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A Multinuclear Magnetic Resonance Investigation of Geometrical and Rotational Isomerism in Difluorophosphine Derivatives of Tetraborane(8)[1]

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A series of $B_4H_8{\cdot}PF_2X$ (X = F, Cl, Br, I, H) molecules has been studied by multinuclear (^1H, ^{11}B, ^{19}F, ^{31}P) NMR techniques. Low-temperature ^{19}F NMR has been found to be of great utility in establishing that in all cases except where X = H the molecules exist as geometrical isomers (endo and exo placement of the phosphine with respect to the folded B_4 framework) at ambient temperature. At low temperatures rotation about the P–B bond in the endo isomer becomes slow with respect to the ^{19}F NMR time scale and rotational isomers are observed. In the PF_3 and PF_2I adducts only one rotational isomer of the endo geometrical isomer is observed. In the PF_2Cl and PF_2Br complexes two rotational isomers of the endo geometrical isomer are found. In all of the above complexes rotation about the P–B bond in the exo isomer remains rapid with respect to the ^{19}F NMR time scale. In agreement with a previous study, no evidence is found for geometrical isomers in $B_4H_8{\cdot}PF_2H$. Long-range P–B and P–H spin–spin coupling is observed in the ^{11}B and ^{31}P NMR spectra of $B_4H_8{\cdot}PF_2H$ and is not observed in spectra of any of the other molecules studied. The anomalous properties of PF_2H as a base relative to other PF_2X molecules are discussed.

Introduction

Recent reports[1,3] from this laboratory of NMR studies of $B_4H_8{\cdot}PF_2N(CH_3)_2$ have confirmed that the isomers observed at room temperature in this compound arise from endo and exo placement of the ligand and not from restricted rotation about the P–B bond which could also be the origin of isomers.[4] The utility of ^{11}B, ^{31}P, and ^{19}F NMR in establishing the presence of the isomers in $B_4H_8{\cdot}PF_2N(CH_3)_2$ was also demonstrated. The ^{19}F NMR spectra of $B_4H_8{\cdot}PF_3$, $B_4H_8{\cdot}PF_2Cl$, $B_4H_8{\cdot}PF_2Br$, and $B_4H_8{\cdot}PF_2I$ have been reported[4] to be similar to that of $B_4H_8{\cdot}PF_2N(CH_3)_2$ in that they indicate the presence of two isomers for each compound. Interestingly, the ^{19}F NMR spectrum of $B_4H_8{\cdot}PF_2H$ shows no evidence for the existence of isomers.[5]

In view of the results for $B_4H_8{\cdot}PF_2N(CH_3)_2$, we have undertaken a multinuclear (^{11}B, ^{19}F, and ^{31}P) variable-temperature NMR study of other $B_4H_8{\cdot}PF_2X$ (X = F, Cl, Br, I, H) compounds. We were particularly interested in investigating the utility of ^{11}B and ^{31}P NMR spectroscopy in the study of these compounds and in investigating the behavior of the molecules at low temperatures by ^{19}F NMR spectroscopy in order to gain insight into the nature of the isomers.

Experimental Section

The B_4H_8L complexes were prepared by reaction of B_5H_{11} with the appropriate bases[4] and by base displacement from B_4H_8CO. B_5H_{11}[6] and B_4H_8CO[7] were prepared by published methods. The bases PF_2Cl, PF_2Br, and PF_2I were prepared from $(CH_3)_2NPF_2$ by published procedures.[8] Difluorophosphine was prepared from PH_3, PF_2I, and Hg as previously reported.[9] The PF_3 was purchased from Ozark-Mahoning. Purity of each base was checked by vapor pressure, IR spectrum, and/or mass spectrum. Standard high-vacuum techniques were employed throughout all preparative procedures.

Syntheses of B_4H_8L complexes from B_4H_8CO seemed to provide better results than did those from B_5H_{11}. In a typical experiment using B_5H_{11}, approximately 1.5 mmol of B_5H_{11} and 3.5 mmol of PF_2X (X = Cl, Br, I) were condensed into an all-glass reaction vessel at −196 °C. The vessel was removed from the vacuum line and held at −78 °C for approximately 4 days. The vessel was then returned to the vacuum line, and the volatile components of the reaction mixture were separated on a low-temperature vacuum fractionation column.[10] The appropriate fraction was then condensed into an NMR tube at −196 °C. No pure samples of $B_4H_8{\cdot}PF_2X$ (X = Cl, Br, I) could be obtained in this way. Initial attempts to prepare these compounds from B_4H_8CO via displacement were also unsuccessful. In a typical experiment, approximately 1.0 mmol of B_4H_8CO and 2.0 mmol of PF_2X were condensed at −196 °C into a small volume reaction vessel and isolated from the vacuum line by a greaseless stopcock. The reactants were allowed to warm slowly to 0 °C and held there for 10 min. The tube was then frozen to −196 °C and the liberated CO was pumped into a calibrated volume by a Toepler pump. This procedure was repeated until CO evolution ceased. The products were pumped directly onto a low-temperature fractionation column. This procedure provided pure $B_4H_8PF_2H$; however, for $B_4H_8PF_2X$ (X = Cl, Br, I) it was not possible to transfer the products under vacuum to an NMR tube (or any other vessel) without significant decomposition. In order to obtain NMR samples without transferring the isolated product, we sealed an NMR tube onto the bottom of the U-trap at the top of the cold column. The appropriate fraction from the separation was collected in the trap and carefully moved down into the NMR tube. The appropriate solvent was then condensed into the tube, and the tube was sealed under dynamic vacuum. This procedure provided reasonably pure (by NMR) samples of $B_4H_8{\cdot}PF_2Cl$ and $B_4H_8{\cdot}PF_2Br$. However, $B_4H_8{\cdot}PF_2I$ is very thermally unstable, and NMR spectra of samples prepared in this way still displayed significant concentrations of impurities.

