

have succeeded in synthesizing $(\text{NH}_3)_5\text{CoNCSCo}(\text{CN})_5$ by reaction of $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ with $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$.¹⁹ We are planning to study these reactions kinetically in order to obtain information about the nucleophilicity of ambidentate ions where one of the donor atoms is already bound to a metal center.

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Synthesis of a 6,9-Deuterium-Labeled Decaborane(14)

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Received July 13, 1970

Procedures for the synthesis of decaboranes(14) which are labeled with deuterium atoms in the bridge (μ),²⁻⁴ 1,2,3,4-terminal,^{5,6} and the $\mu,5,6,7,8,9,10$ -terminal^{3,4,6} positions are well known and commonly used. Recently, during the course of our studies of the structure and ¹¹B nmr spectrum of the $\text{B}_{10}\text{H}_{15}^-$ ion⁷ we have found a method for the preparation of a 6,9-deuterium-labeled decaborane(14). Although the labeled molecule contains slightly less than two deuterium atoms, the new compound is designated nominally as 6,9- $\text{B}_{10}\text{H}_{12}\text{D}_2$ in this communication. The new specifically labeled species should prove to be highly useful for further studies of decaborane chemistry.

Experimental Section

Apparatus.—All work which required inert-atmosphere conditions was done in an N_2 -flushed glove bag. Vacuum-line manipulations were performed on a standard vacuum line.^{8,9}

Boron-11 nmr spectra were obtained using a Varian Associates HA-100 equipped with standard 32.1-MHz probe and radio-frequency unit accessories. Chemical shifts were measured relative to $\text{B}(\text{OCH}_3)_3$ and are reported relative to $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ ($\delta_{\text{B}(\text{OCH}_3)_3} = \delta_{\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2} - 18.1$ ppm). Spectra were calibrated using the audiofrequency integrator side bands and spectral integrals were measured with a planimeter. Infrared spectra were obtained with Perkin-Elmer Model 21 and Beckman IR-5 spectrometers.

Materials.—Decaborane, obtained from a laboratory supply, was sublimed before use. Sodium borodeuteride (Alfa Inorganics) was used without further purification. Deuterium chloride was obtained from the reaction of SiCl_4 with D_2O ¹⁰ and was shown by mass spectral analysis to contain >95% deuterium. Hydrogen chloride was obtained from Matheson Co. and was purified by routine fractional condensation techniques. Mono-

glyme and dioxane were distilled from LiAlH_4 and stored under an N_2 atmosphere prior to use in an experiment.

The $\mu\text{-B}_{10}\text{H}_{10}\text{D}_4$ ¹¹ was prepared according to the method of Miller and Hawthorne.³ The $\mu\text{-B}_{10}\text{H}_{10}\text{D}_4$ contained 3.50 D/molecule. Within experimental error, no deuterium migration into terminal positions could be detected in the ¹¹B nmr spectrum.

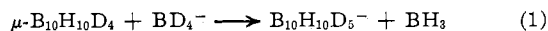
Deuterium analyses were performed by Mr. Josef Nemeth, Urbana, Ill.

Preparation of 6,9- $\text{B}_{10}\text{H}_{12}\text{D}_2$.—In a typical reaction $\mu\text{-B}_{10}\text{H}_{10}\text{D}_4$ (1.0 mmol) in 1 ml of monoglyme was allowed to react under an N_2 atmosphere with NaBD_4 (2.0 mmol). Upon completion of the reaction, as evidenced by the discontinuation of slight gas evolution, the solution was decanted from the excess undissolved NaBD_4 . The monoglyme solution was treated with a 4–5 molar excess of DCl for 1 hr. Hydrogen, unreacted DCl , and monoglyme were removed by passage of the reaction materials through a -30° trap. The intermediate decaborane, nominally described as $\text{B}_{10}\text{H}_8\text{D}_6$, was purified by sublimation. Removal of deuterium from bridging positions was accomplished by a rapid equilibration in H_2O in which the $\text{B}_{10}\text{H}_8\text{D}_6$ was stirred in 5 ml of an equivolume H_2O –dioxane mixture for 3 min. To this mixture several 10-ml portions of ether were added to extract the product. Evaporation of the ether followed by vacuum sublimation of the product yielded 62 mg (0.5 mmol; 50% yield) of 6,9- $\text{B}_{10}\text{H}_{12}\text{D}_2$. A content of 1.90 D/molecule was found.

