with J_{NF} = 232 Hz),[16] which was slowly replaced by the signal of NF_3 (triplet of equal intensity at 145 ppm below $CFCl_3$ with J_{NF} = 290 Hz),[19] suggesting again solvolysis of NF_4XeF_7, followed by decomposition of the unstable NF_4BrF_6 intermediate:

$$NF_4XeF_7 + BrF_5 \rightleftarrows [NF_4BrF_6] + XeF_6 \quad (4)$$

$$[NF_4BrF_6] \rightarrow NF_3 + F_2 + BrF_5 \quad (5)$$

When a sample of NF_4XeF_7 was exposed at room temperature for prolonged time to blue 4880-Å laser light, photolytic decomposition of NF_4XeF_7 occurred, resulting in $(NF_4)_2XeF_8$ formation:

$$2NF_4XeF_7 \xrightarrow{h\nu\ (4880\ Å)} (NF_4)_2XeF_8 + XeF_6 \quad (6)$$

Attempts were unsuccessful to duplicate this reaction by carefully controlled thermal decomposition of NF_4XeF_7. The only products obtained were NF_3, F_2, XeF_6, and unreacted NF_4XeF_7. The selective decomposition of NF_4XeF_7 and stability of $(NF_4)_2XeF_8$ in the laser beam can be explained by the different color of the two compounds. The yellow NF_4XeF_7 strongly absorbs the blue 4880-Å light, whereas the white $(NF_4)_2XeF_8$ does not. Since the output of the available laser was just 75 mW, only very small amounts of $(NF_4)_2XeF_8$ could be produced in this manner, and identification of the product was limited to Raman spectroscopy. As can be seen from traces G–I of Figure 3 and Table II, the spectra clearly show the presence of the NF_4^+[18] and XeF_8^{2-} ions (see above). The observed splittings are due to lifting of the degeneracies for the E and F modes in the solid state.[18]

Conclusion. The present study further demonstrates the unique ability of the NF_4^+ cation to form a host of stable salts. The successful synthesis of NF_4XeF_7 and $(NF_4)_2XeF_8$ provided the first known examples not only of NF_4^+ salts containing noble-gas fluoride anions but also of an NF_4^+ salt containing an octafluoro anion. These salts are very powerful oxidizers and on thermal decomposition generate NF_3, F_2, and only inert gases. The formation of $(NF_4)_2XeF_8$ is an interesting example of a selective laser-induced reaction. The XeF_7^- and XeF_8^{2-} anions were characterized by vibrational spectroscopy. Raman spectroscopic evidence was obtained for the existence of a stable $NaXeF_7$ salt, and the presence of different phases in solid XeF_6 was confirmed.

Acknowledgment. The authors gratefully acknowledge helpful discussions with Drs. C. J. Schack and L. R. Grant and Mr. R. D. Wilson and financial support from the Office of Naval Research and the Army Research Office.

Registry No. $(NF_4)(XeF_7)$, 82963-12-0; CsF, 13400-13-0; $(NF_4)SbF_6$, 16871-76-4; $Cs(XeF_7)$, 19033-04-6; $Cs_2(XeF_8)$, 17501-71-2; XeF_6, 13693-09-9; $Na(XeF_7)$, 82963-13-1; Xe, 7440-63-3; F_2, 7782-41-4; NaF, 7681-49-4; $(NF_4)_2XeF_8$, 82963-15-3; $Na_2(XeF_8)$, 17501-70-1.

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Contribution from the Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

Synthesis of 2-Aryl Derivatives of Pentaborane(9)

JOSEPH A. HEPPERT and DONALD F. GAINES*

Received March 19, 1982

A series of 2-aryl derivatives of B_5H_9 have been prepared via aluminum chloride catalyzed electrophilic substitution by 2-ClB_5H_8 on various alkylbenzenes. Analyses of ^1H NMR spectra suggest that the site of attack of the B_5H_8 moiety is controlled by steric interactions.

Introduction

During the early 1960s, a heavy emphasis was placed on the preparation of alkyl derivatives of the boron hydrides. Much of the impetus for this research came from the demand for suitable borane-based fuels for various aviation and rocket programs.[1] In several of the early syntheses of alkylboranes, simple heating of olefins in the presence of boranes produced varying yields of 2-substituted pentaborane(9) derivatives (eq 1).[2] Subsequent investigations with B_5H_9 disclosed that

$$C_2H_4 + B_5H_9 \xrightarrow{150\ °C} 2\text{-}EtB_5H_8 \quad (1)$$

Friedel–Crafts-catalyzed electrophilic attack by olefins and alkyl halides produced only 1-alkylpentaborane derivatives (eq 2 and 3).[3] The corresponding 2-alkylpentaborane derivatives

$$RCl + B_5H_9 \xrightarrow{AlCl_3} 1\text{-}RB_5H_8 + HCl \quad (2)$$

$$C_2H_4 + B_5H_9 \xrightarrow{AlCl_3} 1\text{-}EtB_5H_8 \quad (3)$$

were then prepared from the 1-substituted isomers in nearly quantitative yield by thermal or Lewis-base-catalyzed isomerization.