The NMR spectra were recorded on a highly modified Varian Associates XL-100-15 spectrometer. Standard variable-temperature accessories were employed. Low-temperature ^{19}F NMR (94.1-MHz) spectra were obtained by using 20% solutions in a 1:1 (v/v) mixture of isopentane and toluene-d_8. The ^{11}B (32.1-MHz), ^{31}P (40.5-MHz), and ^1H (100.1-MHz) NMR spectra were obtained by using 20% solutions in pentane, toluene-d_8, or cyclohexane-d_{12}. The 200.1-MHz ^1H, 64.2-MHz ^{11}B, and 81.0-MHz ^{31}P NMR spectra of $B_4H_8{\cdot}PF_2H$ were obtained on a Bruker WP-200 spectrometer.

Chemical shifts were measured relative to external Me_4Si (^1H), $BF_3{\cdot}O(C_2H_5)_2$ (^{11}B), 85% o-H_3PO_4 (^{31}P), and F_3CCOOH (^{19}F). A negative sign (−) denotes increased shielding. Unless otherwise stated, the chemical shifts are accurate to ±0.5 ppm. Coupling constants were measured directly from the spectra and are accurate to ±1 Hz.

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(1) Part 19 in the series, "Spectra and Structure of Phosphorus–Boron Compounds". For part 18 see J. D. Odom, T. F. Moore, W. H. Dawson, A. R. Garber, and E. J. Stampf, *Inorg. Chem.*, **18**, 2179 (1979).

(2) Taken in part from the thesis of T. F. Moore (Aug 1978), submitted to the Department of Chemistry, University of South Carolina, in partial fulfillment of the requirements for the Ph.D. degree.

(3) J. D. Odom, T. F. Moore, and A. R. Garber, *Inorg. Nucl. Chem. Lett.*, **14**, 45 (1978).

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Table I. NMR Parameters of $B_4H_8{\cdot}PF_2X$ Compounds

	$B_4H_8{\cdot}PF_2N(CH_3)_2$	$B_4H_8{\cdot}PF_3$	$B_4H_8{\cdot}PF_2Cl$	$B_4H_8{\cdot}PF_2Br$	$B_4H_8{\cdot}PF_2I$	$B_4H_8{\cdot}PF_2H$
$\delta(^{11}B_1)^a$	−54.9	−58.5	−50.2	−49.8	−49.3	−54.7
$\delta(^{11}B_{2,4})^a$	−3.9	−3.2	−2.2	−4.2	−4.8	−6.3
$\delta(^{11}B_3)^a$	+3.6 −0.5	+1.9	+4.1	+2.5	+2.3	+1.7
$\delta(^{31}P)^b$	+127.2	+96.6	+136.1	+135.1	+132.5	+123.5
$\delta(^{19}F_A)^c$	+8.0	+23.8	+35.6	+40.3	+41.7	+41.8
$\delta(^{19}F_B)^c$	+6.9	+21.4	+34.6	+38.5	+37.5	
J_{P-F_A}, Hz	1110	1280	1280	1280	1270	1120
J_{P-F_B}, Hz	1155	1370	1330	1325	1300	
J_{P-B}, Hz	175 170	175	147	135	138	135
J_{B-B}, Hz	24	25	25	25	25	24
J_{P-H}, Hz						655
J_{F-H}, Hz						60

[a] Chemical shifts relative to $BF_3{\cdot}O(C_2H_5)_2$. [b] Chemical shifts relative to 85% H_3PO_4. [c] Chemical shifts relative to F_3CCOOH.

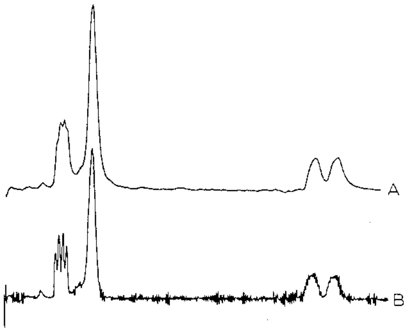

Figure 1. 32.1-MHz proton-decoupled ^{11}B NMR spectrum of $B_4H_8{\cdot}PF_2Cl$ at −20 °C: (A) normal; (B) line narrowed.

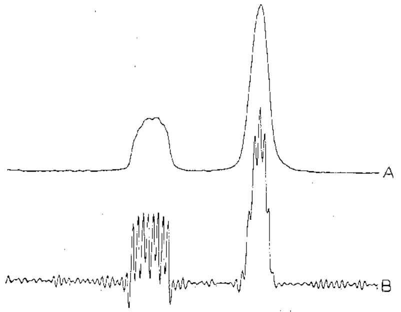

Figure 2. Deshielded resonances (B_3 and $B_{2,4}$) in the 32.1-MHz proton-decoupled ^{11}B NMR spectrum of $B_4H_8{\cdot}PF_2H$: (A) normal; (B) line narrowed.

