on annealing.

Calculations. Although quantum chemical calculations have been done for many of the boron hydride species considered here, isotopic shifts are essential for vibrational assignments and no isotopic frequencies have been reported. Accordingly calculations were repeated at the MBPT(2) level with TZP basis sets using the ACESII program[37] in order to obtain a consistent set of energies for thermochemical calculations and frequencies for the ^{11}B, ^{10}B, H, and D isotopic species. Table 2 summarizes the energies and ^{11}B,H isotopic frequencies of some of the species considered here.

The most important transient intermediates are BH_2 and BH_3, and Table 3 gives the isotopic frequencies. The calculated valence angle for BH_2 is 128.8°, in excellent agreement with the 131° experimental value.[6] The valence angle closes to 103.6° for the

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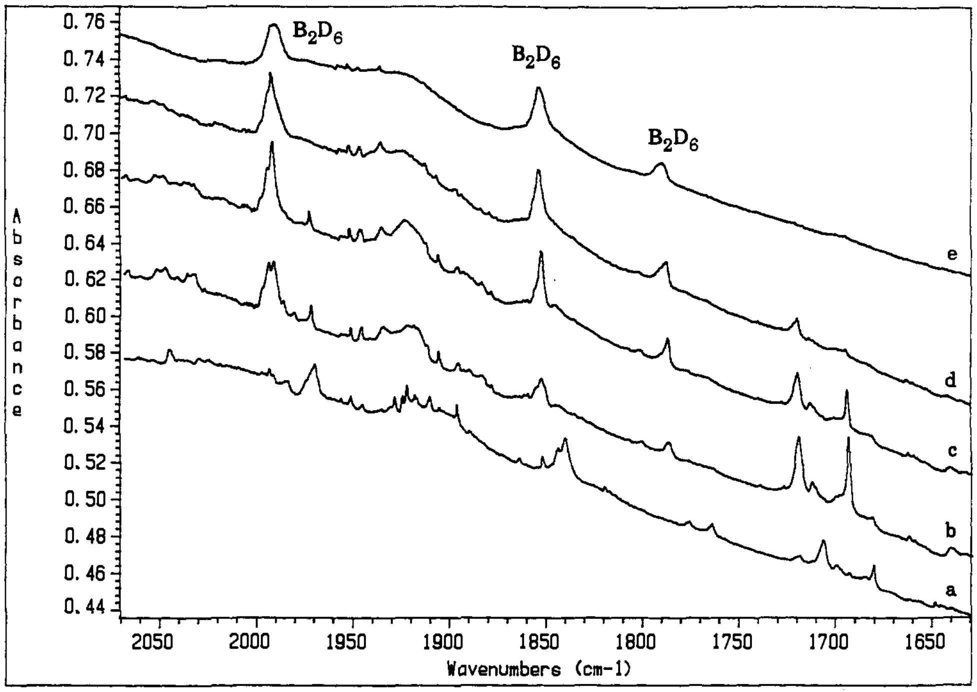

Figure 3. Infrared spectra in the 2070–1630-cm^{-1} region for pulsed-laser evaporated boron atom D_2 reaction products in solid argon at 10 K: (a) ^nB codeposited with 4% D_2 in argon for 5 h, (b) ^{10}B codeposited with 4% D_2 in argon for 4 h, (c) after annealing to 18 K, (d) after annealing to 25 K, and (e) after annealing to 27 K.