A series of 1- and 2-arylpentaborane(9) derivatives is conspicuously absent from the organopentaborane(9) derivatives prepared in previous studies. This absence can be rationalized on the basis of the low Friedel–Crafts activity of the aryl halides.[4] It is clear that an alternate synthetic route is necessary to produce arylpentaboranes. The recent observation that 2-halopentaboranes can function as electrophiles under Friedel–Crafts catalysis conditions[5] suggested a new pathway for the formation of one of the arylpentaborane isomers.

We report the synthesis of a series of 2-ArB_5H_8 derivatives by an $AlCl_3$-catalyzed reaction of 2-ClB_5H_8 with various aromatic hydrocarbons. These compounds have been characterized by mass spectroscopy and ^{11}B, ^{13}C and ^1H NMR spectroscopy.

Experimental Section

Inert-atmosphere manipulations were performed in dry-nitrogen-filled glovebags and on standard high-vacuum lines.[6] All aromatic reagents used were dried over $LiAlH_4$. Benzene and *m*-xylene (Aldrich

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Table I. ^{11}B NMR Data for 2-ArB_5H_8 Compounds

compd	chem shifts[a] B(2) δ	B(3,5) δ	B(3,5) J_{BH}	B(4) δ	B(4) J_{BH}	B(1) δ	B(1) J_{BH}
2-$(C_6H_5)B_5H_8$ (I)	0.56	−14.8	158	−18.6	166	−51.3	172
2-$[(CH_3)C_6H_4]B_5H_8$ (II)	1.07	−14.5	156.2	−18.9	166.0	−51.0	170.9
2-$[m\text{-}(CH_3)_2C_6H_3]B_5H_8$ (III)	1.07	−14.6	175.7	−18.9	175.7	−51.4	175.7
2-$[1,2,3\text{-}(CH_3)_3C_6H_2]B_5H_8$ (IV)	0.57	−15.0	156.2	−19.6	156.2	−52.0	175.7

[a] Reference $BF_3 \cdot OEt_2$; negative values are upfield. J values are given in hertz.

Table II. Mass Spectroscopic Data for 2-ArB_5H_8 Derivatives

compd	high resolution formula	high resolution m/e calcd, found	low resolution formula	low resolution m/e[a]
2-$(C_6H_5)B_5H_8$ (I)	$^{12}C_6{}^1H_{13}{}^{11}B_5$	140.1482, 140.1482	$C_5H_{12}B_5^+$	124
			$C_3H_{10}B_5^+$	96
			$C_6H_6^+$	78
			$B_5H_8^+$	60
2-$(CH_3C_6H_4)B_5H_8$ (II)	$^{12}C_7{}^1H_{15}{}^{11}B_5$	154.1639, 154.1639	$C_6H_{12}B_5^+$	138
			$C_5H_{11}B_5^+$	123
			$C_4H_{10}B_5^+$	110
			$C_3H_9B_5^+$	97
			$C_7H_8^+$	92
			$CH_8B_5^+$	83
2-$[(CH_3)_2C_6H_3]B_5H_8$ (III)	$^{12}C_8{}^1H_{17}{}^{11}B_5$	168.1796, 168.1796	$C_7H_{14}B_5^+$	153
			$C_8H_{10}^+$	106
2-$[(CH_3)_3C_6H_2]B_5H_8$ (IV)	$^{12}C_9{}^1H_{19}{}^{11}B_6$	182.1953, 182.1953	$C_8H_{16}B_5^+$	165
			$C_{10}H_{14}^+$ (impurity)	134
			$C_9H_{12}^+$	120

[a] Represents m/e for the center of envelopes.

analytical grade) and toluene (Fisher reagent grade) were used as obtained. A sample of 1,2,3-$(CH_3)_3C_6H_3$ (90%, technical grade) was obtained from Aldrich and was purified by fractional distillation (boiling range 171–172 °C). 2-ClB_5H_8 was prepared by the literature method.[7] Aluminum chloride (Aldrich technical grade) was purified before use by sublimation in the evacuated reaction vessels. NMR lock solvents, C_6D_6 and CD_2Cl_2, were dried over $LiAlH_4$ and 3-Å molecular sieves, respectively.

