Reactions of 6,9-Bis(dimethyl sulfide)-decaborane(14), 6,9-[$(CH_3)_2S]_2B_{10}H_{12}$: Mechanistic Considerations

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Introduction

The bis(dimethyl sulfide) adduct of decaborane (14), 6,9-$B_{10}H_{12}\cdot 2(CH_3)_2S$ (**I**), is one of several compounds that is easily prepared by reacting decaborane ($B_{10}H_{14}$) and a Lewis base.[1] It is probably best known for its reaction with acetylene to produce *o*-carborane (1,2-dicarbadodecaborane).[2] It also undergoes several other interesting reactions. In this paper we have focused on the reaction that forms 6,9-$[(CH_3)_2S]_2B_{10}H_{12}$ (**I**)

$$B_{10}H_{14} + 2(CH_3)_2S \rightarrow 6{,}9\text{-}[(CH_3)_2S]_2B_{10}H_{12} + H_2$$

the pyrolysis of **I** to form 5-$[(CH_3)_2S]B_{10}H_{12}$[3] (**II**)

$$6{,}9\text{-}[(CH_3)_2S]_2B_{10}H_{12} \rightarrow 5\text{-}[(CH_3)_2S]B_{10}H_{12} + (CH_3)_2S$$

and the hydroboration of **I** with an olefin to form 5-$[(CH_3)_2S]$-9-$RB_{10}H_{11}$[4] (**III**)

$$6{,}9\text{-}[(CH_3)_2S]_2B_{10}H_{12} + (CH_3)_2CC(CH_3)_2 \rightarrow 5\text{-}[(CH_3)_2S]\text{-}9\text{-}(\text{Thx})B_{10}H_{11} + (CH_3)_2S$$

$$\text{Thx} = \text{Me}_2\text{HC}(\text{Me}_2)\text{C}-$$

Boron hydride cluster compounds are known to undergo facile rearrangements, including cases where the boron atoms in the cluster exchange positions. An example of this is the exchange of apical and basal borons in the square pyramidal structure of a pentaborane(9) molecule bearing one methyl group, B_5H_8-CH_3.[5] Various mechanisms have been proposed for these kinds of reactions[6] in which nearest cage neighbor atoms separate from each other in a concerted process throughout the molecule and then re-form the cage in a different arrangement. An elegant proposal for this is the diamond−square−diamond mechanism of Lipscomb and co-workers.[7] In the icosahedral carboranes, the transient intermediate in this mechanism is a cuboctahedron. More recent experimental studies have led to a variety of other mechanistic postulates.[8] An alternative kind of rearrangement is the movement of substituent atoms or groups from one boron of the cage to another with no rearrangement of the atoms in the cage.

The thrust here is to determine the nature of cluster rearrangements that might occur during the reactions described above. The dideuterated adduct of decaborane, 2,4-$D_2B_{10}H_{12}$, produced by electrophilic substitution of $B_{10}H_{14}$,[9] was used, with ^{11}B NMR analysis, to probe the nature of these reactions. We have considered whether the deuterium atoms might migrate around the boron cage under the conditions employed in the reactions reported here. Electrophilic substitution of decaborane(14) requires a Lewis acid catalyst such as $AlCl_3$. The ultimate product of electrophilic deuteration is 1,2,3,4-$D_4B_{10}H_{10}$. (Decaborane(14) can also be deuterated under base-catalyzed conditions, and in this case the ultimate product has deuteriums at all four bridges and at boron atoms 5, 6, 7, 8, 9, and 10.[10]) We have assumed that the conditions of our reactions would not provide circumstances in which H atoms on the B_{10} cage would be labile and thus exchange.

The bis(dimethyl sulfide) adduct, 6,9-$[(CH_3)_2S]_2$-2,4-$D_2B_{10}H_{10}$, was prepared by reaction of 2,4-dideuteriodecaborane(14), 2,4-$D_2B_{10}H_{12}$, with excess dimethyl sulfide for 2 days. Comparison of its ^{11}B NMR spectrum with that of the undeuterated compound (**I**)[11] clearly showed that the absence of $^1H-^{11}B$ splitting of the B(2,4) resonance indicated that the deuterium atoms were still bonded to those atoms and, therefore, the reaction is a hydrogen displacement reaction involving hydrogen rearrangement on the open face of the decaborane cluster but involving no scrambling or rearrangement of the basal boron atoms, B(1,2,3,4).

