Inorg. Chem. **1981**, *20*, 745–748

Table VIII

ρ, e/Å^3	*x*/*a*	*y*/*b*	*z*/*c*	relative location
0.141	0.444	0.344	−0.037	B(2)–B(7)–B(12)
0.130	0.349	0.373	−0.039	B(2)–B(12)–B(13)
0.127	0.391	0.272	−0.167	B(3)–B(11)–B(12)
0.121	0.476	0.310	0.069	B(2)–B(6)–B(7)
0.119	0.432	0.359	0.156	B(1)–B(2)–B(6)
0.117	0.977	0.187	−0.070	[a]
0.116	0.323	0.403	0.160	B(1)–B(13)–B(14)
0.113	0.502	0.290	−0.271	B(3)[b]
0.112	0.369	0.293	−0.142	B(3)–B(11)–B(12)
0.104	0.514	0.029	−0.106	B(8)[b]
0.100	0.402	0.399	0.100	B(1)–B(2)–B(13)

[a] More than 2 Å from any boron atom. [b] Not located in B–B–B face, but close (within 1.5 Å) to designated B.

The resultant strain on the bonding environment around B(7) and B(12) accounts for not only the planarity of the junction but also the rather long B–B distances involving these borons. One might expect this juncture to be a reactive site for the molecule, but the paucity of sample precluded reaction studies. The molecule nearly possesses C_{2v} symmetry in the solid state; however, nonbonded constraints cause significant deviations such that the actual molecular symmetry observed is only C_2. The significance of nonbonded interactions on the structures of boranes is discussed more fully elsewhere.[24] The observance of only five resonances in the room-temperature ^{11}B NMR spectra of $B_{14}H_{20}$ is consistent with a molecule of approximate C_{2v} symmetry.

A final difference Fourier synthesis revealed the 11 peaks over 0.1 e/Å^3 which are listed in Table VIII. It is to be noted that, for all peaks above 0.1 e/Å^3, only one is not associated with the boron cage, and most lie in B–B–B triangles, suggestive of residual electron density from three-center bonding. Similar peaks have been observed in other borane structures,[25] and X–N (X-ray–neutron) difference maps have shown similar features for decaborane(14).[26]

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Registry No. $B_{14}H_{20}$, 55823-36-4; KB_6H_9, 12447-66-4; B_8H_{12}, 19469-16-0.

Supplementary Material Available: Table VI, a listing of angles involving hydrogen atoms, and Table VII, listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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(24) (a) John C. Huffman, Ph.D. Thesis, Indiana University, 1974; (b) John C. Huffman, manuscript in preparation.

(25) (a) J. C. Huffman, L. G. Sneddon, and R. Schaffer, *J. Chem. Soc., Chem. Commun.*, **8**, 474–475 (1972) ($B_{10}H_{13}^-$); (b) M. R. Churchill and B. G. Deboer, *Inorg. Chem.*, **12**, 2674 (1973).

(26) Von R. Brill, H. Dietrich, and H. Dierks, *Acta Crystallogr., Sect. B*, **B27**, 2003 (1971).

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Studies of Boranes. 48.[1] Reactions of Hexaborane(10) with Lewis Acids to Yield Acid–Base Complexes and Synthesis of Halogenated Hexaborane(10) Derivatives via Halogen-Transfer Reactions[2]

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Hexaborane(10) has been shown to complex with a variety of Lewis acids including BCl_3, B_2Cl_4, BBr_3, BI_3, $Al(CH_3)_3$, $Al(C_2H_5)_3$, and $Al(i\text{-}C_4H_9)_3$ and remains uncomplexed in the presence of $(CH_3)_3B$, $(C_2H_5)_3B$, and BF_3. The BBr_3 and BI_3 complexes undergo halogen exchange with B_6H_{10} and its derivatives to form BrB_6H_9, IB_6H_9, $I_2B_6H_8$, and other halogenated species. The reaction of excess B_6H_{10} with BI_3 has also been found to produce $B_{13}H_{19}$ in up to 40% yields. Chlorine gas reacts with KB_6H_9 to form ClB_6H_9.