Results

^{11}B NMR Spectra. $B_4H_8{\cdot}PF_3$. The proton-decoupled ^{11}B NMR spectrum of $B_4H_8{\cdot}PF_3$ is similar to that[1] of $B_4H_8{\cdot}PF_2N(CH_3)_2$ and contains three resonances. The most shielded resonance, a doublet of relative area one, is assigned to the substituted boron atom (B_1, δ −58.5) with the doublet structure arising from coupling to the directly bonded phosphorus nucleus (J_{B-P} = 175 Hz). The deshielded resonances of relative areas one and two are assigned to B_3 (δ +1.9) and $B_{2,4}$ (δ −3.2), respectively. With the aid of computer line narrowing the B_3 resonance appears as a quartet due to B_1–B_3 spin–spin coupling (J_{B-B} = 25 Hz). Due to the thermal instability of $PF_3{\cdot}B_4H_8$, no high-temperature ^{11}B NMR spectra were recorded.

$B_4H_8{\cdot}PF_2Cl$, $B_4H_8{\cdot}PF_2Br$, and $B_4H_8{\cdot}PF_2I$. The proton-coupled ^{11}B NMR spectra of these compounds were reported by Paine and Parry.[4] These spectra are very similar to that[1] of $B_4H_8{\cdot}PF_2N(CH_3)_2$ in that they all consist of a shielded triplet of relative area one (B_1) and a deshielded multiplet arising from overlap of an area two triplet ($B_{2,4}$) and an area one doublet (B_3). Appropriate chemical shifts and coupling constants are given in Table I. The proton-decoupled ^{11}B spectrum of $B_4H_8{\cdot}PF_2Cl$ at −20 °C is shown in Figure 1A. The expected doublet at high shielding, a deshielded singlet, and a poorly resolved quartet are observed. Computer line narrowing completely resolves the boron–boron spin coupling in the B_3 resonance (Figure 1B). However, additional resonances were not observed even with the use of PRFT techniques. An ambient-temperature line-narrowed spectrum exhibited additional multiplicity in the deshielded resonance (B_3), but acquisition of enough transients to obtain an adequate signal to noise ratio for good resolution with line narrowing was prevented by decomposition of the sample.

The ^{11}B NMR spectra of $B_4H_8{\cdot}PF_2Br$ and $B_4H_8{\cdot}PF_2I$ are essentially identical with that of $B_4H_8{\cdot}PF_2Cl$ at low temperature (−25 °C). Increased thermal instability of these compounds relative to $B_4H_8{\cdot}PF_2Cl$ with the concomitant increase in the presence of impurities in the samples preclude extraction of additional information from the spectra of these compounds.

$B_4H_8{\cdot}PF_2H$. The proton-coupled 32.1-MHz ^{11}B NMR spectrum of $B_4H_8{\cdot}PF_2H$ was first reported by Centofanti et al.[5] and is very similar to those of other $B_4H_8{\cdot}PF_2X$ compounds. The spectrum consists of a shielded triplet, B_1, and a deshielded multiplet which arises from overlap of a triplet, $B_{2,4}$, and a doublet, B_3. The proton-decoupled spectrum exhibits the expected doublet at high shielding, B_1 (δ −54.7 (J_{P-B} = 135 Hz)), and singlets at lower shielding, B_3 and $B_{2,4}$ (δ +1.7, −6.3). An expanded view of the B_3 and $B_{2,4}$ resonances is shown in Figure 2. The computer line-narrowed spectrum (Figure 2B) shows the B_3 resonance to be composed of eight lines of approximately equal intensities. The resolution of these lines is solvent dependent: eight lines could not be resolved with toluene-d_8 as solvent while this was easily done with pentane or cyclohexane-d_{12} as solvent. The spacing between each of these lines is 12 Hz. This result is entirely reproducible with different samples on different days.

Because the pattern of the B_3 resonance could be the result of either two overlapping quartets with $J_{B_1B_3}$ = 24 Hz or long-range B–P spin coupling, two experiments were performed. First, a 64.2-MHz ^{11}B line-narrowed spectrum was obtained in C_6D_{12}. The spectrum is identical with that at 32.1 MHz, exhibiting eight lines with a separation of 12 Hz. Second, a triple resonance experiment at 32.1 MHz was performed. Both ^{31}P and ^1H were decoupled while ^{11}B was observed. In this experiment enough power was delivered at 40.5 MHz to almost completely decouple phosphorus from the directly bonded boron B_1. Under these conditions it was not possible to resolve eight lines in the B_3 resonance. However, because of the proximity of the ^{11}B and ^{31}P resonance frequencies (32.1 and 40.5 MHz), there was a significant increase in noise at the receiver under the triple resonance conditions and it is difficult to draw concrete conclusions from this experiment.

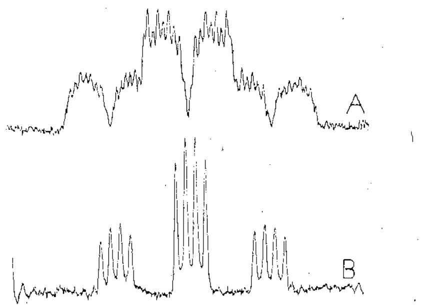

Figure 3. 40.5-MHz ^{31}P NMR spectrum of $B_4H_8{\cdot}PF_2H$: (A) coupled; (B) proton decoupled.

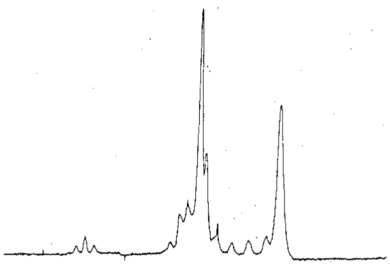

Figure 4. 100-MHz ^{11}B-decoupled ^{1}H NMR spectrum of $B_4H_8{\cdot}PF_2H$.