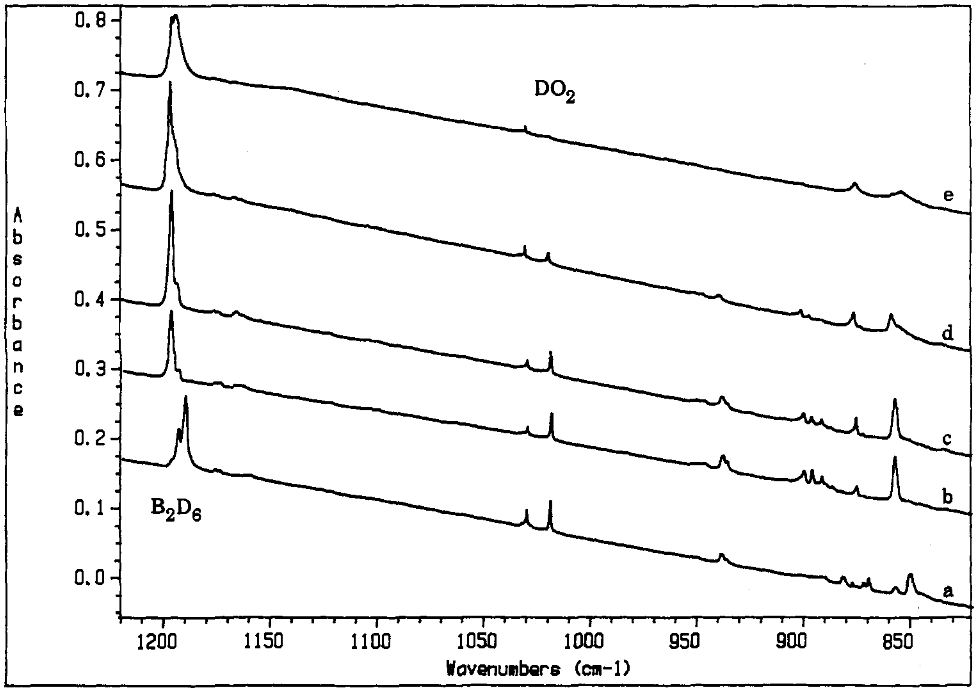

Figure 4. Infrared spectra in the 1220–820-cm^{-1} region for samples in Figure 3.

anion. The BH_3 species is planar (D_{3h}). Calculated isotopic frequencies are listed for the triplet linear HBBH species in Table 4 and for the tetrahedral BH_4^- anion in Table 5. A BH_4 radical with C_{3v} symmetry was less stable than BH_3 + H and exhibited imaginary frequencies. The BH_4 radical lowest energy structure was calculated to be C_{2v} with a terminal BH_2 valence angle of 129.5° and a bridged BH_2 angle of 47.1° enclosing longer 1.282 Å B–H bonds (Table 2).

Discussion

The new product absorptions will be identified with the assistance of isotopic shifts and ab initio calculations of vibrational spectra.

B_2H_6. The strongest product band in the spectrum at 1592.1 cm^{-1} is due to ν_{17} of $^{11}B_2H_6$. This band exhibits a $^{11}B^{10}BH_6$ component at 1594.3 cm^{-1} in natural abundance and a $^{10}B_2H_6$ counterpart at 1597.0 cm^{-1}. These bands are red shifted by the matrix about 9 cm^{-1} from the gas-phase position.[33,34] The deuterium counterparts are illustrated in Figure 4—the $^{11}B_2D_6$, $^{11}B^{10}BD_6$ doublet at 1190.8, 1194.1 cm^{-1} in natural abundance and the $^{10}B_2D_6$ band at 1197.5 cm^{-1} with a 1194.1-cm^{-1} shoulder in the 94% ^{10}B experiment. The five strongest diborane bands are listed in Table 1. These bands are important more for the identification of B_2H_6 as a reaction product than for the spectroscopy itself although the isotopic shifts for the argon matrix bands are more accurately measured than for the early gas-phase