Introduction

The pyrolysis of diborane has traditionally been the method of synthesis of various boranes. One of the unusual features of this reaction is the fact that hydrides containing six to nine boron atoms are almost entirely missing among the pyrolysis products. The Bronsted basicity of hexaborane(10) suggested by Lipscomb and the general Lewis basicity implied by work of Davison and of Shore may play a role in the pyrolysis reaction.[3] Recent investigations in this laboratory provide some support for this suggestion in that it has been shown that hexaborane(10) can be used for the synthesis of $n\text{-}B_9H_{15}$ and the preparation of the new hydrides $B_{14}H_{22}$ and $B_{15}H_{23}$, although at much lower temperature than used in diborane pyrolysis.[4] Furthermore, the basicity of hexaborane(10) is important in the formation of $B_{13}H_{19}$.[5] The present study was undertaken to explore more fully the characteristics of hexaborane(10) as a Lewis base. Several hexaborane derivatives were made and reacted with a range of Lewis acids to accomplish this task.

Experimental Section

Apparatus and Materials. Standard high-vacuum techniques were used throughout this investigation. Mass spectra were measured on an AEI MS-9 mass spectrometer at 70 eV, and ^{11}B nuclear magnetic resonance spectra were recorded on a Varian Associates HR-220

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(1) For part 47 in this series see J. C. Huffman, D. C. Moody, and Riley Schaeffer, *Inorg. Chem.*, preceding paper in this issue.

(2) Riley Schaeffer, David C. Moody, and Patrick J. Dolan, *Pure Appl. Chem.*, **39**, 423 (1974).

(3) W. N. Lipscomb, *J. Chem. Phys.*, **28**, 170 (1958); A. Davison, D. D. Traficante, and S. S. Wreford, *J. Am. Chem. Soc.*, **96**, 2802 (1974); H. D. Johnson, II, V. T. Brice, G. L. Brubaker, and S. G. Shore, *ibid.*, **94**, 6711 (1972).

(4) J. Rathke and R. Schaeffer, *Inorg. Chem.*, **13**, 3008 (1974).

(5) J. Rathke, D. C. Moody, and R. Schaeffer, *Inorg. Chem.*, **13**, 3040 (1974).

0020-1669/81/1320-0745$01.00/0

spectrometer at 70.6 MHz equipped with a "home-built" pulse apparatus. A Perkin-Elmer Infracord spectrophotometer was used for IR identification. Hexaborane(10), methylhexaborane, KB_6H_9, diboron tetrachloride, and octaborane(12) were prepared by literature methods.[6-9] (In the case of substituted hexaboranes, as either reactants or products, all were basal substituted. Since at room temperature, rapid equilibration occurs among several positions, we have avoided specifying a specific isomer in any case; i.e., 2-$CH_3B_6H_9$ is referred to simply as $CH_3B_6H_9$ or methylhexaborane.) Laboratory samples of BBr_3, Me_3B, and Et_3B were used for the reactions described. BI_3 was obtained in low purity from Columbia Organics and purified by sublimation through a 4 in. long tube packed with copper wool. Trimethylaluminum was obtained from Ethyl Corp. and used without purification. Triethyl- and triisobutylaluminum were obtained from Texas Alkyls and transferred in a nitrogen-filled glovebag. Chlorine, BCl_3, and BF_3 were obtained from Matheson Co. and purified by trap to trap fractionation before use. Reagent grade methylene chloride and *n*-pentane solvents were purified by vacuum distillation from P_2O_5.

Reactions of B_6H_{10} with the Boron Trihalides. [All halogenated hexaboranes prepared in this work are basal substituted. We avoid specific designations such as 2-BrB_6H_9 since the molecules are fluxional and more would be implied than is in fact known.] A mixture of B_6H_{10} and excess BF_3 in a sealed tube was a clear solution at temperatures between −64 and −95 °C. Fractionation of that mixture returned the starting materials quantitatively. In contrast, a solid formed when 1 mmol of B_6H_{10} and a 10-fold excess of BCl_3 were condensed together in an NMR tube. The presence of the solid was highly temperature dependent: above −20 °C the mixture was a colorless solution. Recooling the solution below −20 °C caused precipitation. During several weeks at room temperature or on subsequent heating to 60 °C for 1 week, the only reaction that occurred was the decomposition of B_6H_{10}.

