CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN 53706

Isolation and Characterization of Two New Isomers of Pentaboran(9)ylpentaborane(9), $(B_5H_8)_2$

BY DONALD F. GAINES,* TERRY V. IORNS,
AND ELNA N. CLEVENGER

Received August 31, 1970

Several years ago Lipscomb and coworkers[1] prepared 1-[1′-pentaboran(9)yl]pentaborane(9), 1,1′-$(B_5H_8)_2$, by passing a B_5H_9–H_2 mixture through an electrical glow discharge and determined its structure from a single-crystal X-ray diffraction study. Hall and Koski[2] prepared the same compound by deuteron irradiation of B_5H_9, and Pinson and Lin[3] prepared a presumably similar material by gas-phase radiolysis of B_5H_9.

Two other isomers of formula $(B_5H_8)_2$ having a B–B bond between two pentaborane(9) pyramidal groups are possible. We report here the isolation and characterization of these two isomers.

We recently noticed that commercially obtained samples of pentaborane(9), B_5H_9, contained small amounts (~1%) of low-volatility materials that appeared to be organoboranes. Attempted separation of these using standard vacuum-line techniques convinced us that there was at least one new borane present in the mixture in addition to decaborane and the unidentified organoboranes. Further purification using a specially designed low-temperature high-vacuum spinning-band column[4] and final separation using preparative gas chromatography have resulted in the isolation of 2-[2′-pentaboran(9)yl]pentaborane(9), 2,2′-$(B_5H_8)_2$, and 1-[2′-pentaboran(9)yl]pentaborane(9), 1,2′-$(B_5H_8)_2$. The compositions of 2,2′-$(B_5H_8)_2$ and 1,2′-$(B_5H_8)_2$ have been verified by elemental and mass spectroscopic analysis. The structures of the two isomers have been deduced primarily from their ^{11}B nmr spectra (Figure 1), with supporting evidence from their ^1H nmr and infrared spectra (*vide infra*). Schaeffer and coworkers have recently reported the synthesis of *i*-$B_{10}H_{16}$.[5] The physical properties and ^{11}B nmr spectrum of this *i*-$B_{10}H_{16}$ suggest that it is probably a mixture containing primarily 2,2′-$(B_5H_8)_2$ with a small amount of 1,2′-$(B_5H_8)_2$. It is doubtful that any technique less sensitive than vpc would allow separation of these isomers.

The ^{11}B nmr spectrum of 1,2′-$(B_5H_8)_2$ is interesting in that the 2′-pentaboran(9)yl group causes the B(1) resonance of the other pentaborane(9) group to shift upfield, as previously noted for 1,1′-$(B_5H_8)_2$,[6] while the B(2′) resonance is shifted to lower field, and yet there is no observable trans effect. In the case of 2,2′-$(B_5H_8)_2$ a much smaller downfield shift of the B(2,2′) resonance is observed.

The mass spectra of 1,2′-$(B_5H_8)_2$ and 2,2′-$(B_5H_8)_2$ are nearly identical and are very similar to the published spectrum of 1,1′-$(B_5H_8)_2$.[7] It is not apparent that there is any different fragmentation route for any of the isomers, even at low voltages.

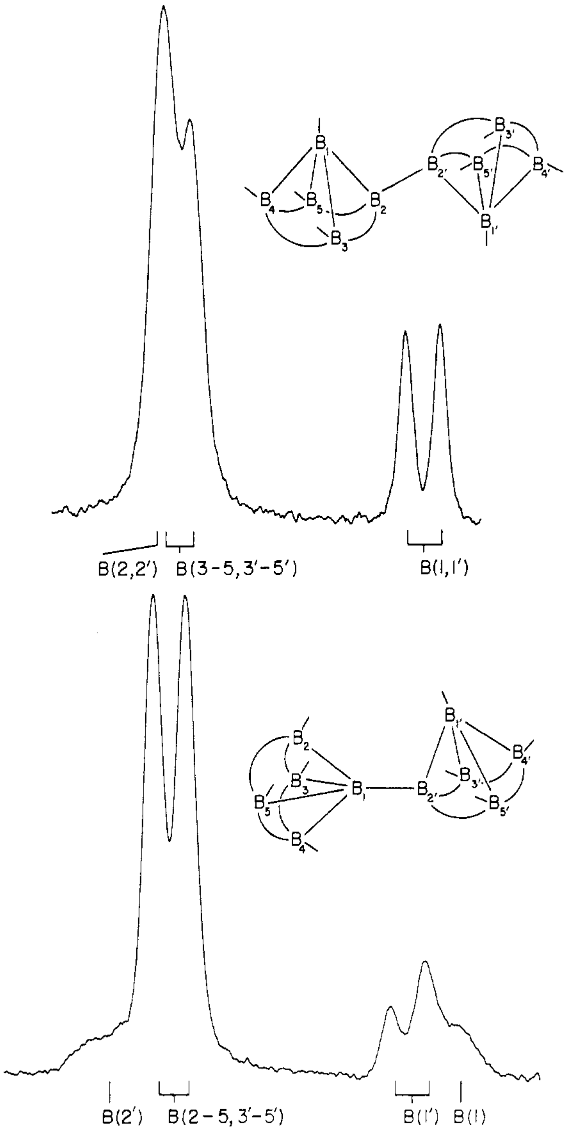

Figure 1.—The ^{11}B nmr spectra of 1,2′-$(B_5H_8)_2$ and 2,2′-$(B_5H_8)_2$ at 32.1 MHz.