6,9-$[(CH_3)_2S]_2$-2,4-$D_2B_{10}H_{10}$ was then dissolved in mesitylene, and the solution was heated at 110 °C for 3 h to form the deuterated derivative of **II**, 5-$[(CH_3)_2S]B_{10}H_{12}$. Comparison of the ^{11}B NMR spectrum of the deuterated product with that of undeuterated **II**[12] showed that the two deuterium atoms were still bonded to boron atoms 2 and 4; thus 6,9-$[(CH_3)_2S]_2$-2,4-$D_2B_{10}H_{10}$ converts to 5-$(CH_3)_2S$-2,4-$D_2B_{10}H_{10}$. This reaction, which includes the loss of one $(CH_3)_2S$ and shift of the other molecule of $(CH_3)_2S$ from boron atom 6 or 9 to boron 5, could involve a rearrangement of the B_{10} cage or a migration of the $(CH_3)_2S$ molecule from one boron atom to another. The NMR results show clearly that the basal atoms of the decaborane cage do not undergo rearrangement. This observation augers for $(CH_3)_2S$ migration unless the boron atoms around the open edge

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(11) For 6,9-$[(CH3)_2S]_2B_{10}H_{12}$, ^{11}B NMR at 160 MHz in CH_2Cl_2 (atom number, chemical shift in ppm (coupling constant in Hz)): 2,4, −3.9 (120); 5,7,8,10, −19.8 (123); 6,9, −24.0 (105); 1,3, −40.2 (131).

(12) For 5-$[(CH_3)_2S]B_{10}H_{12}$, ^{11}B NMR at 160 MHz in CH_2Cl_2 (atom number, chemical shift in ppm (coupling constant in Hz)): 6, +21.8 (br); 1, +5.0 (149); 9, +2.2 (155); 5, +0.3 (br); 3, −3.9 (137); 8, −5.8 (br); 7, −6.2 (br); 10, −11.0 (137); 2, −28.0 (149); 4, −42.0 (160).

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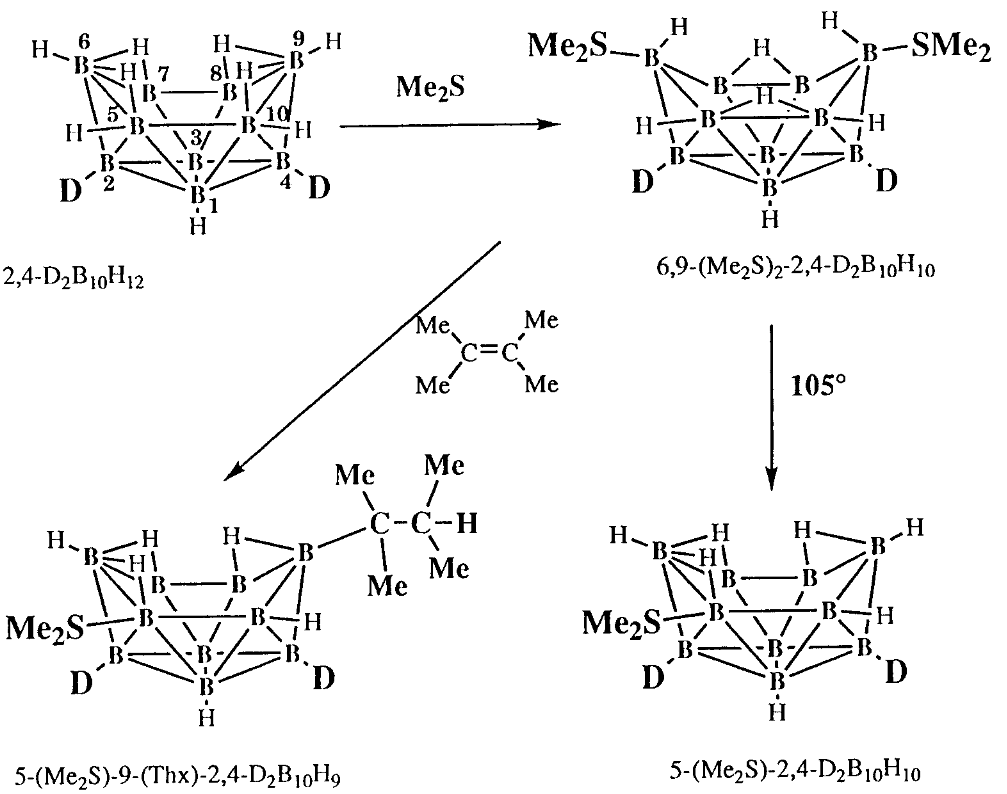
Scheme 1



of the decaborane cluster can interchange without disruption of the basal boron atom positions. To test this possibility will require synthesis of a boron isotopically labeled decaborane in which the boron label is in a regiospecific location in the cluster face, preferably in the B(6,9) location(s). Synthetic routes to such boron isotopically labeled decaboranes are not as yet known.

Another sample of 6,9-$[(CH_3)_2S]_2$-2,4-$D_2B_{10}H_{10}$ was then dissolved in a small amount of methylene chloride, and the solution was placed in an NMR tube. An excess of 2,3-dimethyl-2-butene was added to the tube, and the mixture was allowed to react at room temperature for 3 days. Comparison of the ^{11}B NMR spectrum of the reaction mixture with a known ^{11}B NMR spectrum of 5-$[(CH_3)_2S]$-9-(Thx)$B_{10}H_{11}$[13] showed that the product was 5-$[(CH_3)_2S]$-9-(Thx)-2,4-$D_2B_{10}H_9$ in which the deuterium atoms were still located on the 2- and 4-borons. These observations lead to the suggestion that the hydroboration most likely occurs at the B(9) position and that the movement of the $(CH_3)_2S$ molecule from boron 6 to boron 5 does not involve a concerted rearrangement of the boron cage but rather a migration of hydrogen and $(CH_3)_2S$ on an otherwise static borane cluster.