The 270-MHz ^1H and 86.6-MHz ^{11}B NMR spectra were acquired with a Bruker WH-270 spectrometer. The 50.1-MHz ^{13}C NMR spectra were obtained with a JEOL FX-200 spectrometer in the double-precision mode. Solvent-suppressed ^{13}C NMR spectra were obtained on the same instrument using the Ernst–Doddrell PG-200 programmed-pulse sequence. A delay time (Δ) of 1.5 ms was used to allow for the maximum refocusing of aromatic carbon resonances. The overall pulse delay was 3.32 s. Mass spectra were obtained on an AEI MS-9 spectrometer at 70 eV.

Synthesis of 2-$(C_6H_5)B_5H_8$ (I). In a typical synthesis, 0.2 g of $AlCl_3$ was added to a 250-mL round-bottom flask equipped with a 12-mm Kontes O-ring stopcock and containing a Teflon stirring bar. The flask was evacuated, and 1.07 g (10.7 mmol) of a 2-ClB_5H_8 and 2 mL of C_6H_6 were condensed into it at −196 °C. The reactor was sealed, warmed to 45 °C, and stirred for 6 days. High-vacuum distillation of the reaction mixture through a −22 °C U-trap into a −196 °C U-trap resulted in the isolation of three products in the −22 °C trap. On repeated rapid distillation of the mixture through a −22 °C trap into a −196 °C trap, two of the products remained in the −22 °C U-trap. The third product (^{11}B NMR: singlet, δ 41.2) was stopped in the −196 °C trap and was tentatively identified as $PhBCl_2$. the separation of the remaining two products was effected by distillation of the mixture through a −10 °C U-trap into a −196 °C U-trap. The product isolated in the −196 °C trap had an ^{11}B NMR spectrum consistent with the formulation 2-Cl-1,2′-$(B_5H_7)(B_5H_8)$. Analysis of the product remaining in the −10 °C trap by ^{11}B NMR spectroscopy showed a substitution pattern consistent with that of a 2-alkylpentaborane(9) derivative. A small impurity due to 2-Cl-1,2′-$(B_5H_7)(B_5H_8)$ could also be detected in the ^{11}B NMR spectrum.

The mass spectrum of the 2-aryl product (Table II) was consistent with the proposed formulation $^{12}C_6{}^1H_{13}{}^{11}B_5$, 2-$(C_6H_5)B_5H_8$. The parent region appeared as a "double" envelope with the two maxima being separated by 4 amu. A major peak at m/e 78 can be attributed to the formation of $C_6H_6^+$ ion through recombination reactions in the source. The weight of the isolated 2-$(C_6H_5)B_5H_8$ derivative was 0.018 g, about 1%.

The ^{11}B and ^1H NMR data (collected in Tables I and III, respectively) are consistent with the formulation found by mass spectroscopy. The ^1H spectrum confirmed the ^{11}B NMR findings that only the 2-phenyl isomer is present. $^{13}C\{^1H\}$ NMR spectra data: C(2,2′), 134.0 ppm; C(3,3′), 129.1; C(4), 128.4.

Synthesis of 2-$(CH_3C_6H_4)B_5H_8$ (II). In a typical reaction, 0.2 g of $AlCl_3$ was placed in a 100-mL round-bottom flask equipped with a 12-mm Kontes O-ring stopcock and a Teflon stirring bar. The flask was then evacuated, and 1.10 g (11.0 mmol) of 2-ClB_5H_8 and 2 mL of $CH_3C_6H_5$ were condensed into it. The reactor was sealed and warmed to 45 °C, and the mixture was stirred for 12 days. The reaction mixture was purified by distillation through a 0 °C U-trap into a −196 °C U-trap. A small amount of clear liquid condensed in the 0 °C trap and was again passed through a 0 °C trap into a −196 °C trap. The liquid that condensed in the 0 °C trap was analyzed by ^{11}B NMR spectroscopy. It exhibited a spectrum nearly identical with that of I.

The mass spectrum of the sample (Table II) confirmed its formulation as $^{12}C_7{}^1H_{15}{}^{11}B_5$: 2-$[(CH_3)C_6H_4]B_5H_8$ (II). The characteristic "double" envelope was present in the parent ion region, exhibiting the same 4-amu separation between maxima as was observed in the mass spectrum of I. The weight of the isolated 2-$[(CH_3)C_6H_4]B_5H_8$ product was 0.048 g, a yield of 3%.

The ^{11}B and ^1H spectra (Tables I and III) were consistent with the identification of the product as 2-$[(CH_3)C_6H_4]B_5H_8$. ^{13}C NMR spectra data: C(tertiary aromatic), 138.6, 137.4 ppm; C(aromatic bound to hydrogen), 134.8, 134.1, 131.1, 129.7, 129.0, 128.2; C-(methyl), 21.3.

