duplexes will provide crucial tests of these predictions.[3]

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Boron Atom Reactions with Acetylene. Ab Initio Calculated and Observed Isotopic Infrared Spectra of the Borirene Radical BC_2H_2. A Fingerprint Match

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Boron atom reactions with small molecules such as O_2, H_2O, N_2, CO, and CH_4 have produced new boron species for matrix infrared spectroscopic characterization.[1-7] The boron–acetylene reaction is of particular interest because theoretical calculations suggest that both C—H insertion and C═C addition reactions will proceed readily.[8] The addition product borirene radical BC_2H_2 is expected to be a novel 2π-electron aromatic system like that predicted for borirene (HBC_2H_2)[9-11] and observed for substituted borirene species.[12,13] The infrared spectrum and MP2/DZP calculations on the borirene radical will be presented here.

Mixtures of argon/acetylene (200:1 to 800:1) were codeposited at 12 ± 1 K with laser-evaporated boron atoms [^{n}B: 80% ^{11}B, 20% ^{10}B and ^{10}B: 94% ^{10}B, 6% ^{11}B] using 40 mJ/pulse at the target as described previously.[1,3] Spectra for reaction of each boron sample with C_2H_2, $^{13}C_2H_2$, and C_2D_2 were collected at 0.5-cm^{-1} resolution. Samples were also subjected to UV photolysis and to annealing cycles, and more spectra were recorded.

Two spectral regions are of interest: the 2100–1900-cm^{-1} region shows three species with strong C═C stretching modes, which will be the subject of a full paper, and the 1200–1100-cm^{-1} region reveals two sharp product absorptions at 1175.3 and 1170.6 cm^{-1} (E) and 1122.7 cm^{-1} (F), which will be considered here. Figure 1a shows the latter absorptions after codeposition for 5 h. The E doublet and F band are decreased 40% by λ > 290 nm photolysis, Figure 1b. Further λ > 254 nm irradiation almost destroyed the E and F bands, Figure 1c. Annealing to 18 ± 1 K to allow diffusion and reaction of trapped boron atoms restored some of the 1170.6-cm^{-1} band, and acetylene absorptions did not change (not shown). Further annealing to 28 ± 1 K reproduced the 1170.6-cm^{-1} E band, but not the 1175.3-cm^{-1} band presumed to be a less stable matrix site, sharpened the F band, increased a 1119-cm^{-1} shoulder absorption, Figure 1d, and increased acetylene cluster absorptions. The 1188-cm^{-1} band that also increased on annealing is probably due to species E perturbed by C_2H_2.

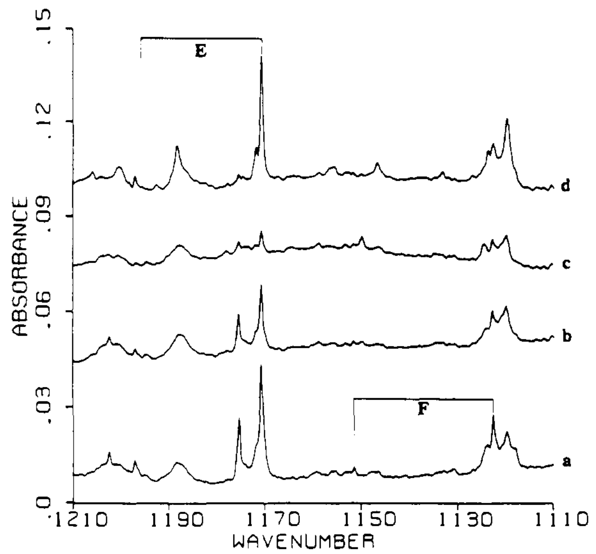

Figure 1. Infrared spectra in the 1210–1110-cm^{-1} region for natural isotopic boron atoms and 400:1 Ar/C_2H_2 sample at 12 ± 1 K: (a) spectrum after 5-h codeposition; (b) spectrum after λ > 290 nm photolysis for 45 min; (c) spectrum after λ > 254 nm photolysis for 45 min; and (d) spectrum after annealing to 28 ± 1 K.