When a tube containing 5.49 mmol of B_6H_{10} and 3.2 mL of BBr_3 was warmed to room temperature, a precipitate formed, yet a ^{11}B NMR spectrum of that slurry both at room temperature and at −45 °C showed only B_6H_{10} and BBr_3. The solid slowly dissolved over a period of hours at room temperature. The mixture was allowed to remain at ambient laboratory temperature for 4 days before it was fractionated to yield 3.86 mmol of H_2, traces of HBr and B_5H_9, and 3.91 mmol of BrB_6H_9 (71% yield). The measured density of BrB_6H_9 is 1.23 ± 0.03 g/mL. The ^{11}B NMR and mass spectra confirmed the identity between BrB_6H_9 formed in our halogen-transfer reaction and that previously reported in 10% yield from reaction of B_6H_{10} with Br_2.[10] Use of a solvent such as CH_2Cl_2 or pentane leads to slower reaction with greater decomposition. Heating the reaction mixture to 70 °C causes sublimation of what appears to be the $B_6H_{10}{\cdot}BBr_3$ adduct and formation of small amounts of $BrB_{13}H_{18}$.

An excess (3.42 mmol) of B_6H_{10} was condensed into a tube containing 0.24 mmol of freshly sublimed BI_3. When the sealed tube was warmed to room temperature, the mixture yellowed and bubbled vigorously. A ^{11}B NMR spectrum of the contents of that tube showed that all the BI_3 had been consumed within 5 h. Hydrogen (0.29 mmol) was removed and the material fractionated through a −35 °C trap. Unreacted B_6H_{10} (2.22 mmols) passed and 0.56 mmol of IB_6H_9 was retained as well as an unmeasured trace of $B_{13}H_{19}$. An increase in the reaction time resulted in an increase in the amount of $B_{13}H_{19}$ formed; yields up to 40% were obtained. If the reaction mixture is heated, trace amounts of $IB_{13}H_{18}$ (detected by a mass spectrum) are formed. The yield of IB_6H_9 based on BI_3 was 78%.

The identity of the IB_6H_9 was established by its mass spectrum, terminating in the molecular ion $^{11}B_6H_9{}^{127}I$ at 202 amu (exact mass 202.0290, calcd mass 202.0307) and with a base peak at 201 amu. The ^{11}B NMR spectrum consists of a doublet of area 2 at −20.2 ppm[11] (J = 153 Hz), a singlet of area 1 at −8.5 ppm, a doublet of area 2 at −7.1 ppm (J = 161 Hz), and a doublet of area 1 at +48.3 ppm (J = 159 Hz). The density at 0 °C is 1.7 ± 0.1 g/mL, and its melting point is −21.5 to −23.0°C. Iodohexaborane(10) decomposes slowly on exposure to air or moisture, or when allowed to remain at room temperature for several hours.

Synthesis of ClB_6H_9. Into a well-stirred solution of 0.5 mmol of KB_6H_9 in dimethyl ether at −80 °C, 0.5 mmol of chlorine gas was admitted *very slowly*. (*Caution*! *Rapid* Introduction *of chlorine into the ether solution results in minor explosions.*) Chlorohexaborane(10) was recovered and was purified (from a $HBCl_2$ etherate byproduct) by passing it through a −30 °C trap into one held at −63°C. The reaction does not proceed in CH_2Cl_2.

A ^{11}B NMR spectrum of ClB_6H_9 consists of a singlet and three doublets, areas 1:2:2:1, at −32.3, −15.9 (J = 160 Hz), −5.6 (J = 160 Hz), and +48.8 ppm (J = 160 Hz), respectively. Its mass spectrum displayed several boron envelopes, the highest of which contained the base peak at 106 amu and the parent at 112 amu (exact mass 112.0918, calcd mass 112.0922).

Reaction of B_6H_{10} and B_2Cl_4. An excess (1 mmol) of B_6H_{10} and 0.4 mmol of B_2Cl_4 were condensed into an NMR tube and the tube was sealed. Although initially colorless, the mixture abruptly turned yellow and bubbled vigorously as it was warmed toward 0 °C.[12] A ^{11}B NMR spectrum revealed mainly the presence of B_6H_{10} and BCl_3; however, fractionation of this reaction mixture also yielded an oily yellow liquid which decomposed to $B_{10}H_{14}$ after a few hours at room temperature. When the reaction was repeated and warmed more slowly a solid formed that did not dissolve before the mixture began to turn yellow and bubble at −30 °C. Other than a trace of $B_{13}H_{19}$, $B_{10}H_{14}$ was the only stable product recovered.