Preliminary investigations of the chemistry of 2,2′-$(B_5H_8)_2$ indicate that it behaves quite differently from 1,1′-$(B_5H_8)_2$.[8] Whereas 1,1′-$(B_5H_8)_2$ reacts with hydrogen iodide at room temperature to give pentaborane(9) and 1-iodopentaborane(9), 2,2′-$(B_5H_8)_2$ does not react with HI under similar conditions. Liquid 2,2′-$(B_5H_8)_2$ is stable for short periods of time in air; it is immiscible with water and slowly hydrolyzes in water. Hydrolysis is more rapid in the presence of acid. The 2,2′-$(B_5H_8)_2$ bubbles vigorously when added to alcohol, in contrast to $B_{10}H_{14}$, which dissolves in alcohol without reaction. The 2,2′-$(B_5H_8)_2$ reacts with 2,6-lutidine and dimethyl sulfide, but the products have not been identified. Owing to the small quantities of 1,2′-$(B_5H_8)_2$ that have been isolated, no chemical studies have been possible.

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It has been observed, however, that 1,2′-$(B_5H_8)_2$ rapidly decomposes in air.

Other examples of boranes in which several polyhedra or polyhedral fragments are attached by a single B–B bond include B_8H_{18}, which most probably consists of two tetraborane units bound by a B–B bond between the 2,2′ positions,[9–11] $B_{20}H_{26}$, which is assumed to consist of two $B_{10}H_{13}$ units (from $B_{10}H_{14}$) bound together by a B–B bond,[2] and all three possible isomers of $B_{20}H_{18}{}^{4-}$.[12]

Experimental Section

A nearly empty B_5H_9 cylinder was attached to the vacuum line and the remaining volatile materials were distilled into a trap at −196° over a period of several days. The materials less volatile than pentaborane(9) were separated by fractional condensation in a U trap at −45°. The materials condensing in this trap were transferred to a high-vacuum reflux cold-finger assembly. The cold finger was cooled to −12° (salt–ice bath) and the bulb of the reflux assembly was heated with a beaker of warm water. The materials were allowed to reflux in the closed apparatus for some time; then the stopcock connecting the reflux assembly to the vacuum line was opened and materials distilling past the cold finger were collected in several fractions. The initial samples had infrared spectra characteristic of alkyl-substituted boron hydrides; these compounds were not characterized. Subsequent samples showed decreasing absorptions in the C–H stretching region of the infrared spectrum, but no samples could be obtained without this absorption. When the amount of liquid material in the reflux assembly became negligible, a solid material began to collect on the cold finger. The solid was subsequently identified as $B_{10}H_{14}$ by its ^{11}B nmr spectrum.

Several samples from the reflux distillation, with only a small C–H stretch absorption, were combined and further purified using a low-temperature, high-vacuum spinning-band distillation column.[4] The first samples collected again showed a strong absorption in the C–H stretching region of the infrared spectrum, but this absorption disappeared as successive fractions were collected. Several samples of material having no absorption in the C–H stretching region of the infrared spectrum were combined and analyzed (Schwarzkopf Microanalytical Laboratories). *Anal.* Calcd for $B_{10}H_{16}$: B, 87.03; H, 12.98. Found: C, 0.00; B, 86.93; H, 12.96.

A gas chromatogram of these samples showed that they were mixtures containing about 85% of one component and 15% of a second component.

Other similar samples, containing approximately 20% of the second component, were purified by preparative gas chromatography using a Loenco Model 160-PMT-2 gas chromatograph. Separation of the components is effected using a $^3/_8$ in. × 10 ft column of 20% Kel-F on Chromosorb W at 60° and a helium flow rate of 200 cm^3/min, with the samples being collected at −196°. Samples were injected as 50% hexane solutions. Owing to severe overloading characteristics of these compounds, sample sizes were restricted to 5 μl or less. The observed retention times were about 6 min for the smaller component and 7.5 min for the major component, compared to about 0.5 min for the hexane solvent. The larger of the two components was subsequently identified as 2-[2′-pentaboran(9)yl]pentaborane(9), 2,2′-$(B_5H_8)_2$, and the smaller as 1-[2′-pentaboran(9)yl]pentaborane(9), 1,2′-$(B_5H_8)_2$. Melting points of both isomers were obtained in sealed capillaries: 1,2′-$(B_5H_8)_2$, 18.4°; 2,2′-$(B_5H_8)_2$, −22.8 to −20.5°.