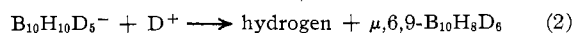
Results and Discussion

In this study, we have found that 6,9- $\text{B}_{10}\text{H}_{12}\text{D}_2$ can be prepared using the following multistep synthetic procedure.

Bridge-deuterium-labeled decaborane ($\mu\text{-B}_{10}\text{H}_{10}\text{D}_4$) is converted to the pentadecahydro-*nido*-decaborate(1-) ion, $\text{B}_{10}\text{H}_{10}\text{D}_5^-$, in a reaction with borodeuteride ion in monoglyme (eq 1). The $\text{B}_{10}\text{H}_{14}\text{-NaBH}_4$



reaction has been reported previously.¹² In the second step of the synthesis the $\text{B}_{10}\text{H}_{10}\text{D}_5^-$ ion is converted back to decaborane by reaction with DCl (eq 2). Finally,



exchange of bridge deuterium for hydrogen by reaction with H_2O results in the final 6,9- $\text{B}_{10}\text{H}_{12}\text{D}_2$.

The deuterium content of 6,9- $\text{B}_{10}\text{H}_{12}\text{D}_2$ is established by deuterium analysis and mass spectral data. Deuterium analysis indicated the presence of 1.90 deuterium atoms/molecule. The mass spectrum exhibits peak envelopes characteristic of a decaborane.¹³ The most intense peak occurs at m/e 123. Small peaks as high as m/e 130 are evident; however, the main spectral cutoff occurs at m/e 126. The cutoff at m/e 126, compared to m/e 124 for normal $\text{B}_{10}\text{H}_{14}$, indicates the absence of large quantities of decaboranes containing more than two deuterium atoms. However, the presence of small quantities of more highly deuterated species is recognized.

The infrared spectrum of 6,9- $\text{B}_{10}\text{H}_{12}\text{D}_2$ exhibits strong absorptions at 2560 and 1920 cm^{-1} which can be assigned to terminal B–H and B–D stretching modes,^{3,14,15} respectively. The B–D bridge absorption in deca-

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borane has not been assigned; however, the absorption at 1885 cm^{-1} verifies the presence of hydrogen in bridging positions.³ The spectrum of the sample was examined two times during a 1-hr period and in this time no evidence of additional deuterium migration into bridging positions was observed.

Terminal substitution of deuterium in the 6,9 positions is clearly evident from the ^{11}B nmr spectrum shown in Figure 1a. The spectrum of normal $\text{B}_{10}\text{H}_{14}$ is also shown (Figure 1b) for comparison purposes.

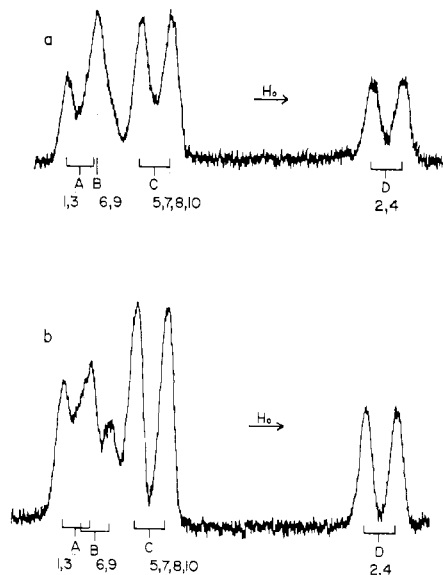


Figure 1.—(a) The ^{11}B nmr spectrum of a 0.3 *M* solution of 6,9- $\text{B}_{10}\text{H}_{12}\text{D}_2$ in heptane. (b) The ^{11}B nmr spectrum of a 0.3 *M* solution of $\text{B}_{10}\text{H}_{14}$ in heptane.