Reaction of 0.49 mmol of B_6H_{10} with an excess (1 mL) of B_2Cl_4 at −80 °C formed a white solid. Materials volatile at −45 °C were removed, and a ^{11}B NMR spectrum of the remaining solid dissolved in CH_2Cl_2 at −45 °C showed no free B_2Cl_4. The NMR pattern appeared to be that of a single species (not ClB_6H_9). When this material was allowed to warm to room temperature, it dissociated into B_6H_{10} and the decomposition products of B_2Cl_4: BCl_3 and B_4Cl_4. Allowing a solution of B_6H_{10} in excess B_2Cl_4 to warm toward 0 °C to encourage the solid adduct to dissolve caused significant yellowing. Nothing other than B_2Cl_4 and boron polymer were recovered from this mixture.

Treatment of B_6H_{10} with $(C_2H_5)_3B$. Approximately 0.5 mmol of B_6H_{10} was condensed together with an excess (about 5 mmol) of $(C_2H_5)_3B$ in an NMR tube, and the tube was sealed. Since no reaction at room temperature was detectable by ^{11}B NMR even after several weeks, the tube was heated to 100 °C for 1 week. Only decomposition of B_6H_{10} was observed.

Reaction of B_6H_{10} with $(CH_3)_3Al$, $(C_2H_5)_3Al$, and $(i\text{-}C_4H_9)_3Al$. Cocondensation of 0.6 mmol of B_6H_{10} with an excess (3 mmol) of $(CH_3)_3Al$ into an NMR tube formed an adduct, detectable both by solid formation and by new resonances observed in a ^{11}B NMR spectrum of this mixture. A large amount of trimethylboron was isolated from the reaction products, but no $CH_3B_6H_9$ was present.

An NMR tube was loaded with 0.5 mmol of B_6H_{10} and excess $(C_2H_5)_3Al$. When the tube was warmed to room temperature, it continued heating of its own accord and became very hot. Though the ^{11}B NMR spectrum of this reaction mixture was similar to that of the complex formed between $(i\text{-}C_4H_9)_3Al$ and B_6H_{10} (see the following paragraph), only $(C_2H_5)_3B$ could be isolated.

Approximately 0.1 mmol of B_6H_{10} was condensed into the bottom of an NMR tube, and an excess (0.45 mL) of triisobutyl aluminum was poured onto this with use of standard Schlenk techniques.[13] The complex that formed and dissolved was stable for 1 week at room temperature in $(i\text{-}C_4H_9)_3Al$ solution. Evidence for the complex is given by its ^{11}B NMR spectrum, which consists of four doublets whose relative areas are 1:2:2:1 at chemical shifts of +8.6 (J = 140 Hz), +12.7 (J = 180 Hz), +16.4 (J = 120 Hz), and +44.6 ppm (J = 180 Hz), respectively.

Treatment of ClB_6H_9 with BCl_3, BBr_3, and BI_3. Treatment of approximately 0.5 mmol of ClB_6H_9 with a large excess (0.25 mL) of BCl_3 in an NMR tube gave no indication of complexation.

Cocondensation of 0.1 mmol of ClB_6H_9 with an excess (0.3 mL) of BBr_3 in an NMR tube showed visual signs of complexation (solid formation). A ^{11}B NMR spectrum of this mixture after it had

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(6) H. D. Johnson, II, V. T. Brice, and S. G. Shore, *Inorg. Chem.*, **12**, 689 (1973).

(7) H. D. Johnson, II, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, **98**, 908 (1970).

(8) J. P. Brennan, Ph.D. Thesis, Indiana University, 1973.

(9) J. E. Dobson, P. C. Keller, and R. Schaeffer, *Inorg. Chem.*, **7**, 399 (1968).

(10) V. T. Brice, H. D. Johnson, II, and S. G. Shore, *J. Am. Chem. Soc.*, **95**, 6629 (1973).

(11) Referenced vs. external $BF_3{\cdot}O(C_2H_5)_2$. Positive shifts are taken to higher field.

(12) The temperature at which B_2Cl_4 disproportionates to BCl_3 and B_4Cl_4.

