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Notes

Deuteration of Decaborane(14) via Exchange with Deuterated Aromatic Solvents

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Introduction

Electrophilic attack on boron hydride clusters in the presence of Friedel−Crafts catalysts has resulted in the regiospecific functionalization of these species.[1] While the chemistry of electrophiles with decaborane(14) has been explored extensively, the regiospecific deuteration of decaborane has been less studied.[2,3] Electrophilic substitution on the decaborane framework occurs at the B1,2,3,4 positions in accordance with calculational studies (Figure 1).[4] Hawthorne et al. published the deuteration of $B_{10}H_{14}$ with DCl in the presence of $AlCl_3$.[3] The exchange is rapid and complete in the presence of excess DCl. However, the handling of DCl requires special equipment, and its facile exchange with proton sources can compromise its isotopic purity.

It has been previously shown that pentaborane(9) deuterates quantitatively in the B1 position in deuterated aromatic solvents in the presence of $AlCl_3$.[5] The byproducts are partially protonated aromatic solvent and small quantities of coupled aromatic species. The exchange here is rapid as well, and the borane product is easily recovered by high-vacuum fractional distillation. While this method has not previously been shown to be efficacious in the deuteration of decaborane, we now report this process as a useful alternative to deuteration via DCl.

Experimental Section

Standard inert atmosphere techniques were utilized unless otherwise noted. Decaborane(14) was acquired from laboratory stock and sublimed prior to use. 6-Thx-$B_{10}H_{13}$ [Thx = tertiary hexyl, 2,3-dimethyl-2-butyl] was synthesized by the published method.[6] Anhydrous $AlCl_3$ (Fisher Scientific) was used as received. Deuterated solvents (C_7D_8, Aldrich Chemicals Co., Inc.; C_6D_6, Cambridge Isotope Laboratories) were distilled from P_2O_5. Benzene (Na) and pentane (CaH_2) were dried using the indicated reagent and distilled immediately prior to use. The ^{11}B NMR (160.4 MHz, referenced externally to $BF_3{\cdot}OEt_2$, $\delta = 0$) and ^2H NMR (76.9 MHz, referenced to solvent resonances) spectra were acquired on a Bruker AM-500 spectrometer. The ^1H NMR (300 MHz) spectra were acquired on a Bruker AC-300 spectrometer and referenced internally to residual solvent peaks.

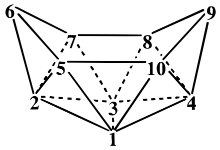

Figure 1. Labeling scheme for decaborane(14). Hydrogens have been omitted for clarity.

NMR-Scale Deuteration Reactions. All NMR-scale deuteration reactions performed were carried out analogously to the reaction of $B_{10}H_{14}$ with C_6D_6 over $AlCl_3$ illustrated here. Under nitrogen, solid $B_{10}H_{14}$ (7.0 mg, 0.06 mmol) and $AlCl_3$ (6.0 mg, 0.05 mmol) were loaded into a 5 mm NMR tube sealed with an O-ring stopcock. The solids were gently tapped to the bottom of the tube, which was then closed, attached to the high-vacuum line, cooled to −78 °C, and evacuated. C_6D_6 (1 mL) was distilled onto the solids and flame-sealed under dynamic vacuum. The tube was thawed and allowed to stand undisturbed except for assay by ^{11}B NMR (every 12 h for the first 4 days and then daily for an additional 14 days).

Synthesis of 1,2,3,4-$D_4B_{10}H_{10}$. Solid $B_{10}H_{14}$ (0.31 g, 2.54 mmol) and excess $AlCl_3$ (0.57 g, 6.84 mmol) were combined in a 50 mL Schlenk flask with a Teflon stir bar. C_6D_6 (10 mL) was distilled into the vessel, which was then fitted with a condenser and refluxed for 14 h during which time the mixture turned dark brown. The benzene was evaporated under nitrogen flow, and the residue was scraped into a sublimator. The solids were sublimed three times under high vacuum at room temperature onto a −78 °C coldfinger to yield 0.24 g (1.90 mmol, 75%) of 1,2,3,4-$D_4B_{10}H_{10}$.