The eight-line pattern observed for B_3 showed no temperature dependence from −20 to +100 °C. No decomposition of the sample was observed during the course of this experiment.

^{31}P NMR Spectra. $B_4H_8{\cdot}PF_3$. The ^{31}P NMR spectrum of $B_4H_8{\cdot}PF_3$ is centered at +96.6 ppm and consists of a quartet (J_{P-F} = 1280 Hz), each member of which is further split into a quartet due to spin–spin coupling to the directly bonded boron nucleus (J_{P-B} = 175 Hz).

$B_4H_8{\cdot}PF_2Cl$, $B_4H_8{\cdot}PF_2Br$, and $B_4H_8{\cdot}PF_2I$. The ^{31}P NMR spectrum of each of these compounds consists of a triplet due to coupling to two fluorine atoms, each member of which is split into a quartet from coupling to the directly bonded boron atom. The values of the chemical shifts and coupling constants for each compound are given in Table I.

$B_4H_8{\cdot}PF_2H$. The ^{31}P NMR spectrum of $B_4H_8{\cdot}PF_2H$ is shown in Figure 3A. This spectrum is basically a triplet (J_{P-F} = 1120 Hz) of doublets (J_{P-H} = 655 Hz), each member of which is further split into a nine-line multiplet. This spectrum is much more complex than the triplet (J_{P-F}) of doublets (J_{P-H}) of quartets (J_{P-B}) which one would predict. Under conditions of proton-decoupling one observes the expected triplet (J_{P-F} = 1120 Hz) of quartets (J_{P-B} = 135 Hz) as shown in Figure 3B. Therefore, the increased multiplicity observed in the proton-coupled spectrum must arise from P–H coupling.

The 81.0-MHz ^{31}P NMR spectra both with and without ^{1}H decoupling are identical with the 40.5-MHz spectra.

^{1}H NMR Spectra. $B_4H_8{\cdot}PF_2H$. The 100-MHz proton NMR spectrum of $B_4H_8{\cdot}PF_2H$ is complex and difficult to interpret. ^{11}B noise decoupling significantly simplifies the spectrum (Figure 4) although it was not possible to simultaneously decouple all four boron nuclei. The ^{11}B resonance of B_1 is shielded by approximately 2000 Hz with respect to the $B_{2,4}$ and B_3 resonances, and it was impossible to deliver enough power over this broad range to simultaneously decouple all the borons. The most shielded resonance (δ −2.7) arises from the two bridging protons. The B_1 nucleus is not decoupled, and the directly bonded ^{1}H appears as a quartet at δ −0.1. The $B_{2,4}$ terminal proton resonance and B_3 terminal proton resonance appear at δ +2.6 and +3.4, respectively. The proton bound to phosphorus appears as a doublet (J_{P-H} = 650 Hz) of triplets (J_{F-H} = 60 Hz) centered at δ +6.1. In the coupled spectrum, each member of this multiplet is further split into a quintet. Centofanti and co-workers[5] described the observed quintet structure as arising from equivalent coupling of 9.4 Hz to B_1 and the proton attached to B_1. Under these conditions overlapping peaks give rise to the observed quintet.

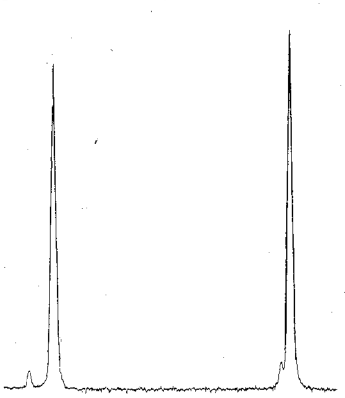

Figure 5. 94.1-MHz ^{19}F NMR spectrum of $B_4H_8{\cdot}PF_3$ at −50 °C.

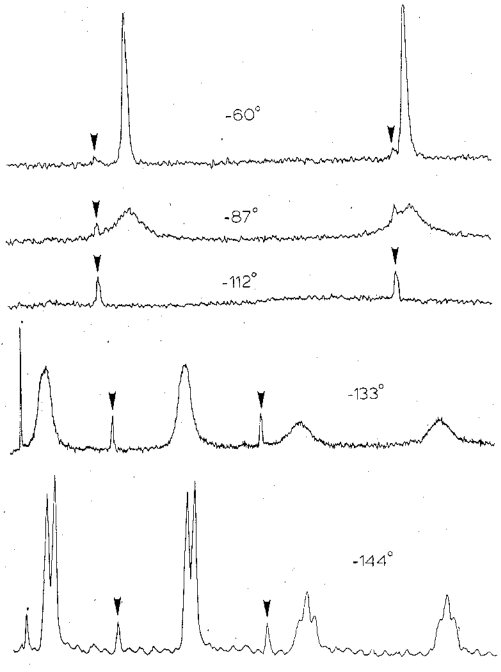

Figure 6. Low-temperature 94.1-MHz ^{19}F spectra of $B_4H_8{\cdot}PF_3$. Sweep width for spectra at −60, −87, and −112 °C is 3000 Hz and for spectra at −133 and −144 °C, 5000 Hz. Doublet marked with an arrowhead represents the exo isomer. Peaks marked with an asterisk result from small amount of PF_3.