Table 2. Energies, Bond Distances, and Frequencies Calculated for the B + H_2 System at the MBPT(2) Level Using the TZP Basic Sets

molecule	r(B–H)	energies, au	frequencies,[a] cm^{-1}
H		−0.49265	
B		−24.58467	
H_2		−1.15593	4645.7
BH	1.226	−25.20738	2476.4
BH_2	1.189	−25.79858	$\underline{2812.5}$, $\underline{2656.7}$, 1071.2
BH_3	1.189	−26.51179	$\underline{2775.1}$, (2630.9), 1260.5, $\underline{1195.2}$
BH_4	1.181 1.282	−27.03498	$\underline{2840}$, 2715, $\underline{2260}$, 2147,$\underline{1443}$, 1092, 1050 ,878, 754
HBBH	1.174	−50.60103	(2871.7), $\underline{2824.2}$, (1275.4), 639.7, (549.3)
BH_2^-	1.243	−25.82702	$\underline{2332.8}$, $\underline{2309.8}$, 1148.3
BH_4^-	1.231	−27.13958	$\underline{2393.4}$, (2365.2), (1253.5), 1140.0

[a] Strongest infrared bands underlined, forbidden bands in parentheses.

Table 3. Frequencies (cm^{-1}) and Intensities (km/mol in parentheses) Calculated for Isotopic BH_3 and BH_2 Molecules at the MBPT(2) Level with the TZP Basis Sets

mode	$^{11}BH_8$	$^{10}BH_3$	$^{11}BD_3$	$^{10}BD_3$
$\nu_3(e')$	2775.1 (90)	2791.3	2077.4 (55)	2100.0
$\nu_1(a_1')$	2630.9 (0)	2630.9	1861.1 (0)	1861.1
$\nu_4(e')$	1260.5 (11)	1266.6	928.8 (5)	934.9
$\nu_2(a_2'')$	1195.2 (85)	1208.0	932.0 (52)	948.3

mode	$^{11}BH_2$	$^{10}BH_2$	$^{11}BD_2$	$^{10}BD_2$
$\nu_3(b_1)$	2812.5 (64)	2830.6	2114.4 (36)	2138.4
$\nu_1(a_1)$	2656.7 (23)	2659.3	1898.5 (10)	1902.4
$\nu_2(a_1)$	1071.2 (32)	1078.4	806.0 (19)	815.0

Table 4. Frequencies (cm^{-1}) and Intensities (km/mol in parentheses) for Isotopic HBBH Molecules at the MBPT(2) Level with the TZP Basis Sets

mode	$H^{11}B^{11}BH$	$H^{11}B^{11}BD$	$D^{11}B^{11}BD$	$H^{10}B^{10}BH$
$\nu_1(\sigma_g)$	2871.7 (10)	2849.2 (10)	2191.4	2891.4
$\nu_3(\sigma_u)$	2824.2 (21)	2136.3 (7)	2079.7	2835.9
$\nu_2(\sigma_g)$	1275.4 (0)	1227.0 (0.0)	1182.3	1328.3
$\nu_5(\pi_u)$	639.7 (0.2)	598.5 (0.1)	471.1	642.4
$\nu_4(\pi_g)$	549.3(0)	460.3 (0.0)	455.3	559.4

Table 5. Frequencies (cm^{-1}) and Intensities (km/mol in parentheses) for Isotopic BH_4^- Molecules at the MBPT(2) Level with the TZP Basis Sets

mode	$^{11}BH_4^-$	$^{10}BH_4^-$	$^{11}BD_4^-$	$^{10}BD_4^-$
$\nu_3(f_2)$	2393.4 (262)	2404.9	1776.4	1793.6
$\nu_1(a_1)$	2365.2 (0)	2365.2	1673.2	1673.2
$\nu_2(e)$	1253.5 (0)	1253.5	886.7	886.7
$\nu_4(f_2)$	1140.0 (10)	1149.6	865.3	875.0

spectra. The sharp satellite features give boron isotopic shifts of 12.8 and 5.4 cm^{-1} for ν_8 and ν_{16}, which involve antisymmetric and symmetric B–H_2 stretching motions, respectively.

