1812 *Inorg. Chem.* **2000,** *39,* 1812−1813

Hydrogen−Deuterium Exchange in Decaborane(14): Mechanistic Studies

Donald F. Gaines*

Department of Chemistry, University of Wisconsin−
Madison, 1101 University Avenue,
Madison, Wisconsin 53706

Herbert Beall*

Department of Chemistry and Biochemistry, Worcester
Polytechnic Institute, 100 Institute Road,
Worcester, Massachusetts 01609

Received August 26, 1999

Introduction

Substitutions on the boron atoms of decaborane(14), $B_{10}H_{14}$, are well-known.[1] The position of substitution of the $B_{10}H_{14}$ cage is dependent on the distribution of charge around the cage (Figure 1). Self-consistent field calculations of the electron density for $B_{10}H_{14}$[2] show clearly that the order from least negative (most positive) to most negative is B6,9, then B5,7,8,10, and then B1,3 and the most negative are B2,4. Thus reactions with nucleophilic reagents can be expected to occur most readily at B6,9 while reactions with electrophilic reagents should occur most readily at B2,4. The positive charge at the open face of $B_{10}H_{14}$ (B6,9 and B5,7,8,10) is elegantly demonstrated by the structure of the charge-transfer complex $B_{10}H_{14}I^-$ in which the negatively charged I^- sits on this open face.[3]

Deuteration reactions of decaborane bear out these conclusions. Under basic conditions, for example, with D_2O in dioxane,[4] the four bridge hydrogen atoms are replaced by deuterium the most rapidly, the terminal hydrogen atoms on B6,9 are replaced next, and then the terminal hydrogen atoms on B5,7,8,10 are replaced.[5] Deuteration stops at this point. The lability of the very acidic bridge hydrogen atoms for deuterium exchange is typical of boron hydrides.

Electrophilic deuterium exchange in $B_{10}H_{14}$ was first observed 40 years ago using deuterium chloride and aluminum chloride in carbon disulfide.[6] Under these conditions, deuteration occurred at the B1,2,3,4 positions. No preference in the rate of deuteration between B1,3 and B2,4 was observed in this early study.

An alternative and interesting method of electrophilic deuteration of $B_{10}H_{14}$ is accomplished using $AlCl_3$ in perdeuteriobenzene.[7] Under these conditions deuteration is observed by ^{11}B NMR to be faster at B2,4 than at B1,3 as would be predicted by the calculated charge distribution. The purpose of this paper is to examine the mechanism for deuterium−hydrogen exchange of $B_{10}H_{14}$ with $AlCl_3$ and deuterio-aromatic hydrocarbons.

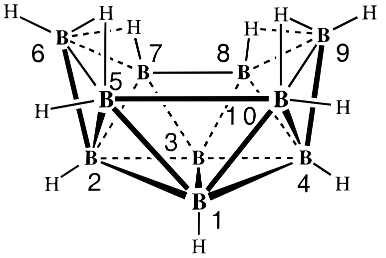

Figure 1. Structure and numbering scheme for $B_{10}H_{14}$.

Experimental Section

Deuterium−hydrogen exchange reactions were run in both directions, that is, using $B_{10}H_{14}$ and a deuterated aromatic compound and using 1,2,3,4-$D_4B_{10}H_{10}$ and an undeuterated aromatic. The purity of the 1,2,3,4-$D_4B_{10}H_{10}$ was ascertained using ^{11}B NMR. $B_{10}H_{14}$, 1,2,3,4-$D_4B_{10}H_{10}$, and $AlCl_3$ were sublimed prior to reaction. The aromatic reagents were distilled and kept dry over molecular sieves. Reactions were performed under nitrogen in NMR tubes, and the results were monitored by ^{11}B NMR recorded at 160.15 MHz on a Bruker AM-500 spectrometer or at 115.15 MHz on a Bruker AM-360 spectrometer.

In a typical reaction under nitrogen, anhydrous $AlCl_3$ (Fisher) from a freshly opened bottle was charged into an NMR tube, which was then attached to the vacuum line. The end of the tube was heated in a water bath at 90−100 °C until about half of the $AlCl_3$ had sublimed up the tube. The bottom of the tube containing the residue from the sublimation was then sealed off from the rest of the tube and discarded. A 1 M solution of sublimed 1,2,3,4-$B_{10}H_{10}D_4$ in benzene dried over 4A Molecular Sieves, 8−12 mesh, was then added to the tube under a stream of nitrogen. The NMR tube was then sealed off and placed on a slow rotator for 160 min. The ^{11}B NMR spectrum of the reaction mixture showed that the product was 1,3-$B_{10}H_{12}D_2$; that is, deuterium−hydrogen exchange had occurred at B2,4, the boron atoms bearing the greatest charge. Other experiments were conducted similarly.