Synthesis of 6-Thx-1,2,3,4-$D_4B_{10}H_9$. A 50 mL Schlenk flask was charged with 6-Thx-$B_{10}H_{13}$ (0.33 g, 1.59 mmol) and $AlCl_3$ (0.14 g, 1.08 mmol). C_6D_6 (10 mL) was distilled directly onto the solids. The pot mixture was refluxed for 16 h, during which time the solution turned brown. The product mixture was cooled, and the benzene was removed under vacuum. The residue was extracted with pentane (3 × 30 mL), concentrated under vaccum, and loaded onto a rotary chromatograph (silica gel). The product was eluted with hexanes and dried in vacuo to give 0.23 g (1.09 mmol, 68%) of the product.

Synthesis of 2,4-$D_2B_{10}H_{12}$. Anhydrous $AlCl_3$ (0.25 g, 1.89 mmol) was placed in a high-vacuum tube and evacuated for 1 h. The vessel was filled with nitrogen, and solid $B_{10}H_{14}$ (0.22 g, 1.80 mmol) was added. The tube was returned to the high-vacuum line, and 4 mL of C_7D_8 was distilled into the tube at −196 °C. The solvent was allowed to melt before the tube was placed in a 5 °C refrigerator. The tube was removed from the refrigerator after 64 h, during which time the contents turned yellow. The volatile components were then separated by fractional distillation (0, −22, and −196 °C) on the high-vacuum line. The product, isolated in the −22 °C trap, was then sublimed under

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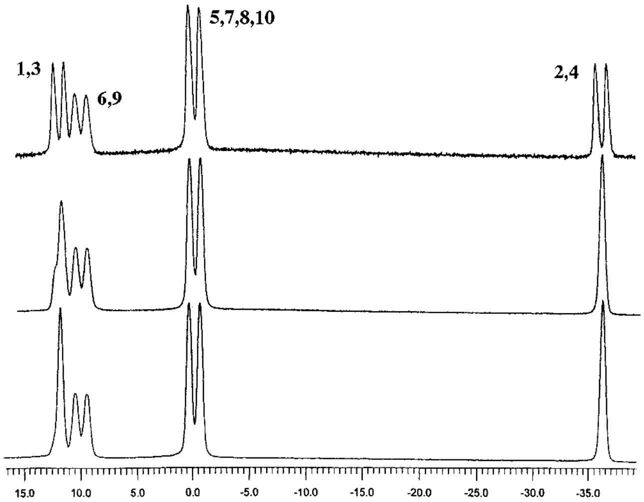

Figure 2. ^{11}B NMR (160 MHz) spectra of $B_{10}H_{14}$ in C_6D_6 in the presence of $AlCl_3$ at room temperature (top), after 2.5 days (middle), and after 13 days (bottom).

high vacuum (−30 and −196 °C) twice to remove residual toluene and provide 2,4-$D_2B_{10}H_{12}$ (0.22 g, 1.77 mmol) in 98% yield.

Results and Discussion

$AlCl_3$ has been shown to facilitate the exchange of deuterium and hydrogen between aromatic solvents and decaborane(14). Furthermore, this process follows the previously established precedent set by other electrophilic substitution chemistry on the $B_{10}H_{14}$ cluster. This conversion is easily monitored by ^{11}B NMR as the B1,2,3,4 doublet resonances collapse to singlets as the protons are replaced by deuterons. No deuterium exchange was noted in samples of $B_{10}H_{14}$ in C_6D_6 over $ZrCl_4$ or $FeCl_3$.