The bands at 1767 and 1788 cm^{-1} that remain on annealing in ^nB and ^{10}B experiments are clearly due to B_2D_6 but not to fundamentals. The $\nu_3 + \nu_{18}$ combination band has been assigned at 1799 cm^{-1} for $^{10}B_2D_6$ in the gas phase,[33] and the 1788-cm^{-1} argon matrix band is so assigned. This combination band has not been observed for $^{11}B_2D_6$ in the gas phase, and the 1767-cm^{-1} argon matrix band is so assigned. Finally, the major bands in ^nB + HD experiments at 1599.4, 2524.5, and 1195.2 cm^{-1} are appropriate for $^{11}B_2H_xD_{6-x}$.

BH. The sharp 1:4 doublet at 2268.4/2259.4 cm^{-1} in natural boron experiments is assigned to BH isolated in solid argon. This assignment is based on isotopic shifts and confirmed by comparison to the gas-phase fundamental[3] of ^{11}BH at 2268.1 cm^{-1} and ab initio frequency calculations. The small 8.7-cm^{-1} red shift by the argon matrix is appropriate for an essentially covalent guest species. The observation of comparable yields of BH and BD in the HD experiments, as compared to H_2 and D_2 experiments, shows that isotopic dilution does not reduce the band intensities and further supports the diatomic molecule identification. Furthermore, the disappearance on annealing to 25 K provides additional support for a small reactive species.

The observed $^{10}BH/^{11}BH$ = 2268.4/2259.4 = 1.00398 anharmonic ratio is just below the calculated harmonic value (1.00420) as expected. Likewise the observed $^{10}BD/^{11}BD$ = 1695.2/1682.6 = 1.00749 ratio is below the harmonic ratio (1.00768). The discrepancy between observed H/D ratios for ^{10}B and ^{11}B (1.3381 and 1.3428) and calculated ratios (1.3532 and 1.3579) is larger because of the greater difference in anharmonicity for BH and BD vibrations as compared to ^{10}BH and ^{11}BH motions.

The MBPT(2) calculations predict the ^{11}BH fundamental at 2476.4 cm^{-1}. The observed/calculated ratio (0.912) is slightly lower than other scale factors determined here. This is common for diatomic metal hydride calculations at the MBPT(2) level of theory.

(H_2)(BH). The broader 1:4 doublet at 2307.0/2298.3 cm^{-1} exhibits almost the same $^{10}B/^{11}B$ ratio (1.00379) and H/D ratio (1.3452) and is also appropriate for a diatomic B–H vibration. The broader doublet remains on annealing to 25 K after the sharp doublet is gone. The 2298.3-cm^{-1} band is assigned to hydrogen-perturbed BH, i.e. the (H_2)(BH) complex. The 38.9-cm^{-1} blue shift for the more repulsive interaction with H_2 is reasonable. Similar blue shifts were observed for (H_2)(AlH) complexes.[27]

Both (H_2)(BH) and isolated BH were observed (±0.3 cm^{-1}) in analogous boron–methane reactions (Figure 2 in ref 24) but not assigned in that study. The observation of the CH_3 radical also points to BH as a decomposition product of the energized CH_3BH insertion product.[24]

HBBH. The broad band with a sharp peak at 2679.9 cm^{-1} in Figure 1 is the highest frequency product band observed here, and the highest fundamental calculated here for a boron hydride (2824.2 cm^{-1}). Several structures for B_2H_2 have been calculated, and linear triplet HBBH is the lowest energy structure.[38] The observed and calculated isotopic frequencies exhibit almost the same relative ^{10}B shift (11.4 cm^{-1}), which is appropriate for a simple B–H stretching mode ($^{10}B/^{11}B$ ratio 1.00425). The observed/calculated ratio (0.949) is in the range expected for the MBPT(2) level of theory. Unfortunately the DBBD bands are masked by B_2D_6, but the strongest HBBD band at 2710.0 cm^{-1}, as predicted by frequency calculations, lends support. As Table 4 shows, the inactive (ν_1) mode is higher than ν_3 for HBBH, so the H–B stretching mode for HBBD is expected above ν_3 of HBBH. The 2679.9-cm^{-1} band is assigned to the antisymmetric B–H stretching mode (ν_3) of HBBH based on agreement of band position and boron isotopic shift with MBPT(2) frequency calculations.