^{19}F NMR Spectra. $B_4H_8{\cdot}PF_3$. The ^{19}F NMR spectrum of $B_4H_8{\cdot}PF_3$ was reported[4] as a pair of widely spaced doublets, indicating the presence of two isomers in solution. The spectrum obtained at −50 °C is shown in Figure 5. There are two widely spaced doublets: δ 23.8 (J_{P-F} = 1370 Hz) and 21.4 (J_{P-F} = 1280 Hz); however, the doublet centered at 21.4 ppm is much more intense than that at 23.8 ppm, indicating a large difference in population for the two isomers. The low-temperature dependence of this spectrum is shown in Figure 6. At −87 °C the doublet which is more intense at −60 °C has broadened extensively while the second doublet is virtually unchanged. At −112 °C the doublet which was more intense has completely collapsed, and all that is seen in the spectrum is the minor doublet. At −133 °C four new resonances (two doublets) have grown into the spectrum. At −144 °C these doublets are in an area ratio of 2:1 and each is further split: the area 2 doublet (δ 30.8) into a doublet of doublets and the area 1 doublet (δ 5.8) into a doublet of triplets. These splittings are equivalent and equal to 70 Hz.

Table II. Low-Temperature ^{19}F NMR Spectral Parameters of $B_4H_8 \cdot PF_2X$ Molecules[a]

$B_4H_8 \cdot PF_2N(CH_3)_2$[1,3] (−125 °C)	$B_4H_8 \cdot PF_3$ (−144 °C)	$B_4H_8 \cdot PF_2Cl$ (−130 °C)	$B_4H_8 \cdot PF_2Br$ (−131 °C)	$B_4H_8 \cdot PF_2I$ (−130 °C)
$\delta(^{19}F)$ 12.5 $J_{P-F} = 1150$ Hz	$\delta(^{19}F)$ 30.8 $J_{P-F} = 1344$ Hz	$\delta(^{19}F)$ 48.9 $J_{P-F} = 1266$ Hz	$\delta(^{19}F)$ 56.8 $J_{P-F} = 1265$ Hz	$\delta(^{19}F)$ 45.3 $J_{P-F} = 1245$ Hz
$\delta(^{19}F)$ 3.0 $J_{P-F} = 1080$ Hz	$\delta(^{19}F)$ 5.8 $J_{P-F} = 1327$ Hz	$\delta(^{19}F)$ 40.2 $J_{P-F} = 1260$	$\delta(^{19}F)$ 45.6 $J_{P-F} = 1262$ Hz	
$J_{F-F} = 40$ Hz	$J_{F-F} = 70$ Hz	$\delta(^{19}F)$ 14.3 $J_{P-F} = 1296$ Hz	$\delta(^{19}F)$ 16.8 $J_{P-F} = 1295$ Hz	

[a] Chemical shifts relative to F_3CCOOH.

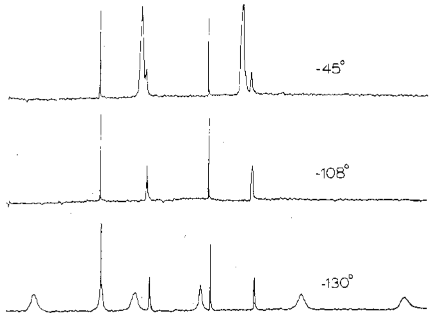

Figure 7. Low-temperature 94.1-MHz ^{19}F spectra of $B_4H_8 \cdot PF_2Cl$. A sharp doublet is in all spectra (the asterisk in −130 °C spectrum) resulting from a small amount of PF_2Cl.

The thermal instability of this compound prevented a study of the ^{19}F spectrum at high temperature.

$B_4H_8 \cdot PF_2Cl$, $B_4H_8 \cdot PF_2Br$, and $B_4H_8 \cdot PF_2I$. The ^{19}F NMR spectra of these compounds were reported by Paine and Parry.[4] The spectrum of each compound was described as a pair of widely spaced doublets (J_{PF} = 1260–1360 Hz) with a small chemical shift difference between members of the doublets. The chemical shifts and coupling constants for each complex are given in Table I. The reversible ^{19}F spectra changes between −40 and +40 °C were reported by Paine and Parry, and thus we have investigated the temperature dependence of the ^{19}F spectra of these compounds below −40 °C. These low-temperature spectra closely resemble those of $B_4H_8 \cdot PF_2N(CH_3)_2$[1] in that one of the doublets broadens and completely collapses as the temperature is lowered and then new resonances grow into the spectrum. However, for $B_4H_8 \cdot PF_2Cl$ (Figure 7) and $B_4H_8 \cdot PF_2Br$, six new resonances, three doublets, appear in the spectra, while for $B_4H_8 \cdot PF_2I$ (Figure 8) only two new resonances, one doublet, appear. The chemical shifts and coupling constants for the limiting low-temperature spectra are given in Table II.

$B_4H_8 \cdot PF_2H$. The ^{19}F NMR spectrum of $B_4H_8 \cdot PF_2H$ was reported by Centofanti et al.[5] The spectrum consists of a widely spaced doublet (J_{P-F} = 1120 Hz) of doublets (J_{H-F} = 54 Hz) centered at 41.8 ppm relative to trifluoroacetic acid. The behavior of this spectrum as a function of temperature has not been reported. There are no significant spectral changes between +90 and −120 °C. The changes which are observed are a sharpening as the temperature is lowered from ambient temperature to −110 °C and a slight broadening between −110 and −124 °C. The sharpening is presumably due to the loss of unresolved B–F coupling as the temperature is lowered. The broadening is the result of shorter relaxation times at lower temperatures (i.e., "viscosity broadening").