Synthesis of 2-$[m\text{-}(CH_3)_2(C_6H_3)]B_5H_8$ (III). In a typical reaction, 1.3 g of $AlCl_3$ was placed in a 500-mL break-tip reactor containing a Teflon stirring bar. Next, the flask was evacuated and 0.50 g (5.0 mmol) of 2-ClB_5H_8 and 2 mL of *m*-xylene were condensed into it at −196 °C. The reactor was sealed and warmed to 40 °C, and the mixture was stirred for 3 days. The reaction mixture was fractionated as above. The ^{11}B NMR spectrum of the liquid product that condensed at 0 °C was very similar to those of I and II and indicated that a single boron-containing product had been obtained.

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Table III. ^{1}H NMR Data for 2-ArB_5H_8 Compounds

compd (solvent)	proton	chem shift, ppm	J, Hz, assignt
2-$(C_6H_5)B_5H_8$ (I) (CD_2Cl_2)	H(7,8)	−2.49	
	H(6,9)	−1.18	
	H(1)	1.60	172, q (^{11}B)
	H(4)	2.14	166, q (^{11}B)
	H(3,5)	2.57	158, q (^{11}B)
"AA'BB'C" Pattern			
		7.30	J_{AB} = 4.8, J_{AC} = 2.2, dd
		7.32	J_{BA} = 4.8, J_{BC} = 1.5, dd
		7.42	
2-[$(CH_3)C_6H_4$]B_5H_8 (II) (C_6D_6)	H(7,8)	−2.48	
	H(6,9)	−1.14	
	H(1)	1.86	174, q (^{11}B)
	H(4)	(2.5)	(166), q (^{11}B)
	H(3,5)	2.58	158, q (^{11}B)
Proposed IIc, AA'BB' Pattern			
		6.96	J_{AB} = 7.8, d
		7.26	J_{AB} = 7.8, d
Proposed IIb, Residual Pattern			
		6.96	7.2, d
		7.08	7.2, t
		7.12	s
		7.15	(C_6D_6)
2-[m-$(CH_3)_2C_6H_3$]B_5H_8 (III) (C_6D_6)	H(7,8)	−2.32	
	H(6,9)	−0.95	
	H(1)	1.44	155, q (^{11}B)
	H(4)	(2.4)	(166), q (^{11}B)
	H(3,5)	2.47	172, q (^{11}B)
Proposed IIIc, A_2X Pattern			
		6.90	s
		7.26	s
Proposed IIIc, ABX Pattern			
		6.93	s
		6.98	J_{AB} = 7.6, d
		7.38	J_{BA} = 7.6, d
Residual Pattern			
		7.05	m
		7.08	7.2 d (?)
		7.31	10.6 d (?)

The mass spectrum of this product (Table II) was consistent with the formulation $^{12}C_8{}^1H_{17}{}^{11}B_5$: 2-[$m$-$(CH_3)_2C_6H_3$]$B_5H_8$ (III). The parent ion region was again found to be a "double" envelope (4-amu separation of maxima), and an intense xylene peak was present at m/e 106. The weight of the isolated 2-[m-$(CH_3)_2C_6H_3$]B_5H_8 product was 0.072 g, a yield of 9%.

The ^{11}B and ^{1}H NMR spectra (Tables I and III) were also consistent with the formulation of the product as 2-[m-$(CH_3)_2C_6H_3$]B_5H_8. ^{13}C NMR spectral data: C(tertiary aromatic), 137.9 ppm; C(aromatic bonded to hydrogen), 135.8, 132.4, 131.2, 128.8; C(methyl), 21.7.

Synthesis of 2-[1,2,3-$(CH_3)_3C_6H_2$]B_5H_8 (IV). Approximately 0.3 g of $AlCl_3$ and 2 mL of 1,2,3-$(CH_3)_3C_6H_3$ were placed in a 250-mL reaction flask containing a Teflon stirring bar. The flask was evacuated and 0.613 g of 2-ClB_5H_8 was condensed into the reactor. The flask was sealed and warmed to 45 °C and the mixture was stirred for 10 days.

Upon fractionation of the reaction mixture a white solid was isolated in the −10 °C U-trap. Analysis of this solid by ^{11}B NMR spectroscopy showed only small amounts of the 2-Cl-1,2'-$(B_5H_7)(B_5H_8)$ product. The bulk of the material was identified as 1,2,4,5-$(CH_3)_4C_6H_2$ (an impurity in the 1,2,3-$(CH_3)_3C_6H_3$ starting material) by ^{1}H NMR and mass spectroscopy.

The ^{11}B NMR spectrum of a benzene extract of the nonvolatile reaction residue, however, suggested the presence of a 2-arylpentaborane(9) product similar to those previously produced. The nonvolatile materials were therefore extracted with benzene. After evaporation of C_6H_6 the residues were heated to 50 °C in a water-cooled sublimator, whereupon the product sublimed. Samples were collected from the sublimate for NMR and mass spectroscopy.