Vacuum-sealed NMR tube samples of $B_{10}H_{14}$ in C_6D_6 in the presence of $AlCl_3$ show complete deuteration at the B2,4 positions within 3 days at room temperature, and complete conversion to 1,2,3,4-$D_4B_{10}H_{10}$ after 13 days (Figure 2). Broadening of the B2,4 doublet is observed within 4 h of the thawing of the reaction tube. No deuterium exchange was noted in samples of $B_{10}H_{14}$ in C_6D_6 in the absence of catalyst over periods greater than one year. Tetradeuteriordecaborane is produced in 14 h in refluxing C_6D_6. Following evaporation of the solvent, the product may be recovered by repeated high-vacuum sublimation in up to 85% yield. If the system is allowed to reflux for extended periods of time (>18 h), some deuterium incorporation in the B5,7,8,10 positions is noted by ^{11}B NMR. As a result, no reactions in refluxing C_7D_8 were pursued. No deuterium incorporation at positions B5,7,8,10 is observed from C_6D_6 in the presence of $AlCl_3$ over a year at room temperature.

Alkyldecaboranes may be deuterated by similar means. Room-temperature reactions of 6-Thx-$B_{10}H_{13}$ with C_6D_6 in the presence of $AlCl_3$ produces 6-Thx-1,2,3,4-$D_4B_{10}H_9$ in 14 days. Purification of the alkylated species is more problematic due to the similar volatility of the product and the residual $AlCl_3$. Elution of the product with hexanes from silica gel on a rotary chromatograph effectively removed all contaminants. As expected, deuteration occurs more rapidly at the B2,4 positions than at the B1,3 positions. The B4 position deuterates slightly more rapidly than the B2 position. This may be attributable to the close proximity of the sterically demanding thexyl moiety residing on the B6 vertex.

Low-temperature reactions were attempted with the intention of isolating regiospecifically deuterated 2,4-$D_2B_{10}H_{12}$ using C_7D_8. Reactions run in a 5 °C refrigerator consistently provided decaborane that was 80% deuterated in the B2,4 positions in 64 h, although deuteration was also observed in the B1,3 positions (∼10% by ^{1}H NMR). The product was separated from residual solvent and $AlCl_3$ and recovered in ca. 95% yield by repeated high-vacuum trap-to-trap sublimation (0, −22, and −196 °C). It is apparent that the lower temperatures have only slightly affected the rate of deuteration, but have not aided in differentiation of the deuteration processes of the B2,4 and B1,3 sites. While the 2,4-$D_2B_{10}H_{12}$ produced by this route may be useful for most labeling experiments, it is unlikely that this route will be effective in the formation of regiospecifically deuterated products as lower temperatures and longer reaction periods are likely necessary.

Samples of 1,2,3,4-$D_4B_{10}H_{10}$ reprotonate when treated with C_6H_6 in the presence of $AlCl_3$ in 13 days, similar to that noted for the deuteration of $B_{10}H_{14}$. Hydrogen incorporation is observed to occur first in the B2,4 positions and then in the B1,3 positions. As a result, one can be expect to synthesize 1,3-$D_2B_{10}H_{12}$ from 1,2,3,4-$D_4B_{10}H_{10}$ in C_7D_8 over $AlCl_3$ at 5 °C. Reactions between 1,2,3,4-$D_4B_{10}H_{10}$ and 6-Thx-$B_{10}H_{13}$ in pentane over $AlCl_3$ showed no definitive evidence for transfer of deuterium between clusters indicating the likelihood that all detuerium transfer is occurring between the solvent and the decaborane moiety.

Conclusion

This study illustrates the facile exchange of deuterium from deuterated aromatic solvent into the basal sites of decaborane in the presence of $AlCl_3$, similar to the deuteration of pentaborane(9). While no investigations into the mechanism for this conversion were undertaken, it is apparent that this process occurs in a fashion similar to that of other electrophilic substitution processes. The availability and relative ease of handling of the reagents make this deuteration procedure a convenient alternative to the previously described DCl/$AlCl_3$ route.

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