Discussion

The ^{11}B and ^{31}P NMR data for the $B_4H_8 \cdot PF_2X$ compounds (X = F, Cl, Br, I) are of little utility in determining the existence and nature of isomers in these compounds. The thermal instability of the compounds prevents acquisition of ^{11}B NMR spectra at temperatures where the resonances are sharp enough for the line-narrowing technique to be used effectively. The ambient-temperature spectrum of $B_4H_8 \cdot PF_2Cl$ does indicate that two quartets are present in the B_3 resonance; however, these data are far from conclusive. The resolution of the multiplicity of the B_3 resonance is of the same magnitude as the nosie level in the spectrum, and this condition makes any conclusions very speculative. The necessity of acquiring the spectra at low temperature reduces the utility of the ^{31}P NMR data also. The relative populations of the two isomers for each of these compounds are temperature dependent (on the basis of ^{19}F NMR data to be discussed later). The difference in populations increases as the temperature is lowered, and for each of these compounds one isomer is present in low concentration at −45 °C. This is especially true for $B_4H_8 \cdot PF_3$ and $B_4H_8 \cdot PF_2Cl$. On the basis of the ^{31}P NMR results for $B_4H_8 \cdot PF_2N(CH_3)_2$,[1] the resonances due to the two isomers in each of these compounds could overlap extensively, and the resonances of the predominant isomer could obscure those of the less predominant isomer.

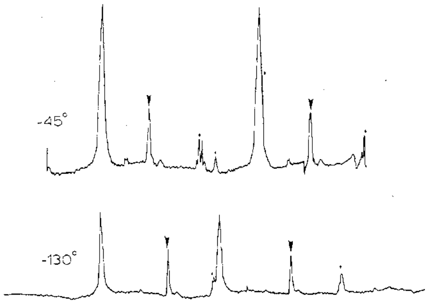

Figure 8. Low-temperature 94.1-MHz ^{19}F NMR spectra of $B_4H_8 \cdot PF_2I$. Sweep width of −45 °C spectrum is 3000 Hz and −130 °C spectrum, 5000 Hz. Doublet marked with an arrowhead represents the exo isomer. Peaks marked with an asterisk result from impurities.

The ^{19}F NMR spectrum of each of these compounds obtained between −40 and −20 °C consists of two doublets and indicates the presence of two isomers. The spectral changes observed below −40 °C are analogous to those observed[1] for $B_4H_8 \cdot PF_2N(CH_3)_2$ and demonstrate conclusively that the isomers observed at higher temperature arise from endo and exo placement of the ligand and not from restricted rotation about the P–B bond. In each case, as the temperature is lowered, the more intense doublet broadens and eventually disappears from the spectrum. As the temperature is lowered further, new resonances grow into the spectrum. In each case, the less intense doublet shows virtually no temperature dependence below −45 °C. As was the case with $B_4H_8 \cdot PF_2N(CH_3)_2$, these spectral changes can be interpreted in terms of two geometrical isomers. As the temperature is lowered, rotation about the P–B bond in one geometrical isomer becomes slow with respect to the experimental time scale, while this rotation remains rapid in the second geometrical isomer.

It is interesting to note that at the low-temperature limit the spectra are not all alike, and none is equivalent to that obtained for $B_4H_8 \cdot PF_2N(CH_3)_2$.[1] For $B_4H_8 \cdot PF_3$ the spectrum at −144 °C (Figure 6) consists of two doublets in an area ratio of 2:1 in addition to the doublet from the second geometrical isomer. The area 2 doublet is further split into a doublet and the area 1 doublet is further split into a triplet. This spectrum can be interpreted in terms of a single rotational isomer in which there are two equivalent fluorine atoms and one unique fluorine atom. The major couplings in this spectrum are P–F coupling, and the minor couplings are F–F coupling. The triplet structure in the area 1 doublet results from coupling with the two equivalent fluorine atoms and the additional doublet structure in the area 2 doublet results from coupling with the unique fluorine atom (J_{FF} = 70 Hz).

For $B_4H_8\cdot PF_2Cl$ (Figure 7) and $B_4H_8\cdot PF_2Br$, the lowest temperature spectra contain six resonances, three doublets, in addition to the doublet from the second geometrical isomer. The spectra are interpreted in terms of two rotational isomers in one geometrical isomer. In one rotational isomer (R_1) the two fluorine atoms are equivalent and a single doublet is observed. In the second rotamer (R_2) the two fluorine atoms are nonequivalent and give rise to two doublets in the spectrum. The members of the doublets at highest and lowest shielding are broader than the doublet at intermediate shielding in each spectrum. This broadness probably results from unresolved fluorine–fluorine coupling, and on this basis these broad resonances are assigned to the nonequivalent fluorines in R_2. This assignment is consistent with the results for $B_4H_8\cdot PF_2N(CH_3)_2$[1] and $B_4H_8\cdot PF_2I$ (vide infra).

The lowest temperature spectrum of $B_4H_8\cdot PF_2I$ (Figure 8) contains a single doublet in addition to the original doublet which remains unchanged. This spectrum indicates the presence of a single rotational isomer in one geometrical isomer, and the two fluorine atoms are equivalent in this rotamer.