BH_3. The three sharpest bands at 2587.3, 2259.4, and 1129.2 cm^{-1} disappeared upon sample annealing to 25 K. The 2259.4-cm^{-1} band is assigned to BH, and the 2587.3- and 1129.2-cm^{-1} bands are clearly due to another very reactive species. The frequency calculations for $^{11}BH_2$ and $^{11}BH_3$ in Table 2 and experimental observations[6] show that the 1129.2-cm^{-1} band is appropriate for BH_3 but not for BH_2. A closer examination of the detailed isotopic shifts (Table 3) predicted for BH_3 reveals an excellent match with the observed values. The sharp 2587.3- and 1129.2-cm^{-1} bands are assigned here to ν_3 and ν_2 of BH_3 isolated in solid argon.

First, the observed/calculated ratios 2587.3/2775.1 and 2601.5/2791.3 for ^{11}B and ^{10}B are the same 0.932 value and the analogous ratios 1953.4/2077.4 and 1973.6/2100.0 are the same 0.940 value for the deuterated species. The slightly lower ratio for BH vibrations as compared to BD vibrations is due to the larger anharmonicity for the former. Second, recent diode laser

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(38) Schaefer, H. F., III. Unpublished results.

spectroscopy of discharged B_2H_6 in He has give ν_3 fundamentals for $^{11}BH_3$ at 2601.57 cm^{-1} and $^{10}BH_3$ at 2615.79 cm^{-1} in the gas phase.[10] The matrix bands are red shifted 14.3 cm^{-1} by the argon matrix; however, the matrix boron isotopic shift (14.2 cm^{-1}) is identical to the gas-phase shift (14.22 cm^{-1}) for BH_3.

The boron isotopic observations also show that the 1134.3- and 1129.2-cm^{-1} bands are due to BH_3 species. The 1:4 doublet in natural isotopic experiments verifies the participation of a single boron atom. The two bands show identical 11.3-cm^{-1} boron isotopic shifts; the broader 1134.3-cm^{-1} band will be considered below for a BH_3 complex and the sharp 1129.2-cm^{-1} band is due to BH_3 isolated in solid argon.

The out-of-plane bending mode ν_2 of the BH_3 molecule (D_{3h}) is subject to quartic anharmonicity, and the observed anharmonic/calculated harmonic ratios for the four observed pure isotopic molecules vary slightly for this reason (0.945 and 0.944 for BH_3 and 0.943 and 0.947 for BD_3). Nevertheless, these ratios are close enough to confirm the assignment to ν_2 of BH_3 based on isotopic shifts. The two very weak sharp bands at 1053.3 and 970.6 cm^{-1} in the ^nB + HD experiment fall intermediate between the 1129.2- and 878.5-cm^{-1} $^{11}BH_3$ and $^{11}BD_3$ values and are appropriate for out-of-plane bending modes of $^{11}BH_2D$ and $^{11}BHD_2$, respectively. The scale factor 0.945 times the calculated frequencies predicts these two bands within 0.2 cm^{-1} of the observed values and confirms this BH_3 assignment. A recent gas-phase observation[9] of ν_2 of $^{11}BH_3$ at 1140.9 cm^{-1} provides further support for the 1129.2 cm^{-1} argon matrix BH_3 assignment.

The present assignments disagree with the BH_3CO pyrolysis work of Kaldor and Porter.[8] The strongest band observed earlier at 1604 cm^{-1} tracked with a strong 2148.9-cm^{-1} band now known to be due to the $(H_2O)(CO)$ complex,[39] hence water is implicated. This band was not observed here. The present weak doublet at 1602.0 and 1599.6 cm^{-1} is probably due to a H_2O complex perhaps with a boron hydride species. Furthermore, the previous 2808-cm^{-1} band was not observed here. The earlier 1125-cm^{-1} band, observed here with the same 6-cm^{-1} boron isotopic shift, leaves a residual absorption on annealing. This small isotopic shift is not appropriate for ν_2 of BH_3, but it is reasonable for a valence angle bending mode, and the 1125-cm^{-1} band could be due to a higher borane species.