The ^{11}B NMR spectrum of the sublimate (Table I) was nearly identical with those of the previously isolated arylboranes and showed no boron-containing impurities.

The mass spectrum of the sample (Table II) confirmed the formulation $^{12}C_9{}^1H_{11}{}^{11}B_5$: 2-[1,2,3-$(CH_3)_3C_6H_2$]$B_5H_8$ (IV). The spectrum of IV contained features similar to those found in the spectra of I, II, and III.

Attempts to obtain a proton spectrum of IV were hampered by the presence of low-volatility impurities. The use of fractional sublimation, which was dictated by the air sensitivity and volatility of the product, was an inadequate purification method to remove proton- and carbon-containing impurities from the sample.

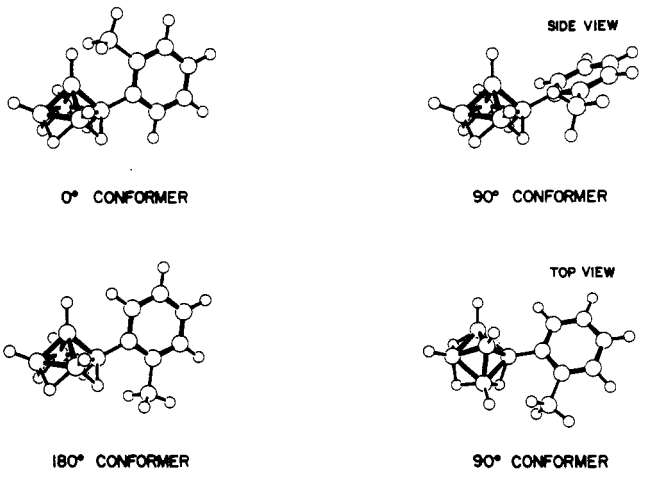

Figure 1. Rotational isomers of IIa (assumed B–C distance 1.6 Å).

Results

Synthesis of I–IV. A series of 2-ArB_5H_8 derivatives were prepared via Friedel–Crafts-catalyzed electrophilic attack of 2-ClB_5H_8 on various aromatic hydrocarbons (eq 4, where ArH = benzene, toluene, m-xylene, 1,2,3-trimethylbenzene).

$$2\text{-}ClB_5H_8 + ArH \xrightarrow{AlCl_3} 2\text{-}ArB_5H_8 + HCl \qquad (4)$$

Previous syntheses of alkylpentaboranes were dependent either on the attack of carbocationic species on the apical boron atom of B_5H_9 (eq 2 and 3)[3] or on the thermolysis of B_5H_9 in the presence of olefins (eq 1).[2] These methods precluded general access to arylpentaborane derivatives. The presence of positive charge density on the basal boron atoms of B_5H_9 predicted by Lipscomb[8] is consistent with the presence of a B(2)-localized "boranocation" acting as the electrophilic intermediate in the 2-ArB_5H_8 syntheses.

Attempts to produce a 2-mesitylpentaborane derivative were unsuccessful under reaction conditions similar to those used in the syntheses of I–IV. Steric constraints imposed by *two* α-methyl groups probably hinder the electrophilic attack by the B_5H_8 moiety. Figure 1 illustrates the potential steric interaction caused by the presence of a methyl substituent α to the site of substitution of the pentaborane cage. Measurements on idealized models of this isomer (constructed from X-ray crystal structure data for pentaborane and toluene[9,10]) indicate serious steric interactions between the methyl group and the borane-bound hydrogens unless the methyl group is positioned adjacent to the bridging protons of the borane (Figure 1: 180° dihedral angle). Positioning the methyl group adjacent to the apical terminal or basal terminal hydrogens (Figure 1: 0 and 90° dihedral angles, respectively) leads to

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minimum interaction distances of 1.0 and 1.3 Å, respectively. The addition of a second α-methyl group would introduce serious steric interactions in all rotational conformations.

The syntheses of 2-arylpentaboranes produced one borane byproduct of volatility similar to that of the desired products. The formulation of 2-Cl-1,2′-$(B_5H_7)(B_5H_8)$ was consistent with the ^{11}B NMR spectrum of the byproduct, which is most likely formed by Friedel–Crafts-catalyzed coupling of 2-ClB_5H_8 (eq 5).[5] The byproduct was easily removed from II and III by

$$2(2\text{-}ClB_5H_8) \xrightarrow{AlCl_3} 2\text{-}Cl\text{-}1,2'\text{-}(B_5H_7)(B_5H_8) + HCl \quad (5)$$

fractional distillation but was never totally removed for I. Excess aromatic reactant and moderate reaction temperatures helped suppress the 2-ClB_5H_8 coupling.