Due to the solvent dependence of the ^{11}B nmr spectrum of $\text{B}_{10}\text{H}_{14}$,¹⁶ both spectra were measured in heptane in order to show most clearly the separation of the 1,3 and 6,9 resonances. The spectrum of 6,9- $\text{B}_{10}\text{H}_{12}\text{D}_2$ consists of a low-field doublet, A ($\delta -11.7$ ppm; $J = 156$ Hz), an overlapped singlet, B ($\delta -9.3$ ppm), a doublet, C ($\delta +0.2$ ppm; $J = 152$ Hz), and a high-field doublet, D ($\delta 37.6$ ppm; $J = 151$ Hz), of relative areas 2:2:4:2, respectively. Based on spectral assignments which have been published previously,^{17,18} resonances A, B, C, and D can be assigned to the 1,3, 6,9, 5,7,8,10, and 2,4 boron atoms, respectively. Comparison of resolution of each doublet in the spectrum of 6,9- $\text{B}_{10}\text{H}_{12}\text{D}_2$ with the corresponding doublets in the spectrum of unsubstituted $\text{B}_{10}\text{H}_{14}$ indicates that a very small amount of deuterium scrambling into the 5,7,8,10 positions has occurred. However, no measurable amount of deuterium is present in the 1,3 or 2,4 positions.

The preparation of 6,9- $\text{B}_{10}\text{H}_{12}\text{D}_2$ in the above sequence of reactions depends on the fact that in $\text{B}_{10}\text{H}_{10}\text{D}_5^-$ rapid equilibration of hydrogen and deuterium atoms between bridge and 6,9 terminal positions occurs.⁷ However, only minimal scrambling of deuterium into 5,7,8,10 terminal positions is evident. When

the $\text{B}_{10}\text{H}_{10}\text{D}_5^-$ is allowed to react with DCl, hydrogen evolution occurs in a reaction which does not give rise to a species in which deuterium scrambling into 5,7,8,10 positions occurs. The exact nature of this reaction is not established at this time.

In order to ensure clean labeling, several modifications of the published experimental techniques were used. In the preparation of $\text{B}_{10}\text{H}_{10}\text{D}_5^-$, monoglyme was added to the $\mu\text{-B}_{10}\text{H}_{10}\text{D}_4\text{-NaBD}_4$ mixture in a container large enough so that good mixing was ensured.¹² Also, the reaction was carried out under an N_2 atmosphere. This procedure minimizes the formation of $\mu\text{-B}_{10}\text{H}_{10}\text{D}_3^-$ in the reaction. The exchange reactions which were used to replace hydrogen or deuterium in the bridging positions of decaborane were allowed to continue for only 3–5 min. Upon completion of the exchange the decaboranes were immediately extracted into diethyl ether, the ether was flash evaporated, and the product was purified by sublimation. These procedures minimized both scrambling and loss of product due to hydrolysis.

Acknowledgment.—Support of this work by a grant from the National Science Foundation (GP-8090) is gratefully acknowledged.

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Tungsten-183 Chemical Shifts in *cis*- and *trans*-Bis(tributylphosphine)tetracarbonyltungsten

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Received June 23, 1970

The first measurement of a tungsten-183 nuclear resonance in a nonconducting material was the double-resonance determination of tungsten hexafluoride (liquid).¹ Apparently the only other compound measured has been tungsten trioxide (solid)² which showed a chemical shift of -1000 ppm from that of tungsten hexafluoride. Because the platinum^{3,4} and rhodium⁵ resonances in square-planar and octahedral *halide* complexes have exhibited a regular dependence on the geometrical form of the complexes, it seemed that a similar measurement on two isomers of a carbonyl complex might prove useful by comparison. Therefore we have measured the tungsten chemical shifts in the compounds *cis*- and *trans*-(CO)₄W((C₄H₉)₃P)₂.

The preparation and phosphorus-31 spectra of the compounds have been reported by Grim and Wheatland.⁶ The method of preparation was the same as

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