(13) D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, 1969.

remained at room temperature for 20 h contained peaks attributable to Br_2BCl and BrB_6H_9 as well as those belonging to ClB_6H_9. After 1 week at room temperature approximately 45% of the ClB_6H_9 had been converted to BrB_6H_9. No evidence was observed for a dihalogen species.

Into a small tube were placed 0.03 mmol of ClB_6H_9, about 0.1 mmol of BI_3, and 1.5 mL of pentane. Fractionation of that mixture after 20 h at room temperature yielded small amounts of BCl_3 and IB_6H_9 which were separated from the remaining ClB_6H_9 and identified by their mass spectra.

Reaction of BrB_6H_9 with BBr_3 and BI_3. One-half millimole of BrB_6H_9 was condensed into a tube with an excess (about 3 mmol) of BBr_3, and the tube was sealed. Although no reaction had occurred after 2 weeks at room temperature, when the tube was heated to 55 °C for several hours, both HBr and $B_{10}H_{14}$ were formed.

Reaction of 0.58 mmol of BrB_6H_9 with 0.19 mmol of BI_3 occurred with immediate bubbling and yellowing, but no IB_6H_9 was obtained. In contrast, reaction of BrB_6H_9 with an excess of BI_3 gave almost exclusively IB_6H_9 (identified by its ^{11}B NMR spectrum) plus some $I_2B_6H_8$ and $IBrB_6H_8$ detected by their mass spectra.

Treatment of BrB_6H_9 with B_3H_7. $B_3H_7{\cdot}(CH_3)_2O$ (0.58 mmol) was generated as described elsewhere.[14] Onto this was condensed 3 mmol of BF_3 and an excess (5 mmol) of BrB_6H_9. Warming to room temperature followed by thorough mixing resulted in some bubbling, but fractionation yielded only $BF_3{\cdot}(CH_3)_2O$, BrB_6H_9, and the known decomposition products of B_3H_7.[14] No evidence for the formation of BrB_9H_{14} was observed, in contrast to known reaction of the parent B_6H_{10}.[4]

Treatment of BrB_6H_9 with B_8H_{12}. Cocondensation of about 3 mmol each of BrB_6H_9 and B_8H_{12} showed no signs of complexation detectable either by visual means or by use of ^{11}B NMR.

Treatment of IB_6H_9 with BCl_3, BBr_3, and BI_3. Cocondensation of about 0.5 mmol of IB_5H_9 with an excess (0.5 mL) of BCl_3 showed no visual or ^{11}B NMR spectral signs of complexation or reaction even after 1 week at room temperature.

An excess of BBr_3 (about 0.75 mL) was condensed onto about 2 mmol of IB_6H_9, and the mixture was allowed to warm to room temperature where it became a colorless solution. A few minutes later a solid began to precipitate. The solid redissolved, and crystals began to form. Hydrogen was evolved in the reaction. Repeated trap to trap fractionation showed (by IR, NMR, and/or mass spectra) that the mixture contained $IBBr_2$, about 35% BrB_6H_9, 60% IB_6H_9, and a trace of what appears to be $IBrB_6H_8$.

Both IB_6H_9 and B_6H_{10} react neat with an excess of BI_3 to form $I_2B_6H_8$. Addition of a solvent does not appear to aid the reaction.[15] The moderately air-stable white needles (mp 101 °C) gave a mass spectrum, whose highest boron envelope contained the base peak at 327 amu and parent at 328 amu. The ^{11}B NMR spectrum of $I_2B_6H_8$ consists of a doublet of area 2 at −19.0 ppm (J = 165 Hz), a singlet of area 2 at −11.4 ppm, and two doublets each of area 1 at +3.47 (J = 160 Hz) and +32.2 ppm (J = 165 Hz). Difficulty retaining mounted crystals allowed us only to begin X-ray analysis. Rapid scan data gave the space group $P2_1/c$ and the cell constants a = 5.942, b = 11.102, and c = 14.546 Å and a β angle of 114.8°.

Reaction of $CH_3B_6H_9$ with BCl_3, BBr_3, and BI_3. About 0.5 mmol of $CH_3B_6H_9$ and 0.5 mL of BCl_3 were condensed into a tube and warmed. A white solid formed which dissolved within 24 h. The ^{11}B NMR spectrum of the solution gave no evidence of a complex.