$(H_2)(BH_3)$. The 2475.2- and 1134.3-cm^{-1} bands appear to track together and are reduced but still evident on annealing to 25 K, while the 2587.3- and 1129.2-cm^{-1} bands due to isolated BH_3 are gone. The ^nB experiments with H_2 reveal 1:4 doublets for both bands with the ^{10}B counterparts in natural abundance confirmed in separate ^{10}B experiments. Hence, the 2475.2- and 1134.3-cm^{-1} bands are due to single boron atoms species. Again, the calculated frequencies eliminate BH_2 as a possibility.

Two remaining candidates are BH_4 and BH_5. The calculated spectrum for the lowest energy BH_4 species (C_{2v}) predicts strong bands at 2150 ± 50 and 1100 ± 50 cm^{-1}, which is not compatible with the observed bands. Ab initio studies[14,40–42] have predicted a C_s structure for BH_5, i.e. $(H_2)(BH_3)$, and the most recent calculation has found a binding energy between H_2 and BH_3 of 6 kcal/mol, a large 70-cm^{-1} red shift for the ν_3, and a small 14-cm^{-1} blue shift for the ν_2 mode of the BH_3 submolecule in the complex. The 2475.2- and 1134.3-cm^{-1} bands are red shifted 112.1 cm^{-1} and blue shifted 5.1 cm^{-1} from isolated BH_3 values, which are in good general agreement with harmonic frequency calculations for BH_5 and BH_3.[14] The calculation further predicts a lifting of degeneracy for the ν_3 mode of the BH_3 submolecule due to symmetry lowering by H_2 in the complex, which is not observed. The $^{10}B/^{11}B$ ratio for the perturbed ν_3 mode (1.00513) is slightly smaller than that for isolated BH_3 (1.00549) and the H/D ratios slightly larger (1.3263, 1.3201) for the perturbed mode than the isolated bands (1.3245, 1.3181), which suggest slightly less stretch–stretch interaction and an approximately 6° smaller H–B–H angle in the complex as compared to isolated BH_3. This is in accord with the structure calculated at the MBPT-(2) level.[14] In summary, the relationship between the 2475.2- and 1134.3-cm^{-1} bands and the isolated BH_3 fundamentals is in general agreement with predictions from ab initio calculations and supports the present identification of $(H_2)(BH_3)$ in solid argon.

BH_4^-. The 2212.8-cm^{-1} band appears just below BH but exhibits a larger $^{10}B/^{11}B$ ratio (2223.5/2212.8 = 1.00484). Calculations (Table 2) show that both BH_4^- and BH_2^- are expected in this region, but BH_2^- exhibits two strong bands with different $^{10}B/^{11}B$ ratios and only one band is observed here. The strong ν_3 fundamental of BH_4^- has a calculated $^{10}B/^{11}B$ ratio of 1.00480, in excellent agreement with the observed ratio. Furthermore, the BH_4^- anion ν_3 fundamental has been observed in this region,[43–46] and in particular at 2382 cm^{-1} in NaCl and down to 2250 cm^{-1} in the more polarizable RbI host.[45] These salt host observations extrapolate[47] to an isolated anion value around 2200 cm^{-1} and point to assignment of the 2212.8-cm^{-1} band to BH_4^- isolated in solid argon. A possible $\nu_2 + \nu_4$ Fermi resonance partner is probably masked by the $(H_2)(BH)$ or BH absorptions. A similar relationship was found for BO_2^- in salt and solid argon hosts.[17] The observed/calculated frequency ratio (0.924) is reasonable for the MBPT(2) level of theory employed here. Unfortunately, the deuterium counterparts were masked by BD absorptions.

