protonation of the nitrogen lone pair in H_3NOSO_3 eliminates the opportunity for stabilization in the transition state by π overlap between the lone pair and low-lying, unfilled orbitals on I^- or $(C_6H_5)_3P$. Thus, the lower reactivity of H_3NOSO_3 can be understood if this effect dominates over the charge effects.[38]

The observed order of nucleophilicity at trivalent nitrogen in $H_2NOSO_3^-$ is $(C_6H_5)_3P > I^- > (C_2H_5)_3N \gg Br^-, Cl^-$. It appears that polarizability and ease of oxidation of the nucleophile play a considerably more important role than does proton basicity in determining reactivity toward this trivalent nitrogen center. The appreciable nitrogen nucleophilicity of $(C_2H_5)_3N$ can be understood in terms of its softness and tendency for strong covalent interactions as a base.[39] Clearly, proton basicity is not an important factor, since OH^- shows little reactivity (pH 10-12) toward $H_2NOSO_3^-$.

Results for a wider range of nucleophiles are required before a detailed comparison of trivalent nitrogen with other acid centers is made. However, with respect to the order of nucleophilicity and possible π interaction of the nonbonded electron pair, there is a resemblance between trivalent nitrogen and Pt(II).

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Registry No. $(C_6H_5)_3PNH_2^+HSO_4^-$, 41380-11-4; $H_2NOSO_3^-$, 41380-12-5; I^-, 20461-54-5; $(C_6H_5)_3P$, 603-35-0; $(C_2H_5)_3N$, 121-44-8; $CH_3NHOSO_3^-$, 41380-13-6; hydroxylamine-*O*-sulfonic acid, 2950-43-8; *N*-methylhydroxylamine-*O*-sulfonic acid, 3400-11-1.

[38] However, in a related system in which $H_2NOSO_3^-$ is coordinated to Ir^{III}, presumably through the nitrogen lone pair,[7,21] $H_2NOSO_3^-$ is subject to slow, but measurable attack by Cl^-, in contrast with the lack of reactivity between Cl^- and free H_3NOSO_3.

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Preparation of Isopropyl and *tert*-Butyl Difluorophosphites

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tert-Butyl difluorophosphite and the previously reported isopropyl difluorophosphite have been prepared by the direct reaction of PF_3, pyridine, and the appropriate alcohol. PF_2O-*i*-Pr forms a stable adduct with borane but PF_2O-*t*-Bu appears to be reduced in the direct reaction with B_2H_6. Base displacement reactions have established the base strength toward borane as PF_2O-*i*-Pr > PF_2OEt > PF_2OMe. The basicity order is mirrored by the series of values for the J_{PB} coupling constants and the BH stretching frequencies.

The utility of the reaction of PF_3, pyridine, and alcohol for the production of difluorophosphites has recently been shown.[1,2] The preparation of PF_2O-*i*-Pr and PF_2O-*t*-Bu extends the generality of the reaction.

To examine the effect of the R (Me, Et, *i*-Pr, *t*-Bu) group[1] upon the basicity of these difluorophosphites toward borane, we have prepared $PF_2O\text{-}i\text{-}Pr{\cdot}BH_3$ and have attempted the preparation of $PF_2O\text{-}t\text{-}Bu{\cdot}BH_3$. The basicity order, as determined by displacement reactions,[1-5] is reported for the methyl, ethyl, and isopropyl derivatives.

Experimental Section

Material. Commercial PF_3 (Ozark-Mahoning), C_5H_5N, isopropyl alcohol and *tert*-butyl alcohol (Mallinckrodt), SbF_3 (Allied Chemical), B_2H_6 (Callery), and $(CH_3)_3SiCl$ (PCR) were used without further purification. Galvinoxyl[6] was prepared by literature methods.

General Techniques. Standard high-vacuum techniques were employed throughout.[7] Molecular weights were determined by *PVT* measurements and mass spectra recorded on a Varian M66 (70 eV). ^{19}F nmr spectra were obtained on a Varian T-60 and a Jeol JNM-C-60 HL operating at 56.4 MHz while proton nmr spectra were determined with a Jeol MN-100 operating at 100 MHz. ^{11}B spectra were recorded at 32.1 MHz on a Varian Associates XL-100 nmr spectrometer. Internal tetramethylsilane (except where noted) and external $CFCl_3$ and $B(C_2H_5)_3$ served as references for ^1H, ^{19}F, and ^{11}B spectra, respectively. Infrared spectra were recorded at a sample pressure of 10 mm on Perkin-Elmer 137 NaCl and 421 grating spectrophotometers using a 10-cm gas cell with KBr windows.