In a similar experiment using BBr_3 in place of BCl_3 a solid was formed. After 3 days the contents of this tube were fractionated through a −35 °C trap to give a mixture of $CH_3B_6H_8Br$ isomers, according to mass spectral and ^{11}B NMR analyses.

When an excess (about 0.5 mL) of $CH_3B_6H_9$ was condensed onto about 0.1 mmol of BI_3, the mixture yellowed rapidly and a precipitate first formed and then redissolved. A purple color (reminiscent of I_2) appeared for a few moments and then disappeared. A large amount of H_2 was generated along with several other products. B_2H_6 and B_5H_9 were detected by IR analysis, in addition to the recovered $CH_3B_6H_9$. There was also a yellow oil of low volatility that could not be characterized. During the several attempts to purify this yellow substance a white solid appeared that was very poorly soluble in CH_2Cl_2. Mass spectra as well as ^{11}B NMR spectra showed that the white solid was a mixture of isomers of $ICH_3B_6H_8$ and $I_2CH_3B_6H_7$.

Reaction of $CH_3B_6H_9$ with B_3H_7. The reaction of B_4H_{10} with tetrahydrofuran was used to make 2.66 mmol of the B_3H_7-THF adduct. A large excess of $CH_3B_6H_9$ and 7 mmol of BF_3 were condensed on top of the solid adduct, and the resulting mixture was held at 0 °C for 1 h. Hydrogen (0.75 mmol) was formed. Trap to trap fractionation of the volatile products (−30 and −80 °C traps) separated excess $CH_3B_6H_9$ from $CH_3B_9H_{14}$. Analysis by ^{11}B NMR indicated the presence of two isomers of $CH_3B_9H_{14}$. This mixture of isomers decomposes above 0 °C.

Reaction of $B_{15}H_{23}$ with Diethyl Ether. Condensation of 2.0 mL of diethyl ether onto about 0.7 mmol of $B_{15}H_{23}$[4] at 0 °C, followed by stirring for 0.5 h at that temperature, gave a slight yellow solution. The volatile products were diethyl ether and B_6H_{10}, and a ^{11}B NMR spectrum of an ether solution of the nonvolatile residue was identical with that of $B_9H_{13}{\cdot}O(C_2H_5)_2$.[9]

Results and Discussion

We felt it worthwhile to compare the Lewis base properties of hexaborane to other Lewis bases. When B_9H_{13} was employed as the Lewis acid, B_6H_{10} was shown to be a weaker base than diethyl ether or CO, since diethyl ether replaced B_6H_{10} from $B_{15}H_{23}$ quantitatively and B_6H_{10} could not displace CO from $B_9H_{13}CO$.[16]

Another way of "measuring" the Lewis basicity of a compound is by noting its reactivity with a series of Lewis acids of varying strength. This is an especially useful technique for weakly basic compounds such as hexaborane, for sufficiently weak acids can be chosen such that a weak base will not react with them. This eliminates the Lewis equivalent of the "leveling effect" of the Bronsted acid–base theory.

Given the experimentally determined[17] increase in Lewis acidity as one proceeds through the series[18] BF_3, BCl_3, BBr_3, BI_3, and B_2Cl_4, one would expect that a complex of B_6H_{10} would be weakest with BF_3. We have found no indication of the formation of a complex between BF_3 and B_6H_{10}, nor did G. L. Brubaker in other experiments with this system.[19] This information has been used advantageously in synthesis, for BF_3 can be used to remove Lewis bases stronger than B_6H_{10} from a reaction mixture without affecting the B_6H_{10}.[4] Although BCl_3 was observed to form a solid complex with B_6H_{10} (as earlier noted by Shore and Brubaker[3,19]), that complex is temperature dependent even in liquid BCl_3. The complex dissociates in a vacuum, and the ^{11}B NMR spectrum of a mixture of B_6H_{10} and BCl_3 shows only peaks attributable to uncomplexed B_6H_{10} and BCl_3—even when the temperature was lowered to −40 °C. The two compounds can be recovered from the complex even after prolonged storage at room temperature. No halogen transfer is seen even under forcing conditions of heat or pressure.