Other Absorptions. There remain absorptions at 2616, 2544, 1538.5, and 1125 cm^{-1} to be considered. The 2616-, 2544-, and 1125-cm^{-1} bands are broader than the sharp BH, BH_3, and $(H_2)(BH_3)$ bands assigned above and leave a broad residual absorption after annealing to 27 K, which destroys the sharp transient bands. The boron isotopic shifts identify antisymmetric B–H_2 stretching and bending modes. Serious consideration was given to B_2H_4 species in D_{2d} and C_{2v} structures.[48–50] Vibrational spectra of these molecules have been calculated and are not compatible with the observed spectra. The D_{2d} structure is expected to give a strong e mode in the 2460–2630-cm^{-1} region with a large boron isotopic shift, a strong b_2 mode in the 2350–2500-cm^{-1} region with a small boron isotopic shift, and a bending mode in the 900–1000-cm^{-1} region.[50] The latter bands are not observed. The C_{2v} structure is expected to exhibit a very strong band in the 1250–1350-cm^{-1} region,[50] which was not observed.

The reaction of BH_3 and B_2H_6 is expected to form a B_3H_9 intermediate, which can eliminate H_2 to give B_3H_7.[13] Either of these molecules could give the absorptions at 2616, 2544, and 1125 cm^{-1}. These bands are therefore attributed to a higher borane species probably formed by the reaction of BH_3 and B_2H_6.

The sharp 1538.5-cm^{-1} band and deuterium counterparts decrease on annealing and exhibit small boron isotopic shifts analogous to the nearby strongest diborane bridged B–H stretching absorption. Clearly, these bands are due to bridged B–H stretching absorptions in another transient molecule. Such a transient could be smaller (B_2H_5) than diborane or larger (B_3H_7), but without more absorptions, this transient cannot be identified.

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Mechanisms. The detailed reaction mechanism of B + H_2 to give B_2H_6 is of fundamental interest. The primary reaction of B and H_2 has two possible products, BH and BH_2, reactions 1 and 2. Reaction 1 is endothermic by 24.4 (spectroscopic)[3] or 25

$$B + H_2 \rightarrow H + BH \qquad (1)$$

$$B + H_2 \rightarrow BH_2 \qquad (2)$$

kcal/mol (calculated from Table 2), but the pulsed laser evaporated boron atom reagent easily possesses more than enough kinetic energy to overcome any reasonable activation energy barrier. Measurements on pulsed laser evaporated Al atoms reveal average kinetic energies in the 110-kcal/mol range,[51] and the B atoms employed here are expected to be similarly energetic. Although reaction 2 is calculated to be exothermic by 36 kcal/mol, no BH_2 is detected in these experiments. Under the present conditions any BH_2 formed is not trapped, as BH_2 is expected to be extremely reactive. The observation of BH_2 in more sensitive ESR experiments[7] is not inconsistent with this conclusion. Further research will include 4 K experiments in an effort to trap the highly reactive BH_2 species.

Two favorable secondary reactions of BH are observed in these experiments, the reaction with hydrogen to give BH_3 and with BH to form HBBH. Reaction 3 is calculated to be exothermic

$$H_2 + BH \rightarrow BH_3 \qquad (3)$$

$$BH + BH \rightarrow HBBH \qquad (4)$$

by 93 kcal/mol and reaction 4 by 117 kcal/mol. The latter value is somewhat lower than the SCF value of 110 kcal/mol as expected.[38] The formation of a hydrogen complex, $(H_2)(BH)$, is also favorable, but this is only a strong van der Waals interaction. Nevertheless, $(H_2)(BH)$ is a major product in these experiments.

$$H_2 + BH \rightarrow (H_2)(BH) \qquad (5)$$

Some of the BH_3 produced here is trapped by the argon matrix and some forms BH_5 or the $(H_2)(BH_3)$ complex, which is stable by 6 kcal/mol,[14] reaction 6. Hydrogen complexes with BH and

$$H_2 + BH_3 \rightarrow (H_2)(BH_3) \qquad (6)$$

BH_3 are important species in the boron/hydrogen system. These complexes are available for further energetic secondary reactions.

The reaction to give B_2H_6 could proceed through HBBH and B_2H_4, but the yield of HBBH is small and B_2H_4 is not detected here. The latter can be formed by the reaction of BH and BH_3, reaction 7, which is exothermic by approximately 85 kcal/mol.[52] Any B_2H_4 formed by reaction 8 would likely add H_2 rapidly to form B_2H_6, which is exothermic by more than 29 kcal/mol. The

$$BH + BH_3 \rightarrow B_2H_4\ (D_{2d}) \qquad (7)$$

$$B_2H_4 + H_2 \rightarrow B_2H_6 \qquad (8)$$

$$BH_3 + BH_3 \rightarrow B_2H_6 \qquad (9)$$

$$(H_2)(BH) + (H_2)(BH) \rightarrow B_2H_6 \qquad (10)$$

dimerization reaction 9 has been calculated to be exothermic by 30 kcal/mol.[15] The BH_3 yield is small and a more likely route to B_2H_6 may start from $(H_2)(BH)$, which exhibits a 10-fold stronger absorption than BH_3 in these experiments.

$$BH + (H_2)(BH_3) \rightarrow B_2H_6 \qquad (11)$$

The yields of BH and $(H_2)(BH)$ are very high in these experiments. This fact coupled with the large exothermicity of reaction 10 seems to indicate that reaction 10 is the predominant pathway for B_2H_6 formation. The overall channel for B_2H_6 production is therefore initial BH formation, subsequent H_2 complexation, and finally dimerization of $(H_2)(BH)$. We note that similar pulsed-laser B atom reactions with pure H_2 gave only the B_2H_6 product.[53] The BH_5 species or $(H_2)(BH_3)$ complex trapped here could form B_2H_6 in a similar reaction with BH, but again the lower yield of $(H_2)(BH_3)$ makes reaction 11 only a minor source of B_2H_6 in these experiments. Recall that diborane increased on annealing in several experiments so at least one of the above reactions proceeds without activation energy.

The observation of HO_2 in these experiments verifies that H atoms are formed yet BH_4 was not detected. Although BH_4 radical (C_{2v}) is more stable than BH_3 + H by 19 kcal/mol (Table 2), the substantial necessary rearrangement would likely prevent this reaction. On the other hand, BH_4 is more stable than BH_2 + H_2 by 50 kcal/mol, and this reaction is expected to be favorable, but the BH_2 reagent is not observed in these experiments.

Ionization processes play a minor role in these experiments as has been shown in similar B + O_2 reactions where BO_2^- was a minor product. The matrix solvated proton Ar_nH^+ species[36] observed here requires substantial energy for its formation. The pulsed-laser excited plume extends from the target to the condensing gases on the matrix surface, and some H_2 is subjected to discharge conditions. Photoionization of H in the matrix[54] by high-energy radiation from the boron/hydrogen plasma emission is also a possibility. Finally, photoelectrons produced in these pulsed-laser experiments are chemically trapped in the matrix. In hydrogen experiments H^- is a likely trap, which can readily react with BH_3 to form the stable closed-shell borohydride species observed here.

$$H^- + BH_3 \rightarrow BH_4^- \qquad (12)$$

Conclusions

Pulsed-laser evaporated B atoms have been reacted with H_2 molecules upon condensation with excess argon. Product molecules have been identified from infrared spectra by ^{10}B and D_2 substitution and MBPT(2) calculations of product vibrational frequencies. The major primary reaction to give BH requires the activation energy present in the ablated B atoms. The BH product undergoes a number of important secondary reactions to form $(H_2)(BH)$, BH_3, $(H_2)(BH_3)$, and HBBH. A $(H_2)(BH)$ complex can probably react with another $(H_2)(BH)$ complex without activation energy to form B_2H_6 in a highly exothermic process. The hydrogen complexes $(H_2)(BH)$ and $(H_2)(BH_3)$ are important intermediates in the boron–hydrogen reaction system.

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