It is interesting to note that in the $B_4H_8\cdot PF_2X$ compounds (X = $(CH_3)_2N$, F, Cl, Br, I), restricted rotation about the P–B bond gives rise to all possible combinations of rotational isomers. In $B_4H_8\cdot PF_2N(CH_3)_2$ a single rotational isomer in which the two fluorine atoms are nonequivalent is observed.[1,3] In $B_4H_8\cdot PF_2Cl$ and $B_4H_8\cdot PF_2Br$ two rotational isomers, one with equivalent fluorine atoms and one with nonequivalent fluorine atoms, are observed. In $B_4H_8\cdot PF_2I$ a single rotomer with two equivalent fluorine atoms is observed. For $B_4H_8\cdot PF_3$ one would expect to observe a single rotational isomer and a single rotamer which contains two equivalent fluorine atoms, and one unique fluorine atom is observed.

Although the result of restricted rotation about the P–B bond differs for the different compounds, in each case it is the predominant isomer which experiences the restricted rotation. On the basis of the results for $B_4H_8\cdot PF_2N(CH_3)_2$ it is the endo isomer of each compound in which the rotation becomes slow.[1]

Questions which must be addressed are: What is the orientation of the ligands in the different rotational isomers and why are the low-temperature spectra different for different compounds? The three possible rotational isomers are shown in Figure 9. Orientation A in Figure 9 would give rise to nonequivalent fluorine atoms. This is the orientation observed in the crystal structure[11] of $B_4H_8\cdot PF_2N(CH_3)_2$ and is undoubtedly the orientation in which the two fluorine atoms are nonequivalent in $B_4H_8\cdot PF_2Cl$ and $B_4H_8\cdot PF_2Br$. The other two ligand orientations shown in Figure 9 would both give rise to a single ^{19}F NMR resonance as observed for $B_4H_8\cdot PF_2Cl$, $B_4H_8\cdot PF_2Br$, and $B_4H_8\cdot PF_2I$. In structure B, the X substituent extends directly over the boron framework, and in structure C the X substituent extends directly away from the boron ring. Structure B is clearly favored. In the other orientation, the ligand fluorine atoms would point almost directly at the terminal hydrogens on B_2 and B_4. Electronic interactions between these groups would be repulsive in nature, and this orientation would maximize this interaction. One can envision the X substituent getting "trapped" over the ring between the $B_{2,4}$ hydrogen atoms. For the iodo compound, this is the only rotational isomer observed. This rotomer is not observed for $B_4H_8\cdot PF_2N(CH_3)_2$, and this fact indicates that the dimethylamino group is too bulky to fit over the V-shaped boron ring.

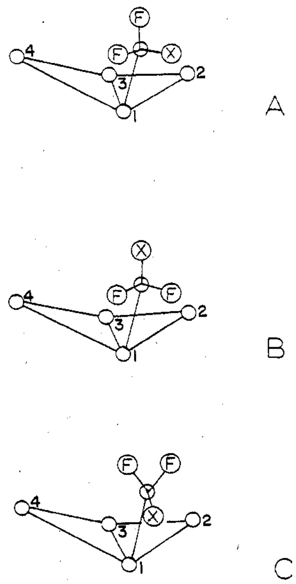

Figure 9. Structures of the three possible rotational isomers in the endo isomer of $B_4H_8\cdot PF_2X$ complexes.

The NMR spectral results of $B_4H_8\cdot PF_2H$ indicate that this compound is the unique member of the series of $B_4H_8\cdot PF_2X$ complexes studied. The ^{11}B NMR data as well as the ^{19}F, ^{31}P, and ^{1}H NMR results show no evidence that more than one isomer is present. The absence of spectral changes in the ^{11}B NMR spectrum at high temperature and the ^{19}F NMR spectrum at high and low temperatures is certainly inconsistent with the data for the other compounds studied but agrees with the conclusions of Centofanti, Kodama, and Parry.[5] The lack of noticeable decomposition of this compound at temperatures above 100 °C indicates that HPF_2 is a much stronger base toward B_4H_8 than is any of the other difluorophosphine bases studied. The unusual base strength of HPF_2 toward BH_3 has also been reported[12] and discussed.[13]

The nucleus most sensitive to an NMR study of the existence of isomers in the other $B_4H_8\cdot PF_2X$ compounds is ^{19}F. An interesting feature of the ^{19}F NMR spectra of these compounds is the change in the chemical shift difference for the two isomers of each compound. For the series $B_4H_8\cdot PF_2I$, $B_4H_8\cdot PF_2Br$, $B_4H_8\cdot PF_2Cl$, and $B_4H_8\cdot PF_2N(CH_3)_2$ the chemical shift differences are 4.2, 1.8, 1.0, and 1.1 ppm, respectively. In each of these spectra the resonance of the predominant endo isomer is deshielded with respect to that of the exo isomer. For $B_4H_8\cdot PF_3$ the exo isomer is deshielded by 2.4 ppm with respect to the endo isomer. For $B_4H_8\cdot PF_2H$ the chemical shifts of the two isomers could be equivalent, and thus the spectrum would appear to result from a single isomer. This reasoning, however, does not account for the lack of spectral changes at low temperature.

The presence of long-range boron–phosphorus spin–spin coupling in the 32.1-MHz ^{11}B NMR spectrum of $B_4H_8\cdot PF_2H$ is, as far as we are aware, the first example of long-range B–P coupling in a phosphine–borane. Initially, it was tempting to explain the presence of eight lines with a separation of 12 Hz as arising from the overlap of two quartets representing two geometrical isomers, each of which had a $J_{B_1B_3}$ value of 24 Hz.

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However, the ^{11}B spectrum at twice the magnetic field strength remains unchanged, proving that the additional multiplicity is a result of long-range coupling and not two separate boron resonances.

Long-range P–H spin–spin coupling in the 40.5-MHz ^{31}P NMR spectrum is also observed in $B_4H_8\cdot PF_2H$ while none of the other PF_2X adducts exhibit this behavior. The proton-coupled 80-MHz ^{31}P NMR spectrum of $B_4H_8\cdot PF_2H$ was identical with that obtained at 40.5 MHz, again indicating that long-range spin–spin coupling is involved rather than nonequivalent ^{31}P resonances. A 200-MHz ^1H NMR spectrum was of no assistance in resolving the ambiguities associated with this compound.

As stated above, PF_2H is known to have unusual base properties toward BH_3.[12] Recently on the basis of the reaction of PF_2H with nickel and the instability of the resulting compound, it has been concluded that the stability of $PF_2H\cdot BH_3$ results from specific hydride–proton interactions involving BH_3 rather than PF_2H being an unusually strong base.[13] This type of interaction could also occur in $B_4H_8\cdot PF_2H$ and, indeed, on the basis of our data it seems probable that the bonding and structural parameters in $B_4H_8\cdot PF_2H$ are different from those of the other PF_2X complexes studied. A single-crystal X-ray diffraction study of this molecule is clearly needed.

While this work has contributed significantly to the understanding of the B_4H_8L complexes, several interesting factors are still not well understood. The anomalous properties of $B_4H_8\cdot PF_2H$, the factors which stabilize the endo isomer relative to the exo isomer, and the importance of the electronic and steric requirements of the ligand in determining the relative stability of the two isomers deserve further study.

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Registry No. $B_4H_8\cdot PF_2N(CH_3)_2$, 60930-18-9; $B_4H_8\cdot PF_3$, 60930-19-0; $B_4H_8\cdot PF_2Cl$, 36907-24-1; $B_4H_8\cdot PF_2Br$, 36907-25-2; $B_4H_8\cdot PF_2I$, 36907-26-3; $B_4H_8\cdot PF_2H$, 24189-89-7.

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Bent Cis d^0 MoO_2^{2+} vs. Linear Trans d^0f^0 UO_2^{2+}: A Significant Role for Nonvalence 6p Orbitals in Uranyl

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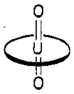
The marked preference of uranyl, UO_2^{2+}, d^0f^0, for linear geometries, while MoO_2^{2+} and isoelectronic d^0 molecules are bent, is not due to oxygen 2p–actinide 5fπ bonding. Instead we trace the geometrical effect to a substantial involvement of formally inner-shell 6p orbitals of σ symmetry on uranium which interact significantly with oxygen pσ orbitals and "activate" these for σ bonding with U 5f.

Enigmatic is the contrast between the ubiquitous *linear* uranyl ion UO_2^{2+} and the common *bent* transition metal dioxo ions such as VO_2^+, MoO_2^{2+}, and WO_2^{2+}. UO_2^{2+}, **1**, in which uranium has a formal $5f^06d^0$ valence configuration, always occurs in crystals or in complexes with trans geometry, having four, five, or six secondary coordinations in an equatorial plane perpendicular to the main O–U–O axis.[1] In contrast, the VO_2^+, MoO_2^{2+}, and WO_2^{2+} ions, **2**, which have a related d^0 valence configuration, occur, mostly in octahedral ligand sets, with exclusive cis geometry (O–M–O angle = 102–114°).[2]



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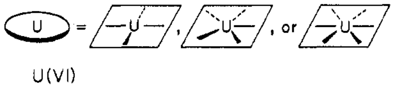

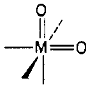

M = V(V), Mo(VI), or W(VI)

2

An obvious difference in electronic structure between the *trans*-UO_2^{2+} and *cis*-VO_2^+, MoO_2^{2+}, or WO_2^{2+} is that the uranium has f orbitals in the valence orbital set while the other metals do not have them. So are the f orbitals in UO_2^{2+} really important in describing its geometrical preference of trans over cis? The numerous theoretical studies on uranyl certainly involve the f orbitals in bonding[3] but do not address themselves to the choice among alternative geometries. We now hypothesize that the answer *is both no and yes* and that nonvalence 6p orbitals on U play a previously unappreciated role in determining the trans geometry.

A feature characteristic of both MoO_2^{2+} and UO_2^{2+} complexes is a very short M–O distance (Mo–O ≈ 1.67 Å, U–O ≈ 1.76 Å) and labile coordination geometries. Thus, as a first approximation, we may consider that the geometrical preferences reside in the naked cations themselves, and not in the auxiliary ligands. We have carried out extended Hückel calculations for MoO_2^{2+} and UO_2^{2+} with a variety of basis sets:[4] for Mo 4d, 5s, 5p separately (d or s or p) or all together

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(4) (a) Mo–O and U–O bond distances are assumed to be 1.67 and 1.76 Å, respectively. (b) Atomic parameters are as follows. H_{ii}: Mo 5s, −9.66 eV; Mo 5p, −6.36 eV; Mo 4d, −12.3 eV; U 7s, −5.50 eV; U 7p, −5.50 eV; U 6d, −5.09 eV; U 5f, −9.01 eV; U 6p, −30.03 eV. Orbital exponents: Mo 5s, 1.96; Mo 5p, 1.90; Mo 4d, 4.54 (0.5899) + 1.90 (0.5899); U 7s, 1.914; U 7p, 1.914; U 6d, 2.581 (0.7608) + 1.207 (0.4126); U 5f, 4.943 (0.7844) + 2.106 (0.3908); U 6p, 4.033. The parameters for U are estimated from the relativistic Dirac–Fock wave functions of Desclaux.[5] Details will be given in a forthcoming paper.[6]

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