Nmr Spectra. 1,2′-$(B_5H_8)_2$.—The 32.1-MHz ^{11}B nmr spectrum of the 1,2′-$(B_5H_8)_2$ has a low-field group that appears to be a composite of a singlet of intensity 1 at about 3.58 ppm (from $BF_3 \cdot O(C_2H_5)_2$), B(2′), and a sharp, well-resolved doublet, B(2–5 and 3′–5′), of intensity 7 at 12.6 ppm, with a coupling constant of 168 Hz (Figure 1). The high-field group appears to be a composite of a singlet of intensity 1, B(1), at 57.3 ppm and a doublet of intensity 1, B(1′), at 50.5 ppm, with a coupling constant of 180 Hz.

The 60- and 100-MHz ^1H nmr spectra of 1,2′-$(B_5H_8)_2$ show both bridging and terminal hydrogens but give no structural information. The following chemical shifts were obtained: H(2–5, 3′–5′), τ 7.82 ppm, J = 165 Hz; H(bridge), τ 12.2 ppm.

2,2′-$(B_5H_8)_2$.—The 32.1-MHz ^{11}B nmr spectrum of 2,2′-$(B_5H_8)_2$ (Figure 1) has a low-field group of intensity 8 which appears to be a doublet, B(3–5, 3′–5′), and a singlet, B(2, 2′), overlapping with the low-field member of the doublet. The resulting two peaks are at 9.6 and 13.4 ppm. The high-field doublet of intensity 2, B(1, 1′), is at 49.9 ppm with a coupling constant of 180 Hz.

The 60- and 100-MHz ^1H nmr spectra of 2,2′-$(B_5H_8)_2$ exhibit two kinds of terminal hydrogens as well as bridging hydrogens. The following chemical shifts and coupling constants were obtained: H (3–5, 3′–5′), τ 7.46 ppm, J = 156 Hz; H(1, 1′), τ 9.5 ppm, J = 171 Hz; H(bridge), τ 12.0 ppm.

Infrared Spectra.—Infrared spectra were obtained in the gas phase, using a Perkin-Elmer 700 spectrometer. In the case of 2,2′-$(B_5H_8)_2$, a thin-film spectrum was also obtained. The infrared spectra of 1,2′-$(B_5H_8)_2$ and 2,2′-$(B_5H_8)_2$, respectively, are (cm^{-1} ± 10 cm^{-1}) as follows: 1,2′-$(B_5H_8)_2$: 2595 (s), 1840 (w), 1790 (vw), 1440 (w), 1395 (m), 1085 (vw), 1010 (w), 890 (m); 2,2′-$(B_5H_8)_2$: 2595 (s), 1805 (m, b), 1495 (sh), 1465 (sh), 1395 (s), 1350 (sh), 1110 (w), 1035 (sh), 1010 (s), 975 (m), 905 (s), 890 (sh), 880 (s), 850 (m), 800 (w).

Mass Spectra.—Mass spectra were obtained using an MS-902 spectrometer. For both isomers, the mass spectra at 70 eV cut off at m/e 126 as expected for $B_{10}H_{16}$. Exact mass measurement gave the following results: calcd for $B_{10}H_{16}$, 126.2183; found, 126.2172. The overall appearance of the spectra of both isomers is nearly identical with the previously reported spectrum of decaborane(16).[5] Mass spectra, obtained at a number of different ionizing voltages in the range 10–20 eV, showed only very slight differences between the two isomers. None of these differences was judged useful in distinguishing between the two isomers on the basis of their mass spectra.

Acknowledgments.—This work was supported in part by the National Science Foundation and the Office of Naval Research. We thank Bill Stebbings for the mass spectra. The mass spectrometer and nmr facilities were purchased in part with funds supplied by National Science Foundation equipment grants.

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CONTRIBUTION FROM THE MATERIALS RESEARCH LABORATORY
AND NOYES CHEMICAL LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

Chlorine Nuclear Quadrupole Resonances in Platinum(II)–Olefin Complexes[1]

BY JAMES P. YESINOWSKI AND THEODORE L. BROWN*

Received September 2, 1970

The trans effect in the substitution reactions of square-planar metal complexes, particularly of platinum(II), has been of interest for many years. The variety of ligands which exert a strong trans effect is quite remarkable. Hydride, H^-, presumably capable of interacting with Pt only through a σ bond, exerts a kinetic effect comparable to that of ethylene,[2] in which interaction with Pt is generally agreed to consist in both σ and π bonding to comparable degrees.

In attempts to account for the kinetic trans effect,

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[1] This research was supported in part by the Advanced Research Projects Agency of the Department of Defense under Contract SD-131 and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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