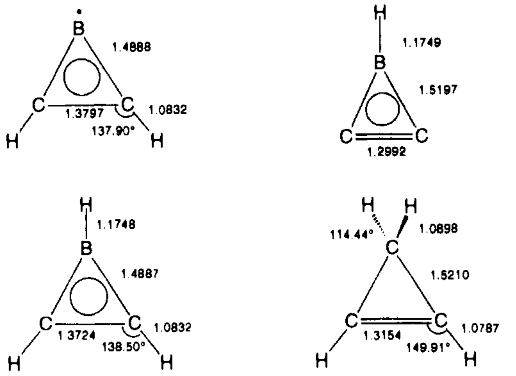

Figure 2. MP2/DZP optimized geometries (Å, deg) for the C_{2v}, molecules HBC_2, BC_2H_2, HBC_2H_2, and C_3H_4.

Isotopic data for the E bands are given in Table I. The 1170.6-cm^{-1} band exhibits 26.4-cm^{-1} boron-10, 22.9-cm^{-1} carbon-13, and 1.2-cm^{-1} deuterium shifts and as such defines a symmetric B–C_2 stretching vibration. The natural boron isotopic 4:1 doublet demonstrates the presence of a single boron atom, and the observation of a single carbon-12,13 peak in a carbon-13 enriched sampled characterizes two equivalent carbon atoms. Species E thus contains one B, two equivalent C atoms, and hydrogen.

Calculations were done at the MP2 level[14] with the DZP (double-ζ plus polarization) basis set[15] using the GAUSSIAN 92

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Table I. Calculated and Observed Isotopic Frequencies (cm^{-1}) for the Strongest E Band

	$^{11}B^{12}C_2H_2$	$^{10}B^{12}C_2H_2$	$^{11}B^{12}C^{13}CH_2$	$^{11}B^{13}C_2H_2$	$^{10}B^{13}CH_2$	$^{11}B^{12}C_2D_2$	$^{10}B^{12}C_2D_2$
$\nu(B-C_2)_{obsd}$	1170.6	1197.4	1161.9	1147.3	1172.0	1169.4	1196.0
$\nu(B-C_2)_{calcd}$	1214.9	1242.8	1206.3	1190.8	1216.4	1211.0	1239.2
ν(scaled 0.964)	1171.2	1198.1	1162.8	1147.9	1172.6	1167.4	1194.6
Δ(obsd–scaled)	–0.6	–0.7	–0.9	–0.6	–0.6	2.0	1.4

Table II. Calculated (MPZ/DZP) Infrared Intensities (km/mol) and Frequencies (cm^{-1}) for $^{11}B^{12}C_2H_2$ (C_{2v} Symmetry)

symmetry	b_1	a_1	b_2	a_2	b_2	a_1	a_1	b_2	a_1
intensity	50	16	31	0	3	65	2	2	0.3
frequency	733.6	910.6	925.9	1010.0	1200.9	1214.9	1506.1	3289.4	3313.0

program.[16] The optimized structures for BC_2H_2, HBC_2, HBC_2H_2, and cyclopropene are given in Figure 2. Calculated vibrational frequencies and intensities are given in Table II for the 11-12-12-1-1 BC_2H_2 isotope. The strong calculated 1214.9-cm^{-1} band dominates the spectrum. Table I also lists the calculated harmonic isotopic fundamentals; multiplying by the average scale factor 0.964 gives calculated bands in agreement within a 1.0-cm^{-1} average for seven isotopic E band frequencies. (The fit for the five hydrogen isotopes with similar anharmonicities is ±0.3 cm^{-1}.) This excellent agreement between calculated and observed isotopic frequencies confirms the identification of BC_2H_2. The out-of-plane deformation calculated at 733.6 cm^{-1} is probably masked by the very strong C_2H_2 band at 720–750 cm^{-1}. Large basis set coupled cluster calculations[17] predict BC_2H_2 to be 74 kcal/mol more stable than $B + C_2H_2$.