Synthesis of PF_2O-*i*-Pr and PF_2O-*t*-Bu. PF_2O-*i*-Pr[8] and PF_2O-*t*-Bu were prepared by the reaction of PF_3, pyridine, and the corresponding alcohol in a manner similar to the preparation of PF_2OCH_3, $PF_2OC_2H_5$, and $PF_2OCH_2CF_3$.[1,2] In the preparation of PF_2O-*t*-Bu, reaction time was 12 rather than 2.5 hr. The yields for the preparation of PF_2O-*i*-Pr and PF_2O-*t*-Bu were 50 and 25%, respectively.

The nmr spectra are consistent with the assigned structures. The ^1H spectrum of PF_2O-*t*-Bu (−40 to 0°, $CHCl_3$) consists of a singlet (δ_{CH_3} 1.49 ppm),[9] while the ^{19}F spectrum (−40°, $CHCl_3$) is a doublet (δ_F 41.3 ppm (d, $J_{PF} = 1345$ Hz)). These values are similar to those reported for other difluorophosphites.[10,11]

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The mass spectrum of PF_2O-*t*-Bu can be fitted very nicely to the compound. A molecular ion peak is not present but the (M − 15) peak corresponding to the loss of a methyl group is very intense. Following are the mass numbers (species) and relative abundances of the mass spectrum of PF_2O-*t*-Bu: 128 ($PF_2OC_3H_7^+$), 17.7; 127 ($PF_2OC_3H_6^+$), 100; 107 ($POC_4H_9^+$), 5.6; 101 ($POC_4H_3^+$), 3; 99 (POC_4H^+), 10.3; 96 ($PF_2OC_2H_6^+$), 10.3; 87 ($POC_3H_4^+$), 26.2; 86 (PF_2HO^+), 4.7; 85 (PF_2O^+), 4.7; 77 ($POC_2H_3^+$), 2.8; 69 (PF_2^+), 74.7; 67 ($PFHO^+$), 2.3; 66 (PFO^+), 2.8; 62 ($POCH_3^+$), 2.3; 61 ($POCH_2^+$), 29.9; 59 (POC^+), 7.5; 58 ($C_4H_{10}^+$), 15.9; 57 ($C_4H_9^+$), 83.1; 56 ($C_4H_8^+$), 19.6; 55 ($C_4H_7^+$), 18.7; 53 ($C_4H_5^+$), 4.7; 51 (PFH^+), 3.7; 50 (PF^+), 7.5; 47 (PO^+), 3.6; 43 ($C_3H_7^+$), 38.3; 42 ($C_3H_6^+$), 19.6; 41 ($C_3H_5^+$), 74.7; 40 ($C_3H_4^+$), 8.4; 39 ($C_3H_3^+$), 36.5; 38 ($C_3H_2^+$), 5.6; 37 (C_3H^+), 2.8; 32 (PH^+, O_2^+), 18.7; 29 ($C_2H_5^+$), 38.3; 28 (CO^+, $C_2H_4^+$, N_2^+), 41.2; 27 ($C_2H_3^+$), 23.3; 26 ($C_2H_2^+$), 3.7; 18 (H_2O^+), 8.4; 15 (CH_3^+), 6.5; 14 (CH_2^+, N^+), 2.8.

Although PF_2O-*i*-Pr has been synthesized,[8] no nmr or ir data have been reported. The compound PF_2O-*i*-Pr exhibits a ^1H nmr spectrum (ambient temperature, $CHCl_3$) consisting of two sets of protons in a 6:1 ratio. The high-field doublet (δ_{CH_3} 1.25 ppm (d, $J_{HCH} = 6.6$ Hz)) has a relative area of 6, while the low-field multiplet (δ_{CH} 4.87 ppm) is a doublet (d, $J_{PCH} = 9.0$ Hz) of septets (septet, $J_{HCH} = 6.6$ Hz). The ^{19}F spectrum confirms the proton spectrum. ^{19}F spectrum ($CHCl_3$, ambient temperature): δ_F 44.2 ppm (d, $J_{PF} = 1312$ Hz).

Synthesis of PF_2O-*i*-Pr·BH_3. PF_2O-*i*-Pr·BH_3 was produced by the direct reaction of B_2H_6 and the ligand.[1,5] The per cent yield was 100%, and BH_3 combined with PF_2O-*i*-Pr in a 1:0.99 ratio.