Reaction of B_6H_{10} with an excess of the stronger Lewis acid BBr_3 results not only in solid formation but also in halogen transfer. This reaction generates BrB_6H_9 in much higher yield than has been previously obtainable from direct bromination of hexaborane(10) by Br_2.[10] Nevertheless, no evidence for a complex is seen in a ^{11}B NMR spectrum of that reaction mixture or in reactions run in a solvent such as pentane or in excess B_6H_{10}—all of which indicates that the complex is significantly dissociated in solution. BI_3, on the other hand, reacts so readily with B_6H_{10} that even in excess B_6H_{10} formation of a solid complex is immediately observed. Halogen transfer also proceeds much faster than in the case of BBr_3, resulting in the generation of IB_6H_9 in high yield. Prolonged reaction

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(14) W. R. Deever and D. M. Ritter, *Inorg. Chem.*, 7, 1036 (1968).

(15) When this reaction was carried out in CH_2Cl_2, BI_3 reacted with the CH_2Cl_2 to form BCl_3, CH_2ClI, and CH_2I_2.

(16) P. J. Dolan, D. C. Moody, and R. Schaeffer, unpublished results; R. Schaeffer and E. Walter, *Inorg. Chem.*, **12**, 2209 (1973).

(17) E. L. Muetterties, "The Chemistry of Boron and Its Compounds", Wiley, New York, 1967, p 333.

(18) Mixed trihalides such as $ClBBr_2$ were not used because they tend to dissociate to the unmixed halides, and this would only complicate the study.

(19) G. L. Brubaker, Ph.D. Thesis, The Ohio State University, 1971.

of BI_3 with excess B_6H_{10} has also been found to yield $B_{13}H_{19}$ in up to 40% yield. Although mechanistically puzzling, this latter reaction constitutes the best currently available procedure for the preparation of $B_{13}H_{19}$. Though there is no doubt that a complex forms between B_6H_{10} and B_2Cl_4, nothing but decomposition products have been isolated at room temperature, and low-temperature investigations were hindered by solubility problems. Perhalogenation of the B_6H_{10} framework by an excess of the strongly Lewis acidic B_2Cl_4 may take place at room temperature, but $B_{10}H_{14}$ is the only stable isolated product from a reaction carried out in excess B_6H_{10}.

An interesting sidelight is the fact that the trialkylboranes $(CH_3)_3B$[20] and $(C_2H_5)_3B$ yield no evidence for complexation, whereas the trialkylaluminum species not only complex but polyalkylate the B_6H_{10}. Neither group of reactions is of synthetic value, however, for a reaction between the boranes and B_6H_{10} cannot be started and the reaction between B_6H_{10} and $(CH_3)_3Al$ or $(C_2H_5)_3Al$ cannot be stopped at intermediates. The only material exhibiting a ^{11}B NMR spectrum consistent with what would be expected for an adduct is the complex of $(i\text{-}C_4H_9)_3Al$ with B_6H_{10}. Apparently either triisobutylaluminum is either too bulky a Lewis acid to transfer an alkyl group or the electron-donating butyl groups neutralize the electropositive character of the aluminum atom enough so that the $(i\text{-}C_4H_9)_3Al{\cdot}B_6H_{10}$ complex is stable in excess triisobutylaluminum.

Reactivity of Hexaborane(10) in Comparison with Its Derivatives. Lewis basicity decreases as one procedes through the series $CH_3B_6H_9 > B_6H_{10} > IB_6H_9 > BrB_6H_9 > ClB_6H_9$, as determined by the rate and extent of reaction between these compounds and the boron trihalides and by the reactions with the borane Lewis acids B_3H_7 and B_8H_{12}. This agrees with the predicted availability of electron density at the B–B bond in these hexaborane derivatives. It also is parallel to the order of Bronsted basicity of hexaborane and its basal methylated derivative observed by Shore et al.[3]

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Registry No. B_6H_{10}, 23777-80-2; BCl_3, 10294-34-5; BBr_3, 10294-33-4; BI_3, 13517-10-7; BrB_6H_9, 50545-82-9; IB_6H_9, 75700-47-9; ClB_6H_9, 75700-48-0; B_2Cl_4, 13701-67-2; $(CH_3)_3Al$, 75-24-1; $(C_2H_5)_3Al$, 97-93-8; $(i\text{-}C_4H_9)_3Al$, 100-99-2; $I_2B_6H_8$, 75700-69-5; $CH_3B_6H_9$, 36863-02-2; $B_3H_7{\cdot}THF$, 52842-96-3; $B_6H_{10}{\cdot}(i\text{-}C_4H_9)_3Al$, 75700-49-1; $B_{13}H_{19}$, 43093-20-5; KB_6H_9, 12447-66-4; Cl_2, 7782-50-5.

