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Some Aspects of the Chemistry of 1,2′-$(B_5H_8)_2$, 2,2′-$(B_5H_8)_2$, and Their Derivatives

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Various derivatives of 1,2′-$(B_5H_8)_2$ and 2,2′-$(B_5H_8)_2$ were produced via halogenation and deprotonation reactions. The rearrangement of the parent compounds and some of their derivatives was studied in the presence of Lewis bases. Cleavage of the intercage σ bond in 1,2′-$(B_5H_8)_2$ was observed in the presence of halogens and hydrogen halides, while boron–boron σ-bond cleavage was not observed in 2,2′-$(B_5H_8)_2$.

Introduction

The binary boron hydrides exist as clusters in which bonding interactions are generally complex. Studies involving discrete boron–boron σ bonding are somewhat out of the ordinary and have been developed more slowly than other areas of boron chemistry. The most common types of boron–boron σ bonds among boranes are those found in diborane(4) derivatives and in σ-bond-coupled polyhedral boranes. Investigation of the chemistry of diborane(4) compounds has shown the B–B σ bonds to be quite reactive; they often undergo cleavage in the presence of diethyl ether or ethylene at −78 °C.[1] In contrast, relatively little is known about the chemistry of intercage boron–boron bonds. It appears that the intercage bonds are much more resistant to cleavage than the boron–boron bonds in diborane(4) derivatives.

We have recently become interested in the chemistry of B–B σ bonds and have, for example, reported the formation and some reactions of 1-Cl_2B-substituted pentaboranes[2] and the specific syntheses of two of the σ-bonded bipentaborane isomers 1,2′-$(B_5H_8)_2$ and 2,2′-$(B_5H_8)_2$.[3] The 1,2′- and 2,2′-$(B_5H_8)_2$ isomers were originally isolated from low-volatility residues present in commercially prepared B_5H_9 and were presumably formed either as byproducts during its synthesis or as degradation products during storage.[4] The syntheses of the above isomers were accomplished by B–B bond-forming reactions: 1,2′-$(B_5H_8)_2$ by a Friedel–Crafts-catalyzed substitution reaction (eq 1) and 2,2′-$(B_5H_8)_2$ by a nucleophilic displacement reaction (eq 2.)[3] A synthesis of 1,1′-$(B_5H_8)_2$ was developed earlier, and consequently, some of its chemistry has been described.[5,6] A serious study of the chemistry of 1,2′-$(B_5H_8)_2$ and 2,2′-$(B_5H_8)_2$ was hampered prior to the development of specific syntheses by the availability of only small quantities of these materials.

$$\text{2-}BrB_5H_8 + B_5H_9 \xrightarrow{AlBr_3} \text{1,2'-}(B_5H_8)_2 + HBr \qquad (1)$$

$$KB_5H_8 + \text{2-}BrB_5H_8 \xrightarrow[-30\ ^\circ C]{\text{pentane}} \text{2,2'-}(B_5H_8)_2 + KBr \qquad (2)$$

We report here the results of further studies of the syntheses and chemical behavior of 1,2′-$(B_5H_8)_2$ and 2,2′-$(B_5H_8)_2$. Striking differences were observed in the rearrangement behavior of the two isomers. While B–B σ-bond cleavage is a dominant feature of the chemistry of 1,2′-$(B_5H_8)_2$, the B–B σ bond in 2,2′-$(B_5H_8)_2$ is more resistant to cleavage.

Results

Synthesis of 1,2′-$(B_5H_8)_2$ and 2,2′-$(B_5H_8)_2$. Continued study of the synthesis of 1,2′-$(B_5H_8)_2$ and 2,2′-$(B_5H_8)_2$[3] has provided further insight into the production of B–B intercage σ bonds. Preliminary results indicate that the use of 2-ClB_5H_8 or 2-IB_5H_8 as reactant leads to approximately 5% yields of 2,2′-$(B_5H_8)_2$, while yields of up to 35% have been obtained by using 2-BrB_5H_8.[3] In contrast, comparable yields of 1,2′-$(B_5H_8)_2$ are obtained regardless of whether 2-BrB_5H_8 or 2-ClB_5H_8 is used as a reactant.

We determined through careful examination of the low-volatility products from the synthesis of 1,2′-$(B_5H_8)_2$ that other pentaborane oligomers are also produced. One example is the 2-Cl-1,2′-$(B_5H_7)(B_5H_8)$ isomer, formed by $AlCl_3$-catalyzed coupling of two 2-ClB_5H_8 molecules (eq 3).[7] Small quantities of both 2-Br-1,2′-$(B_5H_7)(B_5H_8)$ and a "trimeric" pentaborane derivative were observed by ^{11}B NMR and mass spectrometry from syntheses with a 2-BrB_5H_8 reactant.

$$2(\text{2-}ClB_5H_8) \xrightarrow[60\ ^\circ C]{AlCl_3} \text{2-Cl-1,2'-}(B_5H_7)(B_5H_8) + HCl \qquad (3)$$

Halogenation of 1,2′-$(B_5H_8)_2$ and 2,2′-$(B_5H_8)_2$. The Friedel–Crafts-catalyzed halogenation of 1,2′ and 2,2′-$(B_5H_8)_2$ (eq 4 and 5) proceeded under reaction conditions identical with those employed in the halogenation of B_5H_9. The production of 1-substituted isomers of 2,2′- and 1,2′-$(B_5H_8)_2$ (Figure 1) was anticipated as the Friedel–Crafts-catalyzed halogenation of pentaboranes generally leads to 1-halogenated products. Yields of I and II were somewhat reduced by dihalogenation. The yield of V was never comparable to those of the 1-X-2,2′-$(B_5H_7)(B_5H_8)$ derivatives. It is apparent from the reaction byproducts that Friedel–Crafts-catalyzed cleavage of the B–B σ bond competes with halogenation at the apical boron–hydrogen bond in 1,2′-$(B_5H_8)_2$ (eq 6).

$$\text{2,2'-}(B_5H_8)_2 + X_2 \xrightarrow[-78\ ^\circ C\text{ to room temp}]{AlX_3/BX_3} \text{1-X-2,2'-}(B_5H_7)(B_5H_8) + HX \qquad (4)$$

I, X = Cl
II, X = Br

$$\text{1,2'-}(B_5H_8)_2 + Cl_2 \xrightarrow[-78\ ^\circ C\text{ to room temp}]{AlCl_3/BCl_3} \underset{\text{V}}{\text{1'-Cl-1,2'-}(B_5H_8)(B_5H_7)} + HCl \qquad (5)$$

$$\text{1,2'-}(B_5H_8)_2 + Cl_2 \xrightarrow[-78\ ^\circ C\text{ to room temp}]{AlCl_3/BCl_3} \text{1-}ClB_5H_8 + \text{2-}ClB_5H_8 \qquad (6)$$

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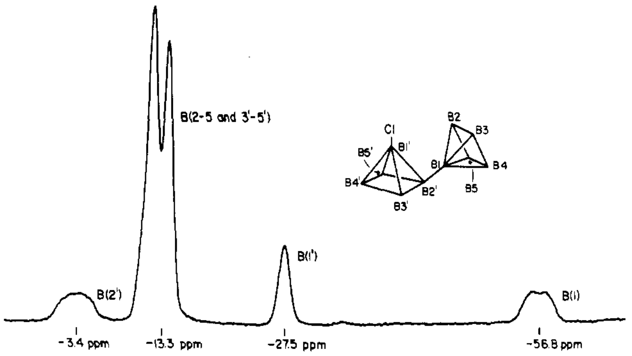

Figure 1. ^{11}B NMR spectrum (86.6 MHz) of 1′-Cl-1,2′-$(B_5H_8)(B_5H_7)$.

Dihalogenation of 2,2′-$(B_5H_8)_2$ produced high yields of the expected 1,1′-disubstituted derivatives (eq 7). The yield

$$2,2'\text{-}(B_5H_8)_2 + 2X_2 \xrightarrow[-78\ ^\circ\text{C to room temp}]{\text{AlX}_3/\text{BX}_3} 1,1'\text{-}X_2\text{-}2,2'\text{-}(B_5H_7) + 2HX \quad (7)$$

$$\text{III, } X = \text{Cl} \qquad \text{IV, } X = \text{Br}$$

obtained for IV is consistent with the results of a recently reported study.[8] A multiple halogenation of 1,2′-$(B_5H_8)_2$ was not attempted. The side reaction detected in the monohalogen reaction (eq 6) would presumably have led to complete disruption of the B–B σ bond (eq 8).

$$1,2'\text{-}(B_5H_8)_2 + 2Cl_2 \xrightarrow{\text{AlCl}_3/\text{BCl}_3} 1,2\text{-}Cl_2B_5H_7 + 2\text{-}ClB_5H_8 + HCl \quad (8)$$

Isomerization of 1,2′-$(B_5H_8)_2$, 2,2′-(B_5H_8), and Their Derivatives. The 2,2′-$(B_5H_8)_2$ isomer and its derivatives rearrange under milder conditions than the 1,2′-$(B_5H_8)_2$ isomer. While neither of the bipentaboranes isomerized in the presence of diethyl ether, 2,2′-$(B_5H_8)_2$ partially rearranged in a benzene solution of Ph_3As. ^{11}B NMR analysis showed that the major rearrangement product was 1,2′-$(B_5H_8)_2$. Whether small quantities of 1,1′-$(B_5H_8)_2$ were part of the reaction products was not determined owing to the coincident chemical shifts of the B(1,1′) and B(1) resonances of 1,1′- and 1,2′-$(B_5H_8)_2$, respectively.[9]

Both the mono- and dichlorinated derivatives of 2,2′-$(B_5H_8)_2$ (I and III) rearrange in diethyl ether solution near ambient temperature. The monochlorinated derivative of 1,2′-$(B_5H_8)_2$ (V), however, showed no evidence of rearrangement after many hours at 95 °C in diethyl ether or in benzene solutions of Ph_3As. The brominated derivatives of 2,2′-$(B_5H_8)_2$ (II and IV) rearranged in diethyl ether at about 50 °C. The ^{11}B NMR evidence suggested that isomerization of the chlorinated derivative produced approximately equal quantities of the 3- and 4-position isomers, while the brominated derivative produced primarily 3-position isomers.

Deprotonation of 1,2′-$(B_5H_8)_2$ and 2,2′-$(B_5H_8)_2$. Experimental evidence suggests that both the 1,2′- and 2,2′-coupled dimers undergo monodeprotonation. The 2,2′-$(B_5H_8)_2$ isomer was deprotonated with excess KH (i.e., 2 equiv), and the anionic product reacted with Me_3SiCl, producing small quantities of monosilylated 2,2′ derivative (eq 9 and 10). The

$$2,2'\text{-}(B_5H_8)_2 + KH \xrightarrow[-78\ ^\circ\text{C}]{\text{Me}_2\text{O}} K\text{-}2,2'\text{-}(B_5H_7)(B_5H_8) + H_2 \quad (9)$$

$$K\text{-}2,2'\text{-}(B_5H_7)(B_5H_8) + Me_3SiCl \xrightarrow[-78\ ^\circ\text{C}]{\text{Me}_2\text{O}} (Me_3Si)\text{-}2,2'\text{-}(B_5H_7)(B_5H_8) \quad (10)$$

^{11}B NMR spectrum of the product suggested that a mixture of a bridge-substituted and a basal–terminal-substituted isomer had been formed. An ^{11}B NMR spectrum of of the product in diethyl ether solution indicated that the bridge-silyl derivative was rapidly converted to the basal–terminal isomer at room temperature. A previous study reported that the 2,2′-$(B_5H_8)_2$ isomer can be deprotonated by methyllithium and that disubstituted products can be obtained by reacting the dianion with R_2BCl.[8] No disubstituted products were isolated from any of our deprotonation studies. This apparent discrepancy may be due to the use in our studies of potassium as the metal counterion and the bulkier Me_3Si group in place of the R_2B group.

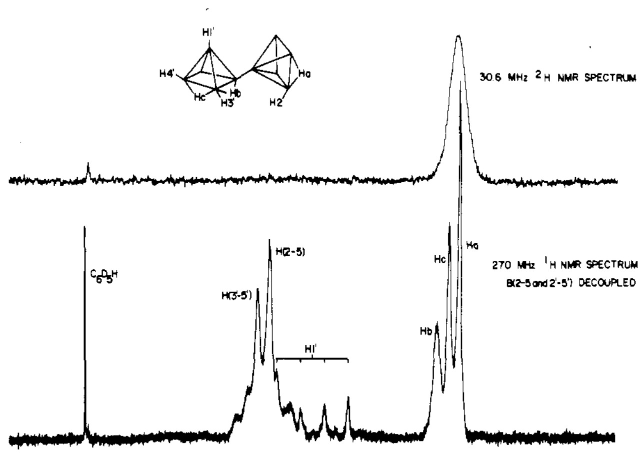

Figure 2. $^1H\{^{11}B\}$ and ^{2}H NMR spectra (270 and 30.6 MHz, respectively) of (μ-D)-1,2′-$(B_5H_7)(B_5H_8)$.

The reaction of 1,2′-$(B_5H_8)_2$ with 2 equiv of methyllithium and the subsequent reaction of the anionic product with DCl led to the recovery of the 1,2′-bipentaborane isomer in good yield. The ^{1}H NMR spectrum of the recovered material indicated that one bridge-hydrogen atom was replaced by a deuterium atom; therefore, the 1,2′-$(B_5H_8)_2$ was only monodeprotonated despite the presence of excess alkyllithium. Comparison of the ^{2}H and $^1H\{^{11}B\}$ NMR spectra of the product (Figure 2) revealed that deprotonation occurs primarily at a bridge-hydrogen position on the cage whose apical boron atom is involved in the boron–boron σ bond (eq 11 and 12).

$$1,2'\text{-}(B_5H_8)_2 + MeLi \xrightarrow[\text{Et}_2\text{O}]{-78\ ^\circ\text{C}} Li\text{-}1,2'\text{-}(B_5H_7)(B_5H_8) + CH_4 \quad (11)$$

$$Li\text{-}1,2'\text{-}(B_5H_7)(B_5H_8) + DCl \xrightarrow{-78\,^\circ\text{C}} (\mu\text{-}D)\text{-}1,2'\text{-}(B_5H_7)(B_5H_8) \quad (12)$$

Boron–Boron σ-Bond Cleavage. The B–B intercage bond of 1,2′-$(B_5H_8)_2$ is far more susceptible to cleavage than the B–B intercage bond of 2,2′-$(B_5H_8)_2$. Hydrogen chloride cleaves the boron–boron σ bond of 1,2′-$(B_5H_8)_2$ in the presence of $AlCl_3$ (eq 13). Preliminary results indicate that the σ bond

$$1,2'\text{-}(B_5H_8)_2 + HCl \xrightarrow[60\ ^\circ\text{C}]{\text{AlCl}_3} B_5H_9 + 2\text{-}ClB_5H_8 \quad (13)$$

of 2,2′-$(B_5H_8)_2$ remains intact under similar reaction conditions.[10] Intercage-bond cleavage is also observed during the chlorination of 1,2′-$(B_5H_8)_2$ (eq 6). The addition of Cl_2 across the boron–boron bond probably accounts for the 60% loss of starting material during chlorination. In contrast, the halogenation of 2,2′-$(B_5H_8)_2$ gave high yields of product and

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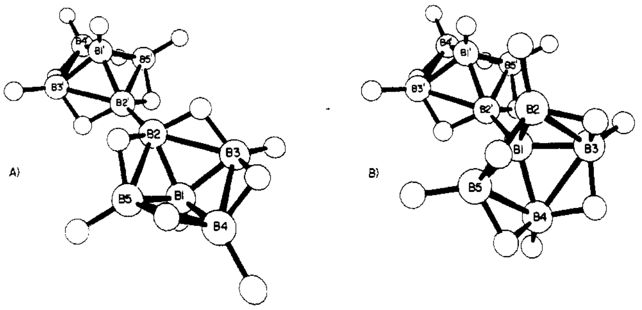

Figure 3. (A) Less hindered B2′ position in 180° rotational conformer of 2,2′-$(B_5H_8)_2$. (B) Steric hindrance at B(2′) caused by the B-(1)-coupled cage in 1,2′-$(B_5H_8)_2$.

showed no evidence of cleavage side reactions.

Discussion

Isomerization of Pentaborane Dimers and Their Derivatives. In the presence of Lewis bases, many of the derivatives of the 1,2′- and 2,2′-bipentaboranes we have studied exhibit behavior similar to analogous derivatives of pentaborane(9). The (μ-Me_3Si)-2,2′-$(B_5H_7)(B_5H_8)$ isomer converts rapidly and quantitatively to a basal-terminal trimethylsilyl 2,2′-bipentaborane in the presence of diethyl ether, as does its counterpart (μ-Me_3Si)B_5H_8. The apically halogenated derivatives of 2,2′-$(B_5H_8)_2$ also mimic their 1-XB_5H_8 analogues by rearranging in diethyl ether at moderate temperature.[11] One apparent rate difference between the two classes is that 1-Br-2,2′-$(B_5H_7)(B_5H_8)$ requires higher isomerization temperatures than 1-Cl-2,2′-$(B_5H_7)(B_5H_8)$. The observation of such a significant rate difference has not been reported for the 1-halopentaboranes. A second difference is the lack of halogen rearrangement in 1-Cl-1,2′-$(B_5H_8)(B_5H_7)$ compared to 1-Cl-2,2′-$(B_5H_7)(B_5H_8)$. If steric effects are the cause of the increased barrier in the 1,2′-(B_5H_8) derivative, they must stem from interference by the B(2–5) and H(2–5) atoms with the trajectory of ether attack at the B(2′) atom (Figure 3). Ether attack at the B(3′-5′) atoms would be unhindered by the change from a 2,2′- to a 1,2′-B–B σ bond. An alternate rationale is that the 1,2′-B–B σ bond electronically stabilizes the dimeric system in a manner that disfavors molecular rearrangements.

The 1,2′-$(B_5H_8)_2$ isomer does not rearrange under conditions suitable for the partial isomerization of 2,2′-$(B_5H_8)_2$ to 1,2-$(B_5H_8)_2$. Similar arguments concerning steric interactions and electronic stabilization can be advanced as an explanation for the barrier to isomerization observed in 1,2′-$(B_5H_8)_2$. In contrast to the other two σ-bonded isomers, 1,1′-$(B_5H_8)_2$ reacts in the presence of strong bases to form Lewis-base adducts of $B_{10}H_{14}$.[6] We observed no such adducts in our NMR tube experiments, and this reinforces our conclusion that 1,1′-$(B_5H_8)_2$ was not formed by the interaction of Ph_3As with 1,2′- or 2,2′-$(B_5H_8)_2$. The 1,1′-$(B_5H_8)_2$ derivative thus appears to be the last energetically accessible isomer by base-catalyzed rearrangement reactions.

Boron–Boron σ-Bond Cleavage. The boron–boron σ bond in 1,1′-$(B_5H_8)_2$ is slowly cleaved by HI at ambient temperature.[6] The boron–boron bond of 1,2′-$(B_5H_8)_2$ is cleaved by HBr at 65 °C in the presence of $AlBr_3$, while the σ bond of 2,2′-$(B_5H_8)_2$ appears unaffected under similar conditions. It appears from these data that the order of kinetic stabilities of the boron–boron σ bonds is

$$1,1'\text{-}(B_5H_8)_2 < 1,2'\text{-}(B_5H_8)_2 < 2,2'\text{-}(B_5H_8)_2$$

This comparison is too simplistic, however, as the Lewis acid essential to bond cleavage in 1,2′-$(B_5H_8)_2$ causes conversion of 1,1′-$(B_5H_8)_2$ to $B_{10}H_{14}$.[6] The formation of $B_{10}H_{14}$ from 1,1′-$(B_5H_8)_2$ occurs in the presence of both Lewis acids and bases via pathways that are apparently unavailable to the 1,2′- and 2,2′-$(B_5H_8)_2$ isomers. The cleavage of the boron–boron σ bond in 1,2′-$(B_5H_8)_2$ by HBr may partially account for the generally low yields obtained in the synthesis of 1,2′-$(B_5H_8)_2$.

A similar ordering of B–B σ-bond stability can be developed for the compounds B_2Cl_4, 1-$(Cl_2B)B_5H_8$, and 1,2′-$(B_5H_8)_2$. In this series, a comparison of the kinetic stability of the σ bonds as represented by the stability of the compounds in diethyl ether solution or the activity of the boron–boron σ bonds toward the ethylene[2] insertion leads to the ordering

$$B_2Cl_4 < 1\text{-}(Cl_2B)B_5H_8 < 1,2'\text{-}(B_5H_8)_2$$

While 1,1′-$(B_5H_8)_2$ cannot be placed in this series on the basis of available data, we conjecture that it should fall between 1-$(Cl_2B)B_5H_8$ and 1,2′-$(B_5H_8)_2$.

Experimental Section

All inert-atmosphere manipulations were performed in dry-nitrogen-filled glovebags or standard high-vacuum apparatus.[12] All solvents were dried over $LiAlH_4$ prior to use. BCl_3, Cl_2, C_2H_4, and HCl were used as obtained from Matheson. $AlCl_3$ was purified in situ by repeated sublimations. $AlBr_3$ was produced in situ from elemental bromine and aluminum foil. Br_2, KH, and MeLi were used as obtained from Fisher, Aldrich, and Alfa, respectively. Me_3SiCl was distilled prior to use and transferred to a high-vacuum storage vessel. 1,2′-$(B_5H_8)_2$ and 2,2′-$(B_5H_8)_2$ were prepared by previously reported methods.[3]

Pump-through reaction flasks and NMR tube fillers employed in these experiments are used extensively in the synthesis and characterization of low-volatility boron hydrides. The pump-through reactor is a modified U-trap attached to the vacuum line in two places. It is generally equipped with two stopcocks, which allow it to be isolated from the vacuum line and removed without exposing the contents to air. The advantage of the pump-through design is that a low-volatility material may be condensed at the reactor inlet while the reactor outlet is open to high vacuum. A pump-through NMR tube filler is a short removable U-trap with an NMR tube sealed to the bottom of the U-trap.

^{11}B (86.6 MHz) and ^1H (270.1 MHz) NMR spectra were acquired on a Bruker WH-270 instrument at spectral widths of 10 000 and 6000 Hz, respectively. ^2H NMR spectra 30.6 MHz were acquired on a JEOL FX-200 instrument with a spectral width of 1000 Hz and a pulse repetition time of 50 s. Mass spectra were obtained on an AEI MS-9 instrument at 70 eV. Infrared spectra were obtained on a Perkin-Elmer 700 spectrophotometer.

Synthesis of 1-Br-2,2′-$(B_5H_7)(B_5H_8)$ (II). In a typical reaction, 2.0 mmol of Br_2 were condensed into a small pump-through reaction flask containing a catalytic amount of $AlBr_3$ and a Teflon-coated stirbar. A 0.5-mL portion of pentane was condensed into the reactor and mixed with the bromine. The mixture was frozen at −196 °C, and 0.25 g (2.0 mmol) of 2,2′-$(B_5H_8)_2$ was condensed into the flask. The reaction mixture was warmed slowly from −78 °C to ambient temperature with stirring. The products were then distilled in a high vacuum through a −22 °C U-trap into a −196 °C U-trap. A 0.8-mmol sample of 2,2′-$(B_5H_8)_2$ was recovered from the −22 °C U-trap. The solid residue in the reaction flask was extracted with C_6H_6 and was transferred to a sublimator. A white solid, 0.122 g, sublimed at room temperature to the −10 °C cold finger after remvoal of the C_6H_6. The product was identified as 1-Br-2,2′-$(B_5H_7)(B_5H_8)$ by ^{11}B and ^1H NMR spectroscopy (Tables I and II) and mass spectrometry. *m/e* for $^{11}B_{10}{}^1H_{15}{}^{79}Br$: calculated, 204.1284; observed, 204.1291. Yield: 0.59 mmol (30%).

After the sublimation of the monobrominated derivative, a solid residue remained. On gentle warming, 0.065 g of white solid sublimed to the cold finger and was identified as 1,1′-Br_2-2,2′-$(B_5H_7)_2$ by ^{11}B and ^1H NMR spectroscopy (Tables I and II) and mass spectrometry. *m/e* for $^{11}B_{10}{}^1H_{14}{}^{79}Br_2$: calculated, 281.0429; observed, 281.0423. Yield: 0.2 mmol (10%). The overall yield of the reaction was 67% based on 2,2′-$(B_5H_8)_2$ consumed.

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Table I. ^{11}B NMR Spectral Data (86.6 MHz): Chemical Shifts and Coupling Constants

	B(1)	B(1′)	B(2–5), B(2′–5′)
1-Cl-2,2′-(B$_5$H$_7$)(B$_5$H$_8$) (I)	−28.6[a]	−51.3 (171)[b]	−11.4, −12.4
1-Br-2,2′-(B$_5$H$_7$)(B$_5$H$_8$) (II)	−35.6	−51.1 (182)	−10.9, −12.0, −13.0

	B(1), B(1′)	B(2–5), B(2′–5′)
1,1′-Cl$_2$-2,2′-(B$_5$H$_7$)$_2$ (III)	−28.7	−10.6, −12.1
1,1′-Br$_2$-2,2′-(B$_5$H$_7$)$_2$ (IV)	−35.7	−9.1, −10.9, −12.2

	B(1)	B(1′)	B(2′)	B(2–5), B(3′–5′)
1′-Cl-1,2′-(B$_5$H$_8$)(B$_5$H$_7$) (V)	−56.8	−27.5	−3.4	−13.3 (156)

[a] Chemical shifts in ppm referenced against an external BF$_3$·OEt$_2$ standard. [b] Coupling constants, in parentheses, in Hz.

Table II. ^{1}H NMR Spectral Data (270.1 MHz): Chemical Shifts and Coupling Constants

	H(1′)	H(2–5), H(2′–5′)	H(6–9)	H(6′–9′)
1-Cl-2,2′-(B$_5$H$_7$)(B$_5$H$_8$) (I)	1.03[a] (176)[b]	2.62 (162)	−2.13	−2.52
1-Br-2,2′-(B$_5$H$_7$)(B$_5$H$_8$) (II)	0.85 (176)	2.52 (154)	−2.43	−2.88

	H(2–5), H(2′–5′)	H(6–9), H(6′–9′)
1,1′-Cl$_2$-2,2′-(B$_5$H$_7$)$_2$ (III)	2.74 (160)	−2.06
1,1′-Br$_2$-2,2′-(B$_5$H$_7$) (V)	2.74 (160)	−2.12

	H(2–5)	H(3′–5′)	H(6–9)	H(6′–9′)
1′-Cl-1,2′-(B$_5$H$_8$)(B$_5$H$_7$) (V)	2.20 (167)	2.79 (159)	−2.76	−1.84

[a] Chemical shifts in ppm referenced against an external Me$_4$Si standard. [b] Coupling constants, in parentheses, in Hz.

Synthesis of 1,1′-Br$_2$-2,2′-(B$_5$H$_7$)$_2$ (IV). Br$_2$ (8.0 mmol) was condensed into a small pump-through reaction flask prepared as above. After dilution of the Br$_2$ with 0.5 mL of pentane, 4.0 mmol of 2,2′-(B$_5$H$_8$)$_2$ were condensed into the flask. The reactor was warmed from −78 °C to ambient temperature over several hours while the solution was stirred. The volatile products were removed from the reactor, and the solid residue was extracted with C$_6$H$_6$. The extract was transferred to a sublimator equipped with a water-cooled cold finger. After removal of the C$_6$H$_6$, the white residue was warmed to 69 °C. A 0.86-g portion of white solid sublimed to the cold finger and was identified by ^{11}B NMR spectroscopy as 1,1′-Br$_2$-2,2′-(B$_5$H$_7$)$_2$. Yield: 3.0 mmol (75%).

Synthesis of 1-Cl-2,2′-(B$_5$H$_7$)(B$_5$H$_8$) (I). Cl$_2$ (1.1 mmol) was condensed into a small reactor containing a Teflon-coated stirbar, a catalytic amount of AlCl$_3$, and 3.0 mL of BCl$_3$ solvent. The reactor was warmed to −78 °C, the Cl$_2$ and BCl$_3$ were mixed, and the flask was frozen at −196 °C. A 2.2-mmol portion of 2,2′-(B$_5$H$_8$)$_2$ was condensed into the vessel. The reactor was sealed and allowed to warm slowly from −78 °C to ambient temperature while the solution was stirred. The volatile products were distilled from the reaction flask, and the residue was extracted as before. A 0.16-g portion of white solid sublimed on a −10 °C cold finger. The product was identified as 1-Cl-2,2′-(B$_5$H$_8$) by ^{11}B and ^{1}H NMR spectroscopy (Tables I and II) and mass spectrometry. *m/e* for ^{11}B$_{10}{}^1$H$_{15}{}^{35}$Cl: calculated 159.1825; observed, 159.1828. Yield: 0.99 mmol (90% based on Cl$_2$).

Synthesis of 1,1′-Cl$_2$-2,2′-(B$_5$H$_7$)$_2$ (III). The equipment and reaction conditions for the synthesis of III were identical with those used in the synthesis of I. A 2.0-mmol sample of 2,2′-(B$_5$H$_8$)$_2$ and 4.0 mmol of Cl$_2$ were used as reactants. The volatile products were removed, and the solid residue was transferred to a sublimator. When it was warmed to 45 °C, 0.33 g of white solid sublimed from the residue to the water-cooled cold finger. The solid was identified as 1,1′-Cl$_2$-2,2′-(B$_5$H$_7$)$_2$ by ^{11}B and ^{1}H NMR spectroscopy (Tables I and II) and mass spectrometry. Yield: 1.7 mmol (85%).

Synthesis of 1′-Cl-1,2′-(B$_5$H$_8$)(B$_5$H$_7$) (V). In a typical synthesis, 0.175 g (1.4 mmol) of 1,2′-(B$_5$H$_8$)$_2$ was condensed into a small pump-through reactor containing a Teflon-coated stirbar and a catalytic amount of AlCl$_3$. A 0.3-mL portion of BCl$_3$ was condensed into the reactor, and the contents were thawed and mixed at ambient temperature. The solution was frozen at −196 °C, and 1.4 mmol of Cl$_2$ was condensed into the reactor. The flask was sealed and warmed slowly from −78 °C to ambient temperature while the mixture was stirred. The color characteristic of Cl$_2$ disappeared before the solution reached room temperature.

The volatile products were removed and distilled through a 0 °C U-trap into a −196 °C U-trap. A 0.095-g portion of white crystalline solid was isolated in the 0 °C U-trap and was identified as 1′-Cl-1,2′-(B$_5$H$_8$)(B$_5$H$_7$) by ^{11}B and ^{1}H NMR spectroscopy (Tables I and II) and mass spectrometry. *m/e* for ^{11}B$_{10}{}^1$H$_{15}{}^{35}$Cl: calculated, 160.1816; observed, 160.1840. Yield: 0.59 mmol (43%).

No unreacted 1,2′-(B$_5$H$_8$)$_2$ starting material was recovered during purification of the remaining products. Small amounts of white solid were isolated by distillation of the residual mixture through a −63 °C U-trap. The ^{11}B NMR spectrum of the solid suggested that it was a mixture of 1-ClB$_5$H$_8$ and 2-ClB$_5$H$_8$.

Isomerization of 1,2′-(B$_5$H$_8$)$_2$ and 2,2′-(B$_5$H$_8$)$_2$. Similar samples containing small quantities of 1,2′- and 2,2′-(B$_5$H$_8$)$_2$ in diethyl ether were prepared in 5-mm NMR tubes. The samples were monitored for isomerization by ^{11}B NMR spectroscopy. No changes were observed in the spectra of the derivatives after several hours at 120 °C.

Small quantities of 1,2′- and 2,2′-(B$_5$H$_8$)$_2$ were then added to NMR tubes containing approximately 10 mg of Ph$_3$As in C$_6$H$_6$. Again, no changes were observed in the NMR spectra of the samples at ambient temperature. After several weeks at 100 °C, the spectrum of the 2,2′-(B$_5$H$_8$)$_2$ sample developed two new resonances at −3.7 and −55.3 ppm.

Isomerization of I and V. An NMR sample of I was prepared by transferring 50 mg of compound into a 5-mm NMR tube under dry-N$_2$ gas, degassing the tube on a high-vacuum line, and distilling 3 mmol of diethyl ether onto the solid. The sample was frozen and sealed under vacuum. An NMR sample of V was prepared by condensing a small sample of the compound and 3 mmol of diethyl ether into an NMR pump-through. The materials were thawed and mixed, the solution was frozen, and the tube was sealed under vacuum.

After 3 days at ambient temperature, several changes occurred in the ^{11}B NMR spectrum of I. A diminution in the intensity of the singlet resonance at −28.0 ppm was accompanied by the appearance of a new singlet at 0.73 ppm and new doublets at −22.0 and −49.2 ppm. After 10 days, the system apparently reached equilibrium, with the singlets at −28.0 and 0.73 ppm having nearly equal intensity. The ^{11}B NMR spectrum of the sample containing V showed no evidence for isomerization after many hours at 95 °C.

A second NMR sample of V was prepared in 3 mmol of C$_6$H$_6$ with 10 mg of Ph$_3$As catalyst. The ^{11}B NMR spectrum of the sample was monitored after warming to progressively higher temperatures. No changes were observed in the spectrum of V though the sample was heated at 95 °C for many hours.

Isomerization of II, III, and IV. The ^{11}B NMR spectrum of a sample containing II in diethyl ether solution, prepared in a manner similar to that for the sample of I above, showed no change after many days at ambient temperature. When the sample was heated at 50 °C for 1 week, two new doublets of comparable intensity appeared at −19.4 and −49.0 ppm. These new doublets appeared with a concurrent loss of intensity in the singlet resonance at −35.1 ppm.

NMR samples containing III and IV in diethyl ether solution were prepared in a manner similar to that for the sample of II above. After 5 h at 50 °C, the ^{11}B NMR spectrum of the sample containing III developed two new doublet resonances at −21.5 and −49.0 ppm and a new singlet resonance at 1.0 ppm. This was accompanied by a loss in the intensity of the singlet resonance at −27.6 ppm. The spectrum of the sample containing IV displayed only minor changes when heated over the same time period.

Deprotonation of 2,2′-(B$_5$H$_8$)$_2$. In a typical reaction, 2.92 mmol of KH was measured as an oil slurry and placed in a pump-through reactor equipped with a Teflon-coated stirbar. The KH was washed repeatedly with pentane to remove the oil. A 2-mL portion of dimethyl ether was condensed onto the KH at −196 °C. The mixture was warmed to −78 °C and stirred for several minutes. A 1.06-mmol portion of 2,2′-$(B_5H_8)_2$ was then condensed into the reactor. The flask was allowed to warm from −78 to −30 °C over several hours while the solution was stirred. The flask was then frozen at −196 °C, and the amount of H_2 gas above the reaction mixture was measured and found to be 0.96 mmol, a 91% yield assuming monodeprotonation of the 2,2′-$(B_5H_8)_2$. Similar reactions employing methyl- and butyllithium in place of KH produced methane and butane, indicating that deprotonation also occurred with those species.

Reaction of K-2,2′-$(B_5H_7)(B_5H_8)$ and Me_3SiCl. An equimolar amount of Me_3SiCl was added to a dimethyl ether solution of K-2,2′-$(B_5H_7)(B_5H_8)$. The mixture was warmed slowly from −78 to −40 °C. The dimethyl ether was then removed by pumping on the reaction mixture overnight at −40 °C. The residues were extracted with C_6H_6 and were transferred by syringe to a −10 °C cold-finger sublimator. After removal of the solvent under high vacuum, a small amount of oil condensed on the cold finger. The ^{11}B NMR spectrum of the oil showed a large pattern of overlapping resonances at −12 ppm and three doublets of approximate intensity 3:2:1 at −51.1, −48.6, and −44.8 ppm, respectively. The −44.8 ppm resonance appears to represent a μ-Me_3Si-substituted 2,2′-$(B_5H_8)_2$, while the −48.6 ppm resonance represents a basal–terminal Me_3Si-substituted 2,2′-$(B_5H_8)_2$.[13] The −51.1 ppm resonance represents the apical boron atom of the unsubstituted cage in the (Me_3Si)-2,2′-$(B_5H_7)(B_5H_8)$ mixture. On treatment of the oil with diethyl ether, the resonance at −44.8 ppm decreased in intensity while the intensity of the resonance at −48.6 ppm increased. The ^{11}B NMR spectrum of the final product had resonances of intensity 1:1 at −48.6 and −51.1 ppm and a complex pattern of overlapping resonances at −12 ppm. These data suggest that the final product was a basal–terminal Me_3Si-substituted 2,2′-$(B_5H_8)_2$ derivative.

Deprotonation of 1,2′-$(B_5H_8)_2$. A 1.2-mmol portion of methyllithium in hexane solution was transferred by syring into a small pump-through reactor equipped with a Teflon-coated stirbar. After the hexane was removed under high vacuum, 0.5 mL of diethyl ether was condensed onto the methyllithium at −196 °C and 0.59 mmol of 1,2′-$(B_5H_8)_2$ was condensed into the reactor. The flask was allowed to warm from −78 to −35 °C while the reaction mixture was stirred. The solution was frozen, and the evolved methane was measured. A 0.4-mmol portion of methane formed during the reaction. The flask was again allowed to warm from −78 to −25 °C, the solution was refrozen, and the reactor was checked for methane. A small quantity of methane was observed; however, the total quantity of methane evolved was less than 1 equiv of the borane starting material. No attempt was made to characterize the presumed anionic intermediate.

Reaction of Li-1,2′-$(B_5H_8)(B_5H_7)$ and DCl. A 1.2-mmol portion of DCl (2 equiv based on 1,2′-$(B_5H_8)_2$ starting material) was condensed into the diethyl ether solution of Li-1,2′-$(B_5H_7)(B_5H_8)$. The flask was warmed to near room temperature while the solution was stirred. The products were distilled through a −22 °C U-trap into a −196 °C U-trap. A 0.055- g portion of white solid was isolated in the −22 °C U-trap. The solid was identified by ^{11}B NMR spectroscopy as the 1,2′-$(B_5H_7D)(B_5H_8)$. Yield: 0.44 mmol (75% based on borane added).

The $^1H\{^{11}B\}$ NMR spectrum of the product was identical with the spectrum of a similar sample of 1,2′-$(B_5H_8)_2$ except for variations in the intensity of resonances in the region characteristic of bridging protons. For the three resonances at −2.12, −2.43, and 2.70 ppm, the normal intensity ratio at 2:2:4 (respectively) was altered to approximately 2:2:3 in the new product. An integration of the ^1H NMR spectrum of the new material indicated that the terminal proton to bridge-proton ratio was 8:7. The ^2H NMR spectrum of the product had a single resonance at −2.74 ppm.

Reaction of 1,2′-$(B_5H_8)_2$ and 2,2′-$(B_5H_8)_2$ with HCl. A catalytic amount of $AlCl_3$ was transferred into an NMR pump-through reactor. A small amount of 2,2′-$(B_5H_8)_2$ and approximately 3.0 mmol of C_6H_6 were condensed into the tube. The sample was thawed and refrozen at the bottom of the tube. A tenfold excess of HCl was condensed into the NMR tube. The sample was sealed and allowed to warm to room temperature. No change in the ^{11}B NMR spectrum of the sample was observed after several days at ambient temperature. Heating at 65 °C for several days also produced no change in the spectrum of the sample.

1,2′-$(B_5H_8)_2$ (0.18 mmol) and HCl (0.18 mmol) were condensed into a small reactor containing a catalyst amount of $AlCl_3$. The flask was sealed and warmed at 60 °C for 1 day. The reaction was opened, and the contents were distilled through a −63 °C U-trap into a −196 °C U-trap. A small amount of liquid isolated in the −63 °C U-trap was identified as a 2-ClB_5H_8 by ^{11}B NMR spectroscopy. The contents of the −196 °C U-trap were identified as B_5H_9 by ^{11}B NMR spectroscopy. Yield: 0.14 mmol (78%). No unreacted 1,2′-$(B_5H_8)_2$ was recovered.

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Registry No. I, 87937-19-7; II, 87937-20-0; III, 80786-88-5; IV, 80786-89-6; V, 82544-59-0; 2,2′-$(B_5H_8)_2$, 28775-81-7; 1,2′-$(B_5H_8)_2$, 31831-99-9; $AlBr_3$, 7727-15-3; $AlCl_3$, 7446-70-0; K-2,2′-$(B_5H_7)(B_5H_8)$, 87884-33-1; Me_3SiCl, 75-77-4; 2,2′-$(B_5H_8)_2$ (Me_3Si derivative), 87901-27-7; Li-1,2′-$(B_5H_8)(B_5H_7)$, 87884-34-2; 1,2′-$(B_5H_7D)(B_5H_8)$, 87937-23-3; Ph_3As, 603-32-7; 2-ClB_5H_8, 19469-14-8; B_5H_9, 19624-22-7.

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Complexes of Aluminum(III) with Hydroxy Carboxylic Acids

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The reactions of the Al(III) ion with citric acid, tartaric acid, gluconic acid, saccharic acid, glyceric acid, bis(hydroxyethyl)glycine, and catechol were studied by potentiometric methods. The equilibrium data were processed with the Fortran computer program BEST. By taking into account all of the known hydrolytic aluminum(III) species, problems associated with previous investigations were avoided. Detailed computations at various ratios of ligands to aluminum(III) now provide a comprehensive description of the Al(III) complexes formed in solution, and formation constants are reported for the various complex species involved. It was found that Al(III) has a very strong tendency toward displacement of protons from the hydroxyl groups of hydroxy acids, a property that previously has not been fully recognized.

Introduction

The Al(III) ion has a strong tendency to undergo complex hydrolytic reactions,[1] and consequently quantitative studies of its reactions in aqueous solution have lagged far behind those of most other common divalent and trivalent metal ions. It is, therefore, not surprising that, except for a few phenolic and multidentate polyamino polycarboxylic acids, quantitative studies[2] of aluminum(III) complexes have been carried out

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