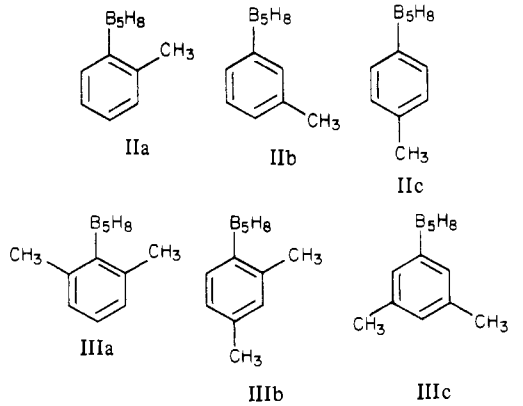
Reactions of 2-ArB_5H_8. Attempts to produce 1-arylpentaborane derivatives via isomerization of the corresponding 2-arylpentaboranes were unsuccessful. No evidence for the isomerization of III was observed after heating samples in diethyl ether and THF for several days. Treatment of II with HMTA at ambient temperature for 1 week also failed to produce isomerization.

These results can be rationalized by comparison with previous isomerization studies on alkylpentaboranes. Equilibria in the interconversion of 1- and 2-alkylpentaboranes greatly favor the 2-substituted species. For example, in the presence of Lewis bases, 1-$(CH_3)B_5H_8$ is converted nearly quantitatively to 2-$(CH_3)B_5H_8$.[6] If the major effect that the aryl substituent exerts on the pentaborane cage is similar to that of an alkyl group, then an equilibrium position greatly favoring the 2-aryl derivative is expected.

Discussion

A representative ^{11}B NMR spectrum of the 2-ArB_5H_8 derivatives is shown in Figure 2. The singlet of intensity 1 at 0 ppm arises from the B(2) boron substituted by the aryl ring, while the doublet near −19 ppm arises from the B(4) boron diagonally across the cage from the point of substitution. The doublets at −14.5 and −51 ppm arise from the B(3,5) and B(1) boron atoms, which are relatively unshifted compared to their positions in B_5H_9. These chemical shift values are nearly identical with those of 2-alkylpentaboranes. This observation supports the conclusion, drawn from the isomerization studies, that the substituent effect of the aryl ring in the B(2) position is similar to that of an alkyl group.

One important structural feature of II and III that cannot be elucidated by ^{11}B NMR spectroscopy is the position of the B_5H_8 moiety relative to that of the alkyl groups of the tolyl (IIa–c) and *m*-xylyl (IIIa–c) derivatives. Analysis of the ^1H and ^{13}C NMR spectra of II and III should give more information about the distribution of substitutional isomers. In addition, the failure of the reaction of 2-ClB_5H_8 with mesitylene suggests that the formation of isomers with fewer methyl groups ortho to the B_5H_8 substituent will be favored. For example, analysis of the ^1H and ^{13}C NMR spectra of III should confirm that IIIb and IIIc are formed in preference to IIIa.



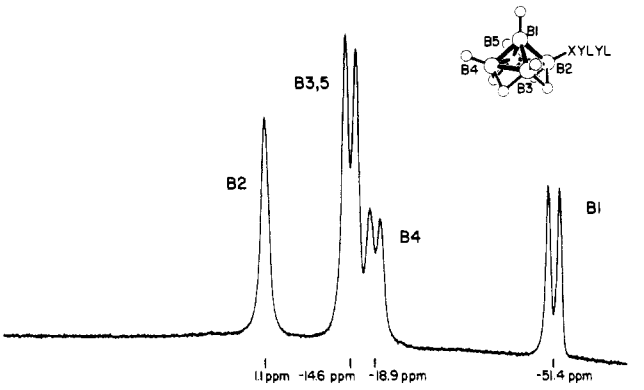


Figure 2. ^{11}B NMR spectrum (86.6 MHz) of III.

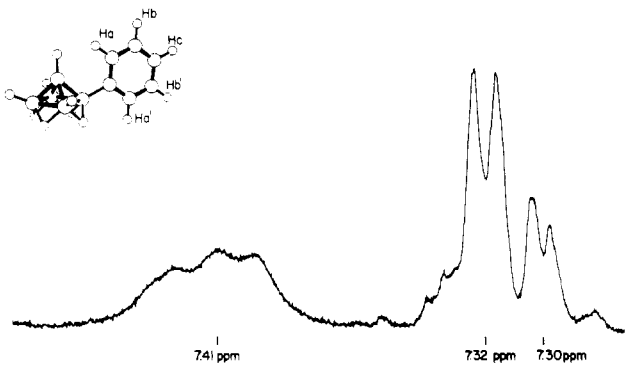


Figure 3. ^1H NMR spectrum (270 MHz) of I (aromatic region).