Results and Discussion

Examination of reactions of strong acids with aromatic hydrocarbons and with $B_{10}H_{14}$ can provide information on the nature of the possible electrophilic species that attacks the decaborane cage in the aromatic−decaborane(14) H−D exchange. Perdeuteriobenzene can be protonated with concentrated H_2SO_4 or 90% H_2SO_4(aq)[8] and also with 83% and 66% H_2SO_4(aq) at 25 °C.[9] Trifluoroacetic acid in D_2O will deuterate aromatic compounds at 70 °C. We have found that hydrogen−deuterium exchange does not occur when H_2SO_4, either concentrated or diluted, or trifluoroacetic acid is reacted with 1,2,3,4-$B_{10}H_{10}D_4$ at room temperature. However, the 1,2,3,4-$B_{10}H_{10}D_4$ molecule can be protonated by a sufficiently strong acid. For example, we observed triflic acid (trifluorosulfonic acid) to react with 1,2,3,4-$B_{10}H_{10}D_4$ causing rapid exchange. Since H_2SO_4 and trifluoroacetic acid can protonate deuteriobenzene, H_2SO_4 and trifluoroacetic acid are stronger acids than protonated benzene. Furthermore, since these acids cannot protonate $B_{10}H_{10}D_4$, it follows that protonated deuteriobenzene cannot effect deuterium−hydrogen exchange on $B_{10}H_{14}$. There-

---

(1) Shore, S. G. In *Boron Hydride Chemistry*; Muetterties, E., Ed.; Academic Press: New York, 1975; pp 154, 155.

(2) Laws, E. A.; Stevens, R. M.; Lipscomb, W. N. *J. Chem. Phys.* **1972**, *94*, 4467.

(3) Wermer, J. R.; Hollander, O.; Huffman, J. C.; Bauer, J. A. K.; Dou, D.; Hsu, L.-Y.; Leussing, D. L.; Shore, S. G. *Inorg. Chem.* **1995**, *34*, 3065−3071.

(4) Hawthorne, M. F.; Miller, J. J. *J. Am. Chem. Soc.* **1958**, *80*, 754. Shapiro, I.; Lustig, M.; Williams, R. E. *J. Am. Chem. Soc.* **1959**, *81*, 1, 838−841.

(5) Shapiro, I.; Lustig, M.; Williams, R. E. *J. Am. Chem. Soc.* **1959**, *81*, 838.

(6) Dupont, J. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1959**, *81*, 1, 4998−4999. Dupont, J. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1962**, *84*, 4, 1804−1808.

(7) Dopke, J. A.; Gaines, D. F. *Inorg. Chem.* **1999**, *38*, 4896−4897.

(8) Ingold, C. K.; Raisin, C. G.; Wilson, C. L. *Nature* **1934**, *134*, 734.

(9) Gold, V.; Satchell, D. P. N. *J. Chem. Soc.* **1955**, 3619−3622.

10.1021/ic991032u CCC: \$19.00

fore, D−H exchange must occur by contact of the decaborane molecule with a deuterium (or hydrogen) species complexed in some way to the $AlCl_3$.

We have observed that no deuterium−hydrogen exchange occurs between C_6D_6 and $B_{10}H_{14}$ using $AlCl_3$ unless there is solid $AlCl_3$ in the reaction vessel. This is true although $AlCl_3$ has a small but significant solubility in benzene, 0.72 g/100 mL at 18 °C and 4.88 g/mL at 108.6 °C.[10] The failure of H−D exchange to take place without solid $AlCl_3$ present is strongly suggestive that this stage of the reaction with $B_{10}H_{14}$ takes place at the surface of the $AlCl_3$. In order for there to be H−D transfer from an Al complex to the $B_{10}H_{14}$, H−D transfer from the deuterated aromatic to the aluminum species must occur before the Al complex reacts with the $B_{10}H_{14}$. Therefore, reaction of an aluminum species with the deuterated aromatic must initiate the overall process.

For Friedel−Crafts alkylations of aromatics, a very small amount of water is necessary to produce a small concentration of HCl.[11] The HCl can interact with the $AlCl_3$ to give an $HCl\cdot AlCl_3$ complex or, perhaps, the postulated but never observed superacid $H(AlCl_4)$.[12] We are postulating that this reaction takes place on the surface of the $AlCl_3$.

We have found that the rate of deuterium−hydrogen exchange between an aromatic and 1,2,3,4-$B_{10}H_{10}D_4$ depends on the substitution on the benzene ring. Our qualitative rate results for deuterium−hydrogen exchange using $AlCl_3$ with methyl-substituted benzenes compared to the rate with benzene are the following: (i) toluene faster than benzene; (ii) *o*-xylene comparable to toluene; (iii) *m*-xylene slower than benzene; (iv) mesitylene no reaction.

In deuterations of aromatics by strong acids toluene is deuterated 127 times faster than benzene.[13] Under the same conditions *o*- and *p*-xylene react about 5 times as fast as toluene, *m*-xylene about 200 times as fast as xylene, and mesitylene about 10^4 times as fast as toluene.[14] We do observe an enhanced rate of deuterium−hydrogen exchange with toluene compared with benzene, and this is presumably an electronic effect. However, as additional methyl groups are added to the benzene ring, the electronic effect appears to be swamped out by a steric effect. Such a steric effect could be expected to occur when the aromatic compound is reacting at the $AlCl_3$ surface, consistent with our contention that it is the $AlCl_3$ surface at which deuterium−hydrogen exchange of the aromatic compound takes place.

We propose that the reaction steps for D−H exchange on $B_{10}H_{14}$ using C_6D_6 and AlCl are the following:

(1) Formation of an $AlCl_3\cdot HCl$ complex at the $AlCl_3$ surface:

$$AlCl_3(\text{surface}) + HCl \rightarrow AlCl_3\cdot HCl(\text{surface})$$

(2) Exchange between C_6D_6 and the complex of $AlCl_3\cdot HCl$ at the $AlCl_3$ surface:

$$AlCl_3\cdot HCl(\text{surface}) + C_6D_6 \rightarrow AlCl_3\cdot DCl(\text{surface}) + C_6D_5H$$

This step would be affected by steric factors depending on the substitution on the aromatic compound, and our observed, qualitative rate results indicate that it is likely rate-determining.

(3) Exchange of the D atom in the $AlCl_3\cdot DCl$(surface) complex with an H atom from the $B_{10}H_{14}$ molecule:

$$AlCl_3\cdot DCl(\text{surface}) + B_{10}H_{14} \rightarrow AlCl_3\cdot HCl(\text{surface}) + B_{10}H_{13}D$$

The facile reaction of $B_{10}H_{14}$ with triflic acid suggests a quick and simple way of converting the boron hydride to either the 2,4-dideuterated or the 1,2,3,4-tetradeuterated compound using deuteriotriflic acid based on length of reaction time. We found that the triflic acid can be removed after reaction by adding the reaction mixture to vacuum-dried NaCl and then separating the products by vacuum fractionation. The triflate salt remains as a nonvolatile solid. The volatile products are passed through a trap at −78 °C and one at −196 °C. The HCl passes the −78 °C trap, and the volatiles trapped at −78 °C are then passed through an ice−salt trap to isolate the desired deuterated decaborane product.

Acknowledgment. The authors wish to express their gratitude to Dr. Joel Dopke and Dr. Dovas Saulys for useful discussions and for providing NMR spectra.

IC991032U

---

(10) Linke, W. F. *Solubilities of Inorganic and Organo-Metallic Substances*, 4th ed.; American Chemical Society: Washington, DC, 1958.

(11) Lippmann, E.; Keppich, E. *Ber. Dtsch. Chem. Ges.* **1900**, *33*, 3086. Scholl, R.; Seer, C.; Weitzenboch, H. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 2202. Froschl, N.; Harlass, J. *Monatsh. Chem.* **1932**, *59*, 275. Fairbrother, F.; Frith, W. C. *J. Chem. Soc.* **1953**, 2975. Nenitzescu, C. D.; Cantuniari, E. I. P. *Ber. Dtsch. Chem. Ges.* **1933**, *66*, 1097.

(12) Brown, H. C.; Pearsall, H. W. *J. Am. Chem. Soc.* **1951**, *73*, 4681.

(13) Lauer, W. M.; Matson, G. W.; Stedman, G. J. *J. Am. Chem. Soc.* **1958**, *80*, 6433−6437.

(14) Lauer, W. M.; G. W.; Stedman, G. J. *J. Am. Chem. Soc.* **1958**, *80*, 6439−6441.