On the other hand, the F bands are assigned to the cyclic HBC_2 species; the different 28.7-cm^{-1} boron-10, 16.5-cm^{-1} carbon-13, and 47.0-cm^{-1} deuterium isotopic shifts are matched (±1.7 cm^{-1}) by quantum chemical calculations for HBC_2.[17] Calculations for the similar borirene molecule HBC_2H_2 reveal still different isotopic shifts for the strong $B-C_2$ fundamental calculated at 1215.8 cm^{-1};26.3-cm^{-1} boron-10, 22.3-cm^{-1} carbon-13, and 50.2-cm^{-1} deuterium shifts. Clearly, each molecule has a unique arrangement of atoms and unique normal vibrational modes, which can be characterized by *isotopic substitution at all atomic positions*. The important conclusion reached from this study is that agreement between scaled calculated and observed isotopic frequencies for *one vibrational fundamental with substitution at all atomic positions* constitutes a *fingerprint match* for identification of the molecule, which is demonstrated here for BC_2H_2.

It is clearly seen that the C=C bonds in BC_2H_2 and HBC_2H_2 are longer than in C_3H_4 (Figure 2). Likewise the B–C bonds are shorter than typical single bonds [1.558 Å in $B(C_2H_3)_3$].[13] Similar evidence has been offered to support delocalization of the two π electrons over the three-membered ring and aromatic character for the BC_2 ring in trimesitylborirene.[12] Furthermore, the BC_2 rings in BC_2H_2 and HBC_2H_2 are seen to be virtually identical. Thus, the σ radical site in BC_2H_2 has no effect on the delocalized π bonding in the BC_2 ring.

The photolysis of BC_2H_2 in the near ultraviolet range indicates a strong absorption band in this region, in agreement with trimesitylborirene.[13] The photolysis behavior also provides evidence for delocalized bonding as acetylene and ethylene absorb at shorter wavelengths.

The appearance of BC_2H_2 on diffusion and reaction of B atoms at 18 K in solid argon follows similar behavior for BO_2.[1] These exothermic reactions proceed without activation energy. The BC_2H_2 radical is the simplest borirene species yet observed and characterized. Further studies are in progress in this laboratory to prepare substituted borirene radicals.

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Cyclopropanation Catalyzed by Osmium Porphyrin Complexes

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Cyclopropanation of alkenes can be accomplished catalytically[2] or stoichiometrically.[3] Catalytic systems typically use a diazo reagent as the carbene source and a metal-containing mediator which forms a postulated metal carbene intermediate. Transfer of the carbene fragment from the metal to an alkene produces the cyclopropane product. Despite the wide variety of catalytic cyclopropanation systems, the putative carbene complex has never been isolated or observed in a catalytic system. This is somewhat surprising since the second category of cyclopropanation reactions involves the stoichiometric reaction of isolated carbene complexes with an alkene to form a cyclopropane. None of the isolated carbene complexes show catalytic cyclopropanation activity. Several years ago Callot demonstrated that rhodium porphyrins catalytically cyclopropanated a variety of alkenes in the presence of ethyl diazoacetate.[4] Kodadek and co-workers have expanded this work and have attempted to prepare synthetically useful enantioselective catalysts for the formation of cyclopropanes.[5] Their approach has been to use rhodium complexes with optically active porphyrins to induce chirality into the product. A similar approach was used for a variety of non-porphyrin copper catalysts.[6] Kodadek has shown that the carbon-bound diazonium complex $[(TTP)RhC(H)(CO_2Et)(N_2)]^+$ is an intermediate in the catalytic cyclopropanation of styrene with ethyl diazoacetate.[7,8] In addition,

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(7) Abbreviations: TTP = meso-tetra-*p*-tolylporphyrinato, Py = pyridine.

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