The proton spectrum of the adduct consists of three sets of peaks: (1) a broad upfield 1:1:1:1 quartet (two peaks hidden under CH_3 doublet) assigned to the BH protons (external reference TMS, ambient temperature, neat, δ_{BH_3} 0.24 ppm (q, $J_{BH} = 102.4$ Hz)); each member of a quartet was further split into a broad quartet (q, $J_{FBH} \approx 15.6$ Hz; $J_{PBH} \approx 17.8$ Hz); (2) a lower field doublet (δ_{CH_3} 1.06 ppm (d, $J_{HCH} = 6.5$ Hz)); (3) a low-field septet (δ_{CH} 4.58 ppm (septet, $J_{HCH} = 6.5$ Hz)) of doublets (d, $J_{PCH} = 1.8$ Hz). The ^{19}F spectrum confirmed the proton spectrum. ^{19}F spectrum (ambient temperature, neat): δ_F 58.3 ppm (d, $J_{PF} = 1286$ Hz)); each member of a doublet was a broad quartet (q, $J_{FBH} = 15.4$ Hz). The boron spectrum confirmed the presence of a PB bond. ^{11}B spectrum (ambient temperature, neat): δ_B 132 ppm (q, $J_{BH} = 102.8$ Hz)); each peak of a quartet was a doublet (d, $J_{PB} = 72.5$ Hz).

Reaction of PF_2O-*t*-Bu and B_2H_6. A 2.56-mmol sample of B_2H_6 was condensed at −196° in a 500-cm^3 reaction bulb with a removable tube. A 3.61-mmol sample of PF_2O-*t*-Bu was frozen on top of the B_2H_6 and the mixture was allowed to warm slowly to room temperature. After 0.5 hr a brilliant yellow solid deposited on the walls of the flask. The mixture remained at ambient temperature for 127 hr. The reaction flask was cooled to −196° and approximately 1 mmol of noncondensable H_2 was pumped away. The mixture was warmed slowly while the volatile contents were led through U traps held at −105, −145, and −196°. The −196° trap contained ~1 mmol of a mixture of BF_3, B_2H_6, and PF_3. The −105° trap held a trace of an unidentified material while the −145° trap contained ~2.4 mmol of a mixture of butane and/or isobutane, tentatively identified by ir analysis.[12-14] A bright yellow solid remained in the flask.

In a separate experiment 3.29-mmol of PF_2O-*t*-Bu was condensed on 5.43 mmol of B_2H_6 and allowed to warm very slowly to room temperature. When yellow solids first began to appear (~0.5 hr) the reaction was frozen and then allowed to warm rapidly while distilling through traps held at −145 and −196°. The −196° trap contained 3.95 mmol of B_2H_6, 104% of theory if PF_2O-*t*-Bu·BH_3 is formed. The −145° trap contained butane and/or isobutane, identified by ir spectroscopy,[12-14] and an unidentified material which exhibited stretches in the 2400-2600-cm^{-1} region (BH). Presumably PF_2O-*t*-Bu·BH_3 is formed during the slow warming period but undergoes decomposition. If the mixture is distilled together and allowed to warm to ambient temperature again, the decomposition continues. No BH stretches are evident in the ir spectrum after this procedure.

Reaction of PF_2O-*t*-Bu and SbF_3. A 1.34-mmol sample of PF_2O-*t*-Bu was condensed at −196° on an excess of SbF_3 and then allowed to warm slowly to room temperature. After 72 hr the only volatile products were SiF_4 and PF_3, identified by ir spectroscopy.

Reaction of PF_2O-*t*-Bu and Galvinoxyl. A 1.48-mmol sample of PF_2O-*t*-Bu was condensed into an nmr tube[5,7] at −196°. A 0.0031-g sample of galvinoxyl had previously been placed into the nmr tube. A 2.0-mmol amount of C_6H_6 was then condensed in and the tube was sealed. ^1H nmr up to 94° showed no species present other than the starting materials.

Reaction of PF_2O-*t*-Bu and $(CH_3)_3SiCl$. A 0.88-mmol sample of PF_2O-*t*-Bu was condensed into a 50-cm^3 reaction tube at −196°. A 0.88-mmol sample of $(CH_3)_3SiCl$ was frozen on top of the PF_2O-*t*-Bu and the mixture was allowed to warm to ambient temperature. After 24 hr no reaction was evident by ir spectroscopy, but after 48 hr a noncondensable species was present. The mixture was distilled through traps held at −135 and −196°. The −196° trap contained 0.5 mmol of PF_3 while the −135° held unreacted Me_3SiCl and an unidentified material. PF_3 and Me_3SiCl were identified by ir spectroscopy. Solids remained in the reaction vessel.

Base Displacement Reactions. Mixtures of an uncoordinated phosphite and a borane adduct were prepared as described previously,[1,5] while integration of the ^{19}F spectra was accomplished by cutting and weighing the resonance absorptions ascribed to the components of the equilibrium mixture. The spectra were obtained at 0° and the equilibrium was approached from both directions.[1,5] The results of these reactions are given in Table I.

Results and Discussion

1. Preparation and Characterization of Ligands and Adducts.

The main route to difluorophosphites has been a two-step procedure involving the preparation of the chloro derivative and its subsequent fluorination.[10,11] The yields for each of these reactions are relatively good but a simpler process would be desirