Inorg. Chem. **1981**, *20*, 3740–3745

concerning computer simulation and complex spectra.

Registry No. $(CF_3)_2PH$, 460-96-8; $(CH_3)_3N$, 75-50-3; $P_2(CF_3)_4$, 2714-60-5; $CHF_2(CF_3)P\text{-}P(CF_3)_2$, 78673-09-3; $CH_2F(CF_3)P\text{-}P(CF_3)_2$, 78673-08-2; $CH_3(CF_3)P\text{-}P(CF_3)_2$, 78673-07-1; $(CF_3)_2PCH_2(CF_3)\text{-}P\text{-}P(CF_3)_2$, 78685-50-4; $(CH_3)_3SiCl$, 75-77-4; $(CH_3)_3SiF$, 420-56-4; $(CH_3)_3NHCl$, 593-81-7; $CH_3(CF_3)PCl$, 4669-76-5; $CH_2F(CF_3)PCl$, 77846-29-8; $CHF_2(CF_3)PCl$, 4669-82-3; $CHF_2(CF_3)PH$, 77846-32-3; $CH_2F(CF_3)PH$, 77846-33-4; $(CF_3)_2PCl$, 650-52-2; $(CH_3)_3SiP(CF_3)_2$, 21658-00-4; $(CF_3)_2PCH_2P(CF_3)Cl$, 77846-30-1; $(CF_3)_2PCH_2P(CF_3)F$, 78673-14-0; $(CF_3)_2PCH_2P(CF_3)N(CH_3)_2$, 78673-15-1; $[(CF_3)_2PCH_2PCF_3]_2$, 78673-16-2.

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Synthesis and Multinuclear Magnetic Resonance Studies of New Difluorophosphine Derivatives of Tetraborane(8)[1]

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Several new difluorophosphine complexes of tetraborane(8) have been prepared and characterized. These new adducts include $B_4H_8{\cdot}PF_2OCH_3$, $B_4H_8{\cdot}PF_2SCH_3$, $B_4H_8{\cdot}PF_2CF_3$, and $B_4H_8{\cdot}PF_2(t\text{-}C_4H_9)$. These specific molecules were prepared to gain additional insight into questions pertaining to the importance of steric and electronic effects of the X substituent in $B_4H_8{\cdot}PF_2X$ molecules on the relative populations of geometrical isomers at ambient temperature and on rotational isomers at low temperature. Multinuclear (^{11}B, ^{13}C, ^{19}F, and ^{31}P) NMR studies employing decoupling, computer line narrowing, and partially relaxed Fourier transform techniques have demonstrated that all molecules except $B_4H_8{\cdot}PF_2CF_3$ exist as two geometrical isomers. Although ^{11}B and ^{31}P NMR spectra indicate the presence of geometrical isomers, the fluorine-19 nucleus is the most sensitive indicator of the presence of these isomers. Rotational isomers were observed for some compounds in low-temperature ^{19}F NMR spectra although only in $B_4H_8PF_2CF_3$ was a limiting low-temperature spectrum obtained. Conclusions concerning relative contributions of steric and electronic factors to the population of endo and exo isomers are discussed.

Introduction

Recently, this laboratory has completed multinuclear NMR studies[1,3,4] of several difluorophosphine derivatives of tetraborane(8), $B_4H_8{\cdot}PF_2X$ (X = F, Cl, Br, I, H, and $N(CH_3)_2$). These studies, particularly low-temperature ^{19}F NMR studies, have conclusively established that all molecules except $B_4H_8{\cdot}PF_2H$ exist as geometrical isomers (endo and exo placement of the phosphine with respect to the B_4 framework as shown in Figure 1) at ambient temperature. Further, at low temperatures restricted rotation about the P–B bond in the endo geometrical isomer of these adducts gives rise to all possible combinations of rotational isomers (Figure 2).

Relative contributions of intramolecular interactions to the stabilization of the endo isomer with respect to the exo isomer are not known. There are still unanswered questions pertaining to the importance of steric and electronic effects of the X substituent of the phosphine on the relative populations of the geometrical isomers at high temperature and on the rotational isomers at low temperature. In order to gain additional insight into these factors, we have synthesized, characterized, and examined several new $B_4H_8{\cdot}PF_2X$ complexes (where X = OCH_3, SCH_3, CH_3, CF_3, and $t\text{-}C_4H_9$) by multinuclear magnetic resonance employing decoupling, computer line-narrowing, and PRFT techniques. The results of this study are reported herein.

Experimental Section

Materials. The preparation and purification of the $B_4H_8{\cdot}PF_2X$ complexes were accomplished with use of standard high-vacuum techniques in an all-glass vacuum system equipped with greaseless stopcocks.[5] The $B_4H_8{\cdot}PF_2X$ complexes were synthesized by base displacement from B_4H_8CO which was prepared directly from the pyrolysis of B_2H_6 in the presence of CO.[6] The phosphine bases were prepared as previously reported. The CH_3PF_2[7] and $(t\text{-}C_4H_9)PF_2$[8] ligands were prepared by the fluorination of CH_3PCl_2 (Alfa) and $(t\text{-}C_4H_9)PCl_2$ (Alfa), with dry NaF (Allied) in sulfolane (Parish). Methyl difluorophosphite,[9] CH_3OPF_2, was synthesized directly from PF_3(Ozark-Mahoning), CH_3OH (Baker), and C_5H_5N (Fisher). The sulfur analogue,[10] CH_3SPF_2, was prepared from PF_2Cl[11] and CH_3SH (Matheson) in the presence of trimethylamine (Matheson). (Trifluoromethyl)difluorophosphine, CF_3PF_2, was obtained from repetitive fluorinations of CF_3PI_2 with freshly sublimed SbF_3 (Ozark-Mahoning) at 100 °C.[12] Sulfolane, methanol, pyridine were dried and distilled before use. The purity of all compounds was monitored by mass spectral and ^{31}P and ^{19}F NMR spectral measurements.

Table I. Melting Points and Vapor Pressure (*P*) for $B_4H_8{\cdot}PF_2X$ Complexes

compd	mp, °C	*P*, torr (*t*, °C)
$B_4H_8{\cdot}PF_2OCH_3$	−76	8 (25.8)
$B_4H_8{\cdot}PF_2SCH_3$	−112 to −110	<1 (24.8)
$B_4H_8{\cdot}PF_2CH_3$	−67 to −66	7 (24.0)
$B_4H_8PF_2CF_3$	−153 to −149	*a*
$B_4H_8{\cdot}PF_2C_4H_9$	−92 to −85	<1 (25.0)

[a] Complex was not available in sufficient quantity for vapor pressure measurement.

The synthesis of $B_4H_8{\cdot}PF_2X$ complexes was accomplished by condensing B_4H_8CO (~2.0 mmol) and the PF_2X ligand (2.2 mol) into a small-volume reaction vessel equipped with a greaseless stopcock.

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(1) Part 20 in the series, "Spectra and Structure of Phosphorus-Boron Compounds". For part 19 see: Odom, J. D.; Moore, T. F. *Inorg. Chem.* **1980**, *19*, 2651.

(2) Taken in part from the thesis of A. J. Zozulin, submitted to the Department of Chemistry, University of South Carolina, in partial fulfillment of the requirements for the Ph.D. degree.

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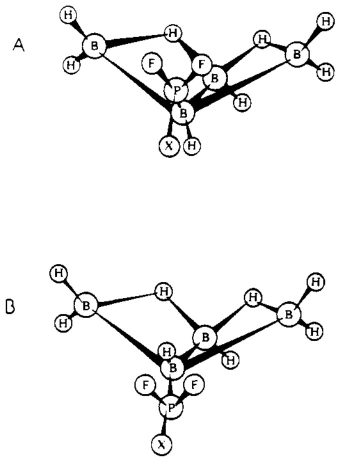

Figure 1. Geometrical isomers of $B_4H_8{\cdot}PF_2X$ molecules: (A) endo placement of the ligand; (B) exo placement of the ligand.

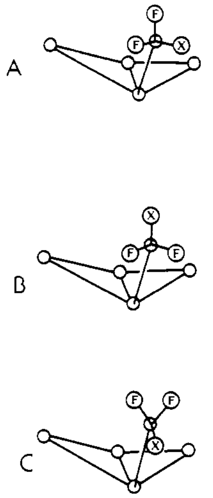

Figure 2. Structures of the three possible rotational isomers in the endo isomer of $B_4H_8{\cdot}PF_2X$ complexes.

The contents were slowly warmed to 0 °C and held at that temperature for 15 min. The tube was then frozen at −196 °C, and the liberated CO was removed. The reaction was continued until CO evolution ceased. The volatiles were reintroduced to the vacuum system and purified on a low-temperature distillation column.

Melting points (Table I) of all complexes were obtained with the use of a Stock melting point apparatus. Temperatures were measured with use of a copper–constantan thermocouple with a reference junction at 0 °C. Low volatilities of the complexes at ambient temperature prevented the determination of meaningful boiling point data. Vapor pressures at ambient temperature for most of the complexes were obtained (Table I).

Instrumental Data. Nuclear magnetic resonance spectra (^{13}C, 25.2 MHz; ^{11}B, 32.1 MHz; ^{31}P, 40.5 MHz; ^{19}F, 94.1 MHz) were obtained on a highly modified Varian Associates XL-100-15 spectrometer operating in the Fourier transform mode. ^{31}P NMR spectra at 81.0 MHz were obtained on a Bruker WP-200 spectrometer. Standard variable-temperature accessories were employed. Spectra were obtained with use of ~20% solutions of the complex in a 1:1 and/or 1:2 (v/v) mixture of toluene-d_8 and isopentane.

Chemical shifts were measured relative to external $Si(CH_3)_4$ (^{13}C), $BF_3{\cdot}O(C_2H_5)_2$ (^{11}B), 85% o-H_3PO_4 (^{31}P), and CF_3COOH (^{19}F). A negative sign (−) denotes increased shielding. Chemical shifts and coupling constants are accurate to ±0.5 ppm and ±1.0 Hz, respectively.

Mass spectral analysis was attempted on Perkin-Elmer RMU-6 (20 and 70 eV) and VG Micromass Model 7070 (The University of North Carolina at Chapel Hill) spectrometers. Analysis by electron impact (Perkin-Elmer) did not yield a parent ion for these compounds even at very low ionizing voltages. Efforts to obtain the exact mass of these compounds by chemical ionization mass spectrometry (VG Micromass) were also futile. Low-resolution spectra were obtained for several of the compounds on a VG Micromass ZAB-2F spectrometer which employed negative ion detection (NIEHS, Research Triangle Park, NC) (compound:ion, m/e (relative intensity)): $B_4H_8{\cdot}PF_2OCH_3$:$^{11}B_4H_8PF_2O^-$, 137 (1.9); $CH_2OPF_2^-$, 99 (0.18); $^{11}B_4H_7^-$, 51 (100); $B_4H_8{\cdot}PF_2SCH_3$: $^{11}B_4H_8{\cdot}PF_2{}^{32}S^-$, 153 (100); $^{11}B_4H_8PF_2^-$, 121 (40.7); $CH_2{}^{32}SPF_2^-$, 115 (42.0); $^{32}SPF_2^-$, 101 (14.8); $^{11}B_4H_8^-$, 52 (18.7); $B_4H_8{\cdot}PF_2CH_3$: $^{11}B_4H_8{\cdot}PF_2CH_2^-$, 135 (0.18); $^{11}B_4H_8{\cdot}PF_2^-$, 121 (0.78); $^{11}B_4H_7^-$, 51 (100); $B_4H_8{\cdot}PF_2C_4H_9$:$^{11}B_4H_8{\cdot}PF_2^-$, 121 (100); $^{11}B_4H_7^-$, 51 (38).

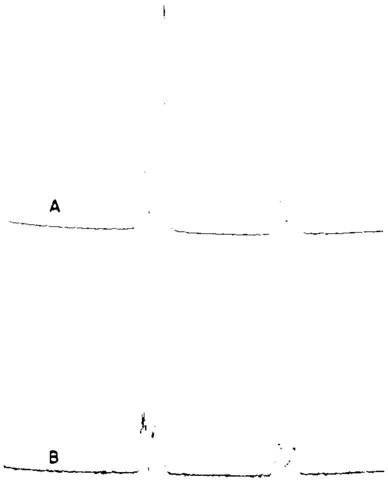

Figure 3. 32.1-MHz ^{11}B NMR spectrum of $B_4H_8{\cdot}PF_2OCH_3$: (A) proton decoupled; (B) proton decoupled, computer line narrowed.

Results

^{11}B NMR Spectra. $B_4H_8{\cdot}PF_2OCH_3$. The proton-decoupled ^{11}B NMR spectrum (Figure 3A) of $B_4H_8PF_2OCH_3$ is consistent with previously reported ^{11}B NMR spectra of $B_4H_8PF_2X$ compounds.[1] Based on these results, the doublet at high field is assigned to the substituted boron atom (B_1, δ −57.0) with the doublet structure arising from boron–phosphorus spin–spin coupling (J_{BP} = 195 Hz). The lowest field resonance, a singlet, is assigned to the B_3 atom (B_3, δ 0.4) with the remaining resonance, also a singlet, assigned to the $B_{2,4}$ atoms ($B_{2,4}$, δ −6.3). An additional resonance which appears as a shoulder on the low-field side of the $B_{2,4}$ resonance is present (δ −3.0). With the application of computer line narrowing (Figure 3B), the resonance for the B_3 atom becomes a well-resolved quartet arising from ^{11}B–^{11}B spin–spin coupling (J_{BB} = 24 Hz) while the shoulder develops into two lines. When partially relaxed Fourier transform (PRFT) techniques are applied at τ = 17 ms, the $B_{2,4}$ resonance is completely nulled, thus leaving two resonances at low field. On the basis of previous results,[1,3,4] the second resonance is assigned to a second geometrical isomer of $B_4H_8PF_2OCH_3$.

$B_4H_8{\cdot}PF_2SCH_3$, $B_4H_8{\cdot}PF_2CH_3$, $B_4H_8{\cdot}PF_2CF_3$, and $B_4H_8{\cdot}PF_2(t\text{-}C_4H_9)$. The proton-decoupled ^{11}B NMR spectra of these compounds are very similar to that of $B_4H_8{\cdot}PF_2OCH_3$ and to the other $B_4H_8{\cdot}PF_2X$ complexes.[1] Each spectrum consists of a shielded doublet (B_1) and two deshielded singlets (B_3, $B_{2,4}$). The chemical shifts and coupling constants are given in Table II. Unlike the $B_4H_8{\cdot}PF_2OCH_3$ complex, the application of computer line narrowing does not yield any additional fine structure nor does the PRFT technique reveal any additional resonances.

^{31}P NMR Spectra. $B_4H_8{\cdot}PF_2OCH_3$, $B_4H_8{\cdot}PF_2SCH_3$, and $B_4H_8{\cdot}PF_2(t\text{-}C_4H_9)$. The ^{31}P NMR spectrum of each of these complexes indicates the presence of two geometrical isomers. The spectra consist of a triplet of quartets and an underlying resonance which is chemically shifted such that only part of the multiplet is clearly identifiable (Figure 4). The triplet structure arises from phosphorus spin–spin coupling to two equivalent fluorine nuclei, while the quartet is due to coupling to the directly bonded boron atom (B_1). The chemical shifts

Table II. NMR Parameters for $B_4H_8 \cdot PF_2X$ Complexes

compd	$\delta(^{11}B)^a$ B$_1$	B$_3$	B$_{2,4}$	$\delta(^{31}P)^b$	$\delta(^{19}F)^c$	$\delta(^{13}C)^d$	J_{PB}, Hz	J_{PF}, Hz
$B_4H_8 \cdot PF_2OCH_3$	−57.0	0.4	−6.3	102.5	12.8	57.2	180	1201
		−3.0		98.5	11.7		172	1266
$B_4H_8 \cdot PF_2SCH_3$	−51.0	1.3	−5.2	172.7	21.2	12.5	144	1205
				181.1	15.0	10.3	130	1239
$B_4H_8 \cdot PF_2CH_3$	−52.5	1.2	−5.5	174.3	12.2		140	1080
					1.5			1130
$B_4H_8 \cdot PF_2CF_3$^{e}	−58.0	0.2	−5.6	125.1	−6.3 (PF_2)		125	1177
					10.2 (CF_3)			
$B_4H_8 \cdot PF_2C_4H_9$	−55.4	1.3	−5.8	183.0	−18.6		135	1145
				185.5	−23.6		128	1158

[a] Chemical shifts relative to $BF_3 \cdot O(C_2H_5)_2$. Negative sign denotes increased shielding. [b] Chemical shifts relative to 85% o-H_3PO_4. Negative sign denotes increased shielding. [c] Chemical shifts relative to F_3CCOOH. Negative sign denotes increased shielding. [d] Chemical shifts relative to $Si(CH_3)_4$. Negative sign denotes increased shielding. [e] $^2J_{FCP} = 108$.

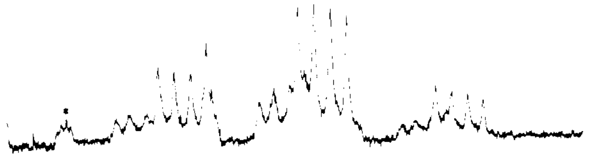

Figure 4. Proton-decoupled 40.5-MHz ^{31}P NMR spectrum of $B_4H_8 \cdot PF_2SCH_3$. Resonance marked with an asterisk corresponds to the ^{31}P resonance of $H_3B \cdot PF_2SCH_3$.[10]

and coupling constants are given in Table II.

$B_4H_8 \cdot PF_2CH_3$. The proton-decoupled ^{31}P NMR spectrum of this compound consists of a single triplet of quartets, indicating the presence of only one geometrical isomer. The triplet structure results from phosphorus spin–spin coupling to two equivalent fluorine nuclei with each of these lines split into a quartet due to phosphorus spin–spin coupling to the directly bonded boron atom. The values of the chemical shifts and coupling constant for each compound are given in Table II.

$B_4H_8 \cdot PF_2CF_3$. The ^{31}P NMR spectrum at −27 °C of $B_4H_8 \cdot PF_2CF_3$ consists of a triplet of septets. The triplet structure arises from phosphorus spin–spin coupling to two equivalent fluorine atoms. The septet structure results from the overlapping of a 1:3:3:1 quartet arising from a two-bond spin–spin coupling of phosphorus to the fluorine atoms of the trifluoromethyl group and a 1:1:1:1 quartet arising from phosphorus spin–spin coupling to the directly bonded boron atom. When single-frequency ^{19}F decoupling of the trifluoromethyl fluorine atoms is performed, the expected triplet of quartets is observed. Chemical shift and coupling constant values are given in Table II.

^{13}C NMR Spectra. $B_4H_8 \cdot PF_2OCH_3$ and $B_4H_8 \cdot PF_2SCH_3$. The proton-decoupled ^{13}C NMR spectrum consists of a single resonance for $B_4H_8 \cdot PF_2OCH_3$ and two resonances for $B_4H_8 \cdot PF_2SCH_3$. As expected, these resonances are deshielded with respect to the free base. The following parameters were obtained in this laboratory from the ^{13}C NMR spectra of the free bases: $B_4H_8 \cdot PF_2OCH_3$, $\delta(^{13}C)$ 48.9 deshielded from Me_4Si; $B_4H_8 \cdot PF_2SCH_3$, $\delta(^{13}C)$ 7.5 deshielded from Me_4Si ($^2J_{CP}$=23 Hz, $^4J_{CF}$ = 8 Hz). (See Table II for NMR parameters of the adduct.)

^{19}F NMR Spectra. $B_4H_8 \cdot PF_2OCH_3$ and $B_4H_8 \cdot PF_2SCH_3$. The ^{19}F NMR spectrum of each of these compounds consists of a pair of doublets resulting from the presence of two geometrical isomers in solution with the doublet structure arising from phosphorus–fluorine spin–spin coupling. The values of the chemical shifts and coupling constants are listed in Table II. Both compounds show similar spectral changes at low temperature. For $B_4H_8 \cdot PF_2OCH_3$, one of the doublets broadens significantly at −99 °C while the other resonance is unchanged (Figure 5). At −110 °C the resonance has continued to broaden and collapse, until at −120 °C it has completely disappeared. Similarly, one of the doublets for $B_4H_8 \cdot PF_2SCH_3$ begins to broaden and collapse at −112 °C. At −120 °C this resonance has broadened significantly while the other remains unchanged (Figure 6). The spectrum at −125 °C is identical with the one at −120 °C. The acquisition of data at temperatures lower than −125 °C was not possible because the adducts precipitated from solution.

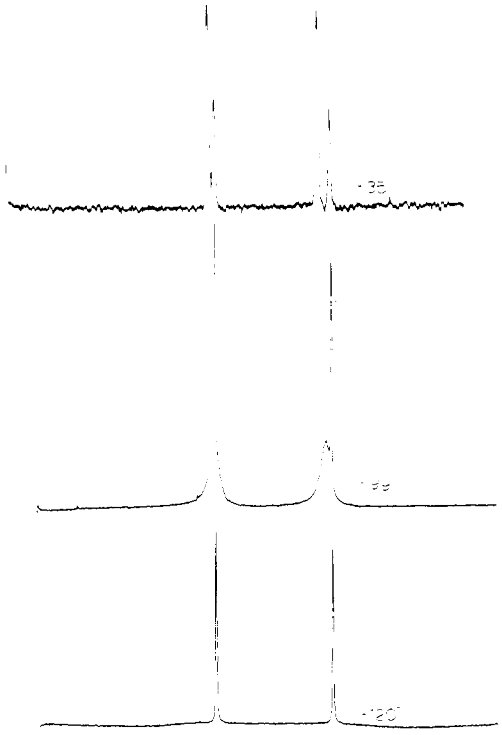

Figure 5. 94.1-MHz ^{19}F NMR spectra of $B_4H_8 \cdot PF_2OCH_3$.

$B_4H_8 \cdot PF_2CH_3$. The ^{19}F NMR spectrum of $B_4H_8 \cdot PF_2CH_3$ at ambient temperature consists of a pair of doublets resulting from phosphorus–fluorine spin–spin coupling. The low-temperature ^{19}F NMR spectra show no major spectral changes as the temperature is lowered from 35 to −120 °C. A slight broadening of one of the doublets occurs at −99 °C and remains nearly constant to the lowest temperature recorded. At temperatures below −120 °C the compound precipitates from solution, and attempts to use other solvents for lower temperature studies were unsuccessful.

$B_4H_8 \cdot PF_2CF_3$. The ^{19}F NMR spectrum at −21 °C of $B_4H_8 \cdot PF_2CF_3$ consists of a pair of doublets (Table II). The high-field doublet, assigned to the fluorine atoms of the PF_2 group, results from phosphorus–fluorine spin–spin coupling. The low-field doublet is assigned to the fluorine atoms of the

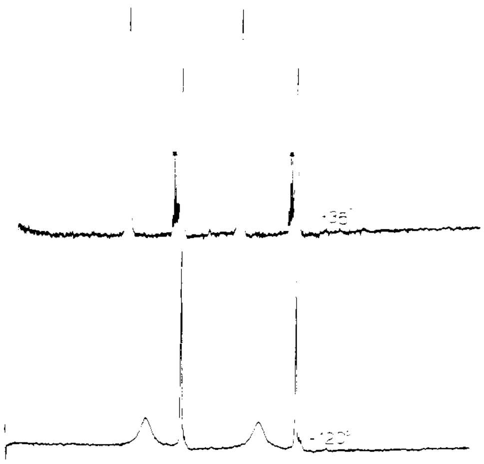

Figure 6. 94.1-MHz ^{19}F NMR spectra of $B_4H_8{\cdot}PF_2SCH_3$. Resonances marked with an asterisk correspond to the ^{19}F resonance of $H_3B{\cdot}PF_2SCH_3$.[10]

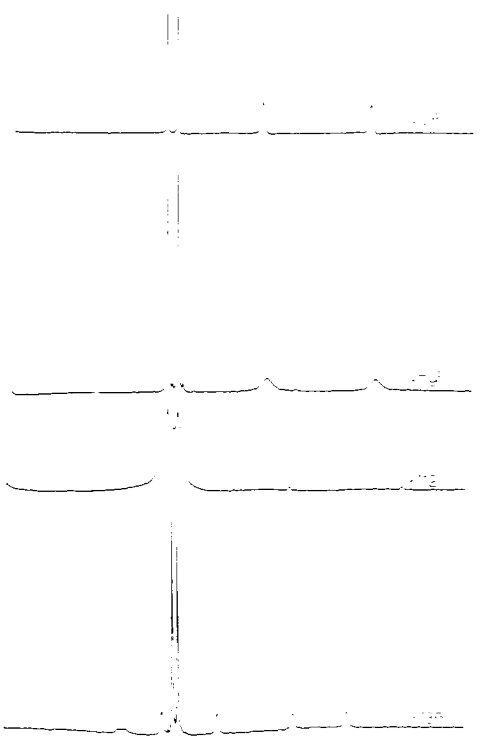

Figure 7. 94.1-MHz ^{19}F NMR spectra of $B_4H_8{\cdot}PF_2CF_3$.

trifluoromethyl group with the doublet structure arising from two bond phosphorus–fluorine spin–spin coupling. The low-temperature ^{19}F NMR spectrum remains essentially unchanged until at −79 °C the PF_2 resonance broadens (Figure 7). At −112 °C the PF_2 resonance has disappeared and the CF_3 resonance has broadened considerably. At −125 °C two new features are apparent, i.e., the CF_3 resonance has sharpened and four new resonances have appeared, a pair of doublets. No further spectral changes are observed except for a sharpening of the resonances at −135 °C. The two new doublets are attributed to the presence of two nonequivalent fluorine atoms, each of which is spin–spin coupled to a phosphorus atom (δ −24.6, J_{PF} = 1170 Hz; δ 5.1, J_{PF} = 1180 Hz). The chemical shift and coupling constant for the CF_3 resonance at −135 °C are δ 8.2 and $^2J_{FCP}$ = 110 Hz.

$B_4H_8{\cdot}PF_2(t\text{-}C_4H_9)$. The proton-decoupled ^{19}F NMR spectrum of $B_4H_8{\cdot}PF_2(t\text{-}C_4H_9)$ consists of a pair of doublets which arise from phosphorus–fluorine spin–spin coupling to a phosphorus atom (Table II). The low-temperature proton-coupled ^{19}F NMR spectra are shown in Figure 8. At −25 °C a new resonance has appeared as a broad doublet (J_{PF} = 1162 Hz) at δ −28.9. The resonances assigned to the $B_4H_8{\cdot}PF_2(t\text{-}C_4H_9)$ complex have shifted by δ −1.5 although the $\Delta\delta$ between the two resonances is unchanged. At −50 °C the broad resonance at δ −28.9 has developed into a doublet of doublets (J = 54 Hz). In addition, the resonance at δ −23.6 has developed into a doublet of doublets (J = 18 Hz). When the temperature is lowered to −75 °C, the resonance due to the predominant isomer at ambient temperature begins to broaden slightly while the minor fine structure on the resonance due to the second isomer has sharpened. The proton-decoupled ^{19}F NMR spectrum at −75 °C indicates the minor coupling on the second isomer is due to a fluorine atom spin–spin coupled to a hydrogen atom, possibly that bonded to the B_1 atom. It appears that proton decoupling has no effect on the resonance at δ −28.9; however, the signal to noise ratio for this resonance is very poor. As the temperature is lowered further, the resonance due to one of the isomers begins to broaden and finally disappears at −125 °C. The fluorine–hydrogen spin–spin coupling of the second isomer continues to collapse until at −135 °C it has nearly disappeared. At temperatures below −135 °C, the compound precipitated from solution, preventing the acquisition of additional information.

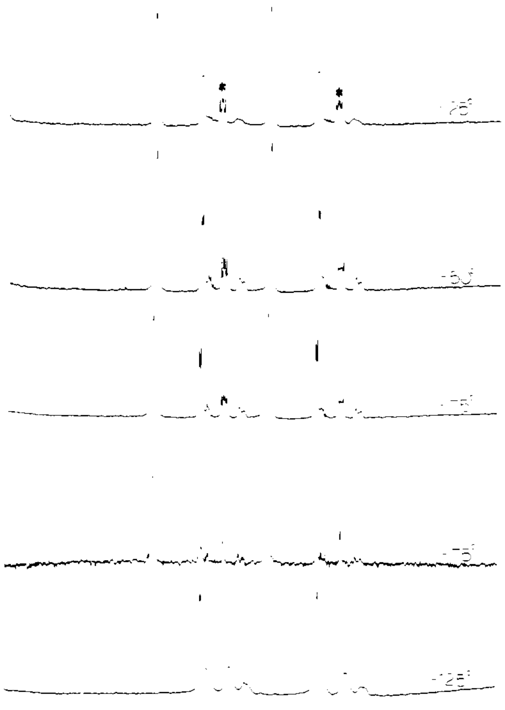

Figure 8. 94.1-MHz ^{19}F NMR spectra of $B_4H_8{\cdot}PF_2tC_4H_9$. Resonances marked with asterisks are assigned to $H_3B{\cdot}PF_2(t\text{-}C_4H_9)$ impurity.

Discussion

Since these $B_4H_8{\cdot}PF_2X$ complexes (X = OCH_3, SCH_3, CH_3, CF_3, and $t\text{-}C_4H_9$) have not been previously reported, characterization has been established from ^{11}B, ^{31}P, ^{19}F, and ^{13}C NMR and mass spectral measurements. The ^1H-decoupled ^{11}B NMR spectrum for each complex consists of a doublet at high field which is assigned to the substituted boron atom (B_1). The doublet structure arises from boron–phosphorus spin–spin coupling. Two additional resonances which are deshielded with respect to the doublet are assigned to the B_3 and $B_{2,4}$ atoms. This interpretation is consistent with the ^{11}B NMR spectra of known $B_4H_8{\cdot}PF_2X$ complexes (X = $N(CH_3)_2$, F, Cl, Br, I, and H)[1,3,4] as well as the X-ray structure for $B_4H_8{\cdot}PF_2N(CH_3)_2$.[15] The ^{31}P NMR spectra are also in accordance with a phosphorus atom spin coupled to two equivalent fluorine atoms and one boron atom. The doublet(s) observed in the ^{19}F NMR spectrum confirms that a fluorine nucleus is spin coupled to another nucleus of spin $^1/_2$ with the magnitude of this coupling constant being consistent with phosphorus–fluorine coupling in other $B_4H_8{\cdot}PF_2X$ complexes. Therefore, the phosphorus and fluorine NMR spectra confirm the presence of a PF_2 group while the boron NMR spectrum characterizes the B_4H_8 moiety. Additionally, the typical fragmentation pattern from electron-impact mass spectrometry exhibited cleavage of the X substituent and of the entire phosphine base while the entire fragmentation pattern was consistent for compounds of the type $B_4H_8{\cdot}PF_2X$.

In recent multinuclear NMR studies of $B_4H_8{\cdot}PF_2X$ compounds (X = F, Cl, Br, I, $N(CH_3)_2$, and H),[1,4] the ^{11}B and ^{31}P NMR data were found to be of limited assistance in determining the presence of geometric isomers. Similarly, in this study the ^{11}B NMR data only indicated the existence of isomers for $B_4H_8{\cdot}PF_2OCH_3$. It is interesting that when resonances due to two geometrical isomers are observed in ^{11}B NMR spectra of B_4H_8L molecules[1,4,13] the B_3 resonance indicates the presence of these isomers. Only in the ^{11}B spectrum of B_4H_8CO have we been able to observe[13] two lines for the $B_{2,4}$ resonance and at no time has the resonance of the substituted boron (B_1) indicated the presence of isomers. It should also be noted that the B_1–B_3 coupling constant remains constant at approximately 24 Hz in all compounds studied.[1,4,13] This is in contrast to the substantial substituent effect which exists for J_{BB} in apically substituted pentaborane(9) molecules.[14]

The ^{31}P NMR spectra clearly demonstrate the presence of two isomers for $B_4H_8{\cdot}PF_2OCH_3$, $B_4H_8{\cdot}PF_2SCH_3$, and $B_4H_8{\cdot}PF_2(t\text{-}C_4H_9)$. No isomers were observed in the ^{31}P spectra for the $B_4H_8{\cdot}PF_2CH_3$ and $B_4H_8{\cdot}PF_2CF_3$ complexes. The ^{31}P chemical shifts in these complexes are in the same relative order as the ^{31}P shifts of the ligands themselves. That is, the ^{31}P resonance in the methyl complex is deshielded with respect to the ^{31}P resonance of the trifluoromethyl and the resonance of the SCH_3 complex is deshielded with respect to that of the OCH_3 complex.

As observed previously,[1,3,4] the fluorine nucleus is the most sensitive NMR indicator with regard to geometric isomers in these $B_4H_8{\cdot}PF_2X$ molecules. All compounds except $B_4H_8{\cdot}PF_2CF_3$ are shown by ^{19}F NMR to exist as two isomers. The ^{19}F NMR spectrum of each of these compounds obtained from +35 to −40 °C consists of two doublets. The spectral changes observed below −40 °C are similar to those observed for other $B_4H_8{\cdot}PF_2X$ complexes[1,3,4] and demonstrate that the isomers arise from endo and exo placement of the ligand with respect to the boron framework. Only in the spectrum of the $B_4H_8{\cdot}PF_2CF_3$ molecule is the limiting low-temperature spectrum obtained. This spectrum arises from one rotational isomer at low temperature. The configuration of this rotamer which would yield two nonequivalent fluorine resonances for the PF_2 group is similar to that found for $B_4H_8{\cdot}PF_2N(CH_3)_2$[3] in which one fluorine atom is over the folded B_4 ring, and one fluorine atom is directed away from the ring. It is possible to speculate on the rotational conformation of the isomers for the other compounds. On the basis of the results of the low-temperature ^{19}F NMR spectra for the $B_4H_8{\cdot}PF_2CH_3$ complex and a comparison of the steric requirements of the X substituent, it would be anticipated that at low temperature all compounds would have one rotational isomer in which the X substituent would not reside over the B_4 ring. This, of course, assumes that steric requirements assume a significant role in the stability of various rotamers.

At this point one can draw some conclusions regarding the relative contributions of steric and electronic contributions to the population of endo and exo geometric isomers. We have observed[1] in the halodifluorophosphine complexes of tetraborane(8) ($B_4H_8{\cdot}PF_2X$) that the population of the endo and exo isomers follow, for the most part, the steric requirement for the X substituent. The ratio of the endo to exo isomer for each of the compounds in this study are $B_4H_8{\cdot}PF_2(t\text{-}C_4H_9)$ 58:42, $B_4H_8{\cdot}PF_2OCH_3$ 58:42, $B_4H_8{\cdot}PF_2SCH_3$ 70:30, $B_4H_8{\cdot}PF_2CH_3$ 88:12, and $B_4H_8{\cdot}PF_2CF_3$, 100:0. If steric effects were the sole factor in determining the relative populations, the endo:exo ratio for the $B_4H_8{\cdot}PF_2OCH_3$ complex suggest that the steric requirements of OCH_3 are comparable to the $t\text{-}C_4H_9$ substituent which is highly improbable. The similarities of the values for the OCH_3 and $t\text{-}C_4H_9$ substituents as well as similarities for other X substituents suggest that steric and electronic effects are both important in determining isomer ratios. It is interesting to note that crystalline $B_4H_8{\cdot}PF_2N(CH_3)_2$ exists only as the endo isomer as shown by its crystal structure.[15] The interactions which are responsible for the all endo configuration in the crystalline state may also be important for the complexes in solution.

The trends in restricted rotation about the B–P bond for these complexes are not so clear. Intuitively, if steric effects are the primary consideration, the compound which should have the greatest restriction to rotation would be expected to be $B_4H_8{\cdot}PF_2(t\text{-}C_4H_9)$. The remaining compounds can probably be ordered as $B_4H_8{\cdot}PF_2SCH_3$, $B_4H_8{\cdot}PF_2OCH_3$, $B_4H_8{\cdot}PF_2CF_3$, and $B_4H_8{\cdot}PF_2CH_3$. If one compares the sulfur and oxygen compounds, the sulfur complex would be expected to experience a more hindered rotation about the B–P bond than the methoxy complex on the basis of the size of sulfur and the presumed greater diffuseness of the sulfur lone pairs. However, from the low-temperature ^{19}F NMR spectra, the $B_4H_8{\cdot}PF_2OCH_3$ complex apparently experiences more hindered rotation.

In this regard it is interesting to compare the magnitude of J_{BP} for these compounds. Several recent reports have addressed this question. Cowley and Damasco[16] have indicated that for a given boron reference acid, BH_3, the magnitude of J_{BP} qualitatively correlates with the strength of a series of phosphine bases while Rudolph and Schultz[17] have shown that the magnitude of J_{BP} empirically correlates with the dative bond strength of borane adducts of a series of smoothly varying phosphine bases. A further study of Rapp and Drake[18] which was concerned with NMR parameters of some alkyl- and arylphosphine adducts of borane acids supported the conclusions of the above studies although an exception to the general relationship has been reported.[10] In our case we are using the same reference acid and similar Lewis bases and if the value of J_{BP} can be used as a measure of the stability of the complex or the strength of the bond between the boron atom and the phosphorus atom, a stronger bond, and possibly a slightly shorter one, would be predicted for the OCH_3 complex (J_{BP} = 180 Hz vs. 144 Hz for the SCH_3 complex). This would increase the steric hindrance of the PF_2OCH_3 ligand and result in a higher barrier to rotation. Another explanation for the observed low-temperature ^{19}F NMR spectra could involve a positive interaction between the methyl hydrogen atoms and the hydridic hydrogen atoms of the $B_{2,4}$ atoms in the boron cage. Due to the greater electronegativity of the oxygen, the carbon atom in $B_4H_8{\cdot}PF_2OCH_3$ should be more negatively charged with respect to the carbon atom of $B_4H_8{\cdot}PF_2SCH_3$. This is experimentally observed in the ^{13}C NMR spectrum of the two compounds in which the OCH_3 shift is 45 ppm deshielded with respect to the SCH_3 shift. This shift of electron

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density should also influence the methyl hydrogen atoms and would be expected to be greater for $B_4H_8{\cdot}PF_2OCH_3$ than for $B_4H_8{\cdot}PF_2SCH_3$. Thus, an attractive, albeit small, interaction can be envisioned as occurring between the methyl group hydrogens and the hydridic hydrogens of the $B_{2,4}$ atoms. This would create a more hindered rotation for the $B_4H_8{\cdot}PF_2OCH_3$ complex. Furthermore, this interaction would not necessarily predict a different order for the population of the two isomers at ambient temperature. If such an interaction exists in these compounds, then a repulsive interaction would probably exist between the fluorines of the CF_3 group and the hydridic hydrogens of the $B_{2,4}$ atoms in $B_4H_8{\cdot}PF_2CF_3$. This should also result in a more hindered rotation, and this complex is the only compound of those prepared in this study in which rotation is clearly slow with respect to the NMR time scale at low temperatures.

A barrier calculation for the restricted rotation about the boron–phosphorus bond for a series of these complexes would be useful. Unfortunately, programs which calculate barriers to rotation from NMR line shapes require a low-temperature spectrum in which the limiting spectrum is obtained and the rotation has been stopped. Experimentally, this could not be accomplished. X-ray structure determinations of several of these compounds are clearly desirable. Correlations between B–P bond distance, interatomic distances between the hydrogens of the $B_{2,4}$ atoms and the phosphine substituents, and determinations of the dihedral angle between the boron rings as a function of the X substituent would be of interest.

Finally, it is now clear that from the wide range of substituents in $B_4H_8{\cdot}PF_2X$ complexes which have been studied geometric isomers are usually formed. The only two compounds which have not exhibited isomers have been $B_4H_8{\cdot}PF_2H$[1] and $B_4H_8{\cdot}PF_2CF_3$ while $B_4H_8{\cdot}PF_3$[1] and $B_4H_8{\cdot}PF_2CH_3$ exist primarily as one isomer (the endo isomer). Several factors are obviously important in determining whether or not isomers are formed and what their relative populations will be. Interestingly, the PF_2H complex exhibited no hindered rotation at low temperatures while the PF_2CF_3 complex clearly exists as one rotamer at low temperatures. Also, the PF_2H complex is the only $B_4H_8{\cdot}PF_2X$ complex which exhibits long range coupling between the phosphorus atom and the ring hydrogens.[1] This implies that the electronic structure of the PF_2H complex may be different and this point deserves further study.

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Registry No. $B_4H_8{\cdot}PF_2OCH_3$, 78890-52-5; $B_4H_8{\cdot}PF_2SCH_3$, 78890-50-3; $B_4H_8{\cdot}PF_2CH_3$, 78890-51-4; $B_4H_8{\cdot}PF_2CF_3$, 78920-38-4; $B_4H_8{\cdot}PF_2C_4H_9$, 78965-40-9; B_4H_8CO, 12539-64-9.

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Reduction of Peroxomonosulfate by Oxovanadium(IV) in Acidic Solution. Role of the Sulfate Radical Anion

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The reduction of HSO_5^- by the 1-equiv reducing agent VO^{2+} cleanly obeys the rate expression $-d(HSO_5^-)/dt = k(HSO_5^-)(VO^{2+})$, although a mild inverse hydrogen ion dependence was observed over the range 0.010–1.0 M H^+. Competition studies utilizing the trapping agents HN_3 and Ce(III) strongly indicate a free-radical mechanism involving the $SO_4^-{\cdot}$ radical. A cursory stoichiometric study of the HSO_5^-–Cr^{2+} reaction provides additional support for this mechanistic feature. The straightforward kinetic results obtained in this study are contrasted with the complicated profiles frequently encountered in analogous reductions of hydrogen peroxide by 1-equiv species. The principal difference in the two systems is proposed to be the rare HSO_5^-–$HSO_5{\cdot}$ transformation in peroxomonosulfate reactions compared to the common H_2O_2–$HO_2{\cdot}$ involvement in hydrogen peroxide chemistry.

Introduction

Peroxomonosulfate, O_3SOOH^-, is an intermediate in the outdated electrolytic preparation of hydrogen peroxide. A convenient source of this oxidant is the commercial product OXONE, although several syntheses of reasonably pure aqueous solutions have been described.[1] A number of oxidations by peroxomonosulfate have been studied with potentially 2-equiv reducing agents.[2] The general mechanistic feature that has emerged is a nonradical reaction involving nucleophilic attack by the substrate at the peroxo moiety.[3] Oxygen transfer from the terminal peroxide position has been demonstrated in several cases.[2,4] Analogous mechanisms have been proposed for a number of peroxides including hydrogen peroxide.[3a] The principal exception is peroxodisulfate, in that radical mechanisms involving the sulfate radical anion, $SO_4^-{\cdot}$, predominate.[5]

Conversely, free-radical reactions may be anticipated in oxidations by peroxomonosulfate if 1-equiv reductants are used. Suprisingly, scant attention has been given to these systems, but the formation of the sulfate radical anion has been proposed in pulse radiolysis studies of the reduction of peroxomonosulfate by the hydrated electron.[6] In this communication we report the results of a study of the reaction of oxovanadium(IV), VO^{2+}, and HSO_5^- in acidic solution. Competition studies strongly indicate a free-radical mechanism

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