Analyses of the ^1H and ^{13}C NMR spectra of I are helpful in the assignment of the more complex systems presented by II and III. The protons bound to the borane portion of I (Table III), which are quite similar to the corresponding protons of II and III, appear in a pattern consistent with 2-substitution at pentaborane. The ^1H NMR aromatic region of I, shown in Figure 3, is an AA′BB′C pattern. Simple assignments, based on a first-order approximation of the spin system, are compiled in Table III. The $^{13}C\{^1H\}$ NMR spectrum of I exhibits only three resonances in the aromatic region. The resonance corresponding to the C(4) carbon, which is σ bonded to the B(2) boron atom, is expected to be split into a quartet and broadened by scalar coupling relaxation from the quadrupolar ^{11}B nucleus. Because of these two effects, the resonance representing the C(4) carbon atom is not observed (similarly, carbon atoms involved in carbon–boron σ bonds in II and III are not observed). Absolute assignments of the remaining resonances were not possible as insufficient sample was available for T_1 studies. However, the resonances may be assigned by analogy to toluene, with the assumption of a B_5H_8 substituent effect similar to that of a methyl group, increasing chemical shift values representing increasing proximity to the pentaborane substituent. Such assignments are proposed for discussion only and are not considered to be absolute.

The aromatic region of the ^1H NMR spectrum of II (Figure 4) is not consistent with the presence of a single isomer; however, selective proton-decoupling experiments have helped in the assignment of the overlapping patterns. Decoupling of the high-field doublet at 6.96 ppm collapses the low-field doublet at 7.26 ppm to a singlet. Similarly, when the low-field doublet is irradiated, about half of the intensity of the high-field doublet collapses to a singlet. These two resonances represent an AA′BB′ pattern, a result consistent with the expected pattern from isomer IIc. The residual doublet at 6.96

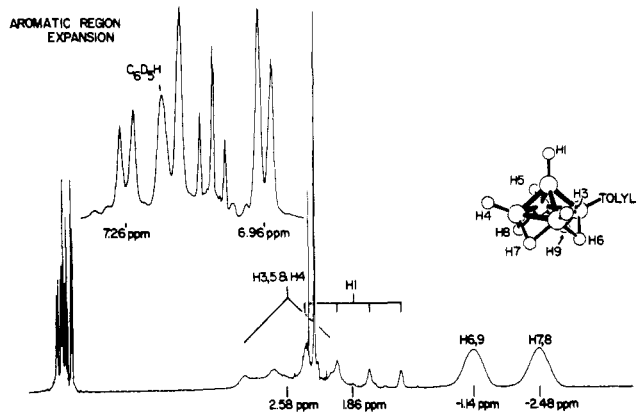


Figure 4. ^1H NMR spectrum (270 MHz) of II (aromatic region expanded).

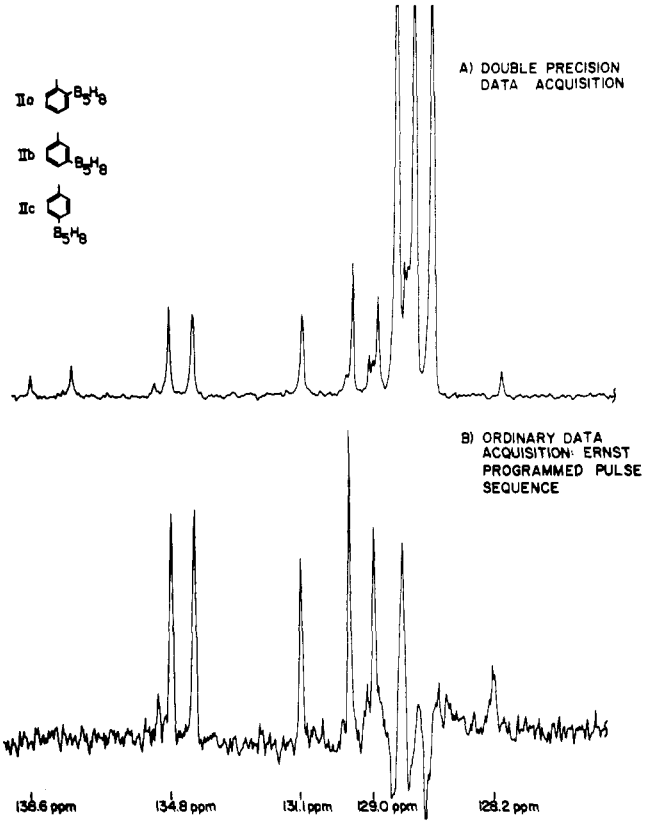


Figure 5. $^{13}C\{^1H\}$ and $^{13}C\{^1H\}$ Ernst-Doddrell NMR spectra (50.1 MHz) of II (aromatic region).

ppm has a coupling constant of 7.2 Hz, which is identical with the coupling constant of the pseudotriplet at 7.08 ppm. The remaining unobscured resonance is a pseudosinglet at 7.12 ppm. Of the two remaining isomers, IIa would be expected to display two pseudotriplet (or doublet of doublet) patterns and two doublet patterns, while IIb would be expected to display one pseudotriplet, two doublet, and one pseudosinglet pattern. The two patterns *suggest* that these remaining signals arise from isomer IIb, in part because a more complex pattern would be expected from isomer IIc. An attempt to simplify the pattern around 7.1 ppm by changing lock solvents to CD_2Cl_2 was unsuccessful due to significant solvent shifts.