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(20) This lack of complexation was observed in the reaction of $(CH_3)_3Al$ with B_6H_{10}, where $(CH_3)_3B$ was a major product of the reaction.

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Kinetics of Formation of (Thiourea)pentacyanoferrate(II) Complexes in Aqueous Perchlorate Media

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The kinetics of formation of complexes of the type $LFe(CN)_5^{3-}$ (L = thiourea and N-substituted derivatives) have been studied over the pH range 2.5–10. Second-order substitution rate constants show a hydrogen ion dependence, and at 25 °C, $k_0 = (k_a[H^+] + k_bK_a)/([H^+] + K_a)$, where $k_a \approx 1\ M^{-1}\ s^{-1}$ is the rate constant for the reaction of $HFe(CN)_5OH_2^{2-}$ with thioureas and k_b ($\sim$186–240 $M^{-1}\ s^{-1}$) governs the corresponding reactions of $Fe(CN)_5OH_2^{3-}$. Activation parameters have been measured for k_b and are similar to those for reaction of other uncharged ligands. The data show some differences at high pH from a previous study, there being no decrease in rate at pH >6. Comparisons are made of the dissociation rates of S- and N-bonded complexes.

In a previous paper,[1] we reported the results of a kinetic investigation of the substitution reactions of pentacyanaquoferrate(II) with thiourea and N-substituted derivatives. The dependence of the rates of substitution on acidity was attributed to three pH-related iron(II) species: $HFe(CN)_5OH_2^{2-}$, $Fe(CN)_5OH_2^{3-}$, and $Fe(CN)_5OH^{4-}$. The protonated aquo ion ($K_a = 2.35 \times 10^{-3}$ M)[2] was found to be much less reactive ($k_{25\,°C} \approx 2\ M^{-1}\ s^{-1}$) than the aquo form ($k_{25\,°C} \approx 200\ M^{-1}\ s^{-1}$), a difference which has also been observed in the pH-dependent reactions of $Fe(CN)_5OH_2^{3-}$ with *N*-methylpyrazinium ion.[2] At high pHs (>8), however, we attributed an apparent decrease in the observed reaction rate to a slower substitution process involving the hydroxy form. Other studies[3] with a number of ligands have reported essentially no change in the rates with acidity in the range pH 6–12. As was indicated earlier,[4] our observations are probably attributable to the presence of small (nonanalytically detectable) amounts of a dimeric impurity resulting from our preparation procedure. Recently, studies have been made involving the dimeric ion and rates in the pH range under consideration are $\sim 10^2$ slower than those for the monomeric species.[5] In this paper we report the results of a further investigation of the reaction of pentacyanoaquoferrate(II) with thioureas.

Experimental Section

Solutions of pentacyanoaquoferrate(II) ion were prepared by dissolution of solid $Na_3[Fe(CN)_5NH_3]{\cdot}3H_2O$ in deoxygenated distilled water. Three samples of the complex were used. Those from Fisher Chemical and one prepared from sodium nitroprusside by the conventional method[6] were recrystallized several times from saturated ammonia at 0 °C. Some data points were derived with use of a preparation by Dr. A. G. Lappin. In all cases the observed rate constants agreed to within ±3%. With the low concentrations of iron(II) used ((2–4) × 10^{-5} M), substitution processes due to the

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(1) D. H. Macartney and A. McAuley, *Inorg. Chem.*, **18**, 2891 (1979).
(2) J. M. Malin and R. C. Koch, *Inorg. Chem.*, **17**, 752 (1978).
(3) G. Davies and A. Garafalo, *Inorg. Chem.*, **15**, 1101 (1976).
(4) Dr. G. Davies, personal communication, submitted for publication in *Inorg. Chem.*
(5) P. Juretic, D. Pavlovic, and S. Asperger, *J. Chem. Soc., Dalton Trans.*, 2029 (1979).
(6) G. Brauer, "Handbook of Preparative Inorganic Chemistry", 2nd ed., Academic Press, New York, 1965, p 1511.