Conclusion

Scheme 1 shows the structural representations of the reactions in this investigation. We are not aware of any experimentally verified indications of rearrangements of the boron atoms of the decaborane(14) cage under any reaction conditions, in contrast to the rather facile cluster rearrangements of some other borane clusters, such as pentaborane(9) derivatives. In fact, the decaborane(14) cage appears to be essentially static under ordinarily encountered reaction conditions. At this juncture, it appears that nucleophilic hydrogen displacement (formation of **I**), thermal adduct loss (formation of **II**), and hydroboration of **I** (formation of **III**) most likely occur with local hydrogen migration, but with no movement of basal boron atoms or their substituents, and that dimethyl sulfide movement during the formation of **II** and **III** occurs via group migration. Apparently, the *nido* structure of decaborane(14) is less easily isomerized by cage rearrangement than the *closo* structures of the icosahedral carboranes.

Experimental Section

All operations were conducted in a conventional high-vacuum line or under a nitrogen atmosphere. Decaborane was sublimed in high vacuum prior to use. Other reagents were used as received from the manufacturers. The ^{11}B NMR spectra were recorded at 160.15 MHz on a Bruker AM-500 spectrometer or at 115.15 MHz on a Bruker AM-360 spectrometer. $^{11}B-^{11}B$ COSY spectra were recorded and analyzed by methods standard in this research group.[14] 2,4-$D_2B_{10}H_{12}$ was prepared by exchange of $B_{10}H_{14}$ with C_6D_6 in the presence of $AlCl_3$.[15] 6,9-$[(CH_3)_2S]_2$-2,4-$D_2B_{10}H_{10}$ was prepared by the method first described by Schaeffer[1] to prepare 6,9-$(CH_3CN)_2B_{10}H_{12}$ except that the reaction occurred at room temperature over several days. In a typical experiment 2,4-$D_2B_{10}H_{12}$ was condensed into an NMR tube sealed to a U-tube on the vacuum line. An excess of dry $(CH_3)_2S$ (dried over CaH_2 and distilled through a −63 °C cold trap before use) was condensed into the NMR tube. Upon warming of the sample to room temperature, a clear solution formed that slowly produced H_2 and a precipitate. Excess $(CH_3)_2S$ was subsequently evaporated, and the product, 6,9-$[(CH_3)_2S]_2$-2,4-$D_2B_{10}H_{10}$, was dissolved in CH_2Cl_2. The NMR tube was sealed, and the product was verified by ^{11}B NMR analysis.

The method of Knoth and Muetterties[3] for preparation of 5-$[(CH_3)_2S]$-$B_{10}H_{12}$ was used to prepare 5-$[(CH_3)_2S]$-2,4-$D_2B_{10}H_{10}$ from 6,9-

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(13) For 5-$[(CH_3)_2S]$-9-(Thx)$B_{10}H_{11}$, ^{11}B NMR at 115 MHz in CH_2Cl_2 (atom number, chemical shift in ppm (coupling constant in Hz)): 6, +19.0 (br); 9, +11.7; 1, +4.4 (137); 8, +0.4; 5, +0.4 (br); 7, −4.6 (137); 3, −5.8 (146); 10, −13.5 (137); 2, −31.4 (142); 4, −41.0 (147).

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$[(CH_3)_2S]_2$-2,4-$D_2B_{10}H_{10}$. The product composition was determined by comparison of its ^{11}B NMR spectrum with that of authentic 5-$[(CH_3)_2S]$-$B_{10}H_{11}$.[16]

Likewise, the method of Bridges et al.[17] was used to prepare 5-$[(CH_3)_2S]$-9-(Thx)-2,4-$D_2B_{10}H_9$ from 6,9-$[(CH_3)_2S]_2$-2,4-$D_2B_{10}H_{10}$ by reaction with 2,3-dimethyl-2-butene. The product composition was determined by comparison of its ^{11}B NMR spectrum with that of authentic 5-$[(CH_3)_2S]$-9-(Thx)$B_{10}H_{11}$.

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Supporting Information Available: ^{11}B NMR spectra of 6,9-$[(CH_3)_2S]_2$-2,4-$D_2B_{10}H_{10}$, 5-$[(CH_3)_2S]$-2,4-$D_2B_{10}H_{10}$, and 5-$[(CH_3)_2S]$-9-(Thx)-2,4-$D_2B_{10}H_9$ (3 pages). Ordering information is given on any current masthead page.

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