The $^{13}C\{^1H\}$ NMR spectrum of II (Figure 5) also suggests that only two isomers are present in any significant quantity. A normal double-precision acquisition spectrum shows the presence of two different $^{13}C-CH_3$ resonances at 138.6 and 137.4 ppm. Acquisition in the Ernst–Doddrell mode identifies

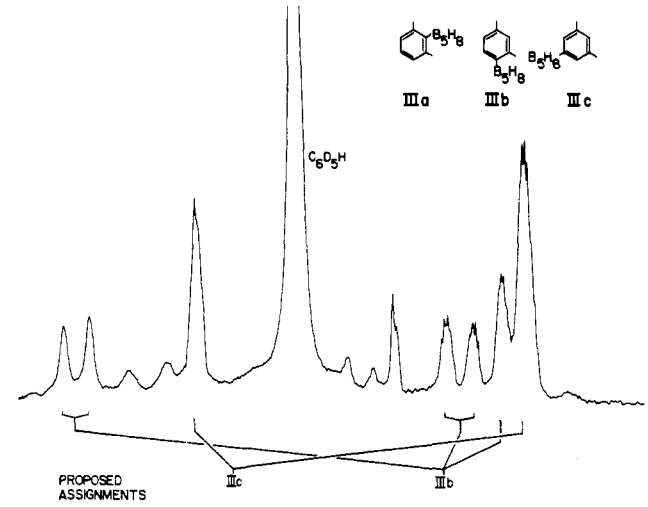


Figure 6. ^1H NMR spectrum (270 MHz) of III (aromatic region).

six separate types of $^{13}C-^1H$ aromatic carbons, which is consistent with the presence of only two isomers of II. From these data, it is apparent that only two of the possible three isomers of II are present in significant quantities. The ^1H NMR spectrum confirms the presence of IIc, and the remaining resonances appear more consistent with IIb than with IIa. This would indicate that the weak directive effect of the methyl group for substitution at ortho positions may be overcome by steric interactions with the B_5H_8 group.

The ^1H NMR spectrum of III (Figure 6) is again consistent with the presence of two major isomers in the product mixture. The pseudosinglets at 6.90 and 7.26 ppm, with approximate intensities of 1:2, respectively, are consistent with the expected pattern of IIIc. The doublet resonances at 6.98 and 7.38 ppm make up an AB pattern, as confirmed by selective decoupling. These two resonances plus the pseudosinglet of similar intensity at 6.93 ppm comprise a pattern consistent with that expected from IIb. The ^1H NMR spectrum of isomer IIa should appear as an A_2B pattern. Some of the weak resonances in the aromatic region that remain unassigned may arise from this isomer. The $^{13}C\{^1H\}$ NMR spectrum of III was very weak, and the identity and number of the resonances present are difficult to assign with certainty.

Substitution of the B_5H_8 moiety on *m*-xylene also appears to be sterically controlled. Formation of the IIIa isomer, at an electronically activated position, seems not to occur. Instead, isomers IIIb and IIIc appear to form via substitution at the less sterically hindered positions.

Conclusion

Various 2-substituted aromatic derivatives of pentaborane should now be accessible via Friedel–Crafts syntheses. In the absence of strongly directing substituents the B_5H_8 group interacts with the aromatic ring to form mixtures of the least sterically hindered isomers. The 2-ArB_5H_8 derivatives show no tendency to isomerize in the presence of Lewis bases. This behavior is consistent with other data, which suggest that the substituent effect of the aryl moiety is similar to that of an alkyl moiety.

Acknowledgment. This work was supported in part by grants, including departmental instrument grants for NMR and mass spectral facilities, from the National Science Foundation. We thank Dr. David F. Hillenbrand for helpful discussions.

Registry No. I, 83076-42-0; IIb, 83076-44-2; IIc, 83076-43-1; IIIb, 83076-46-4; IIIc, 83076-45-3; IV, 83076-47-5; 2-ClB_5H_8, 19469-14-8; C_6H_6, 71-43-2; $CH_3C_6H_5$, 108-88-3; *m*-xylene, 108-38-3; 1,2,3-$(CH_3)_3C_6H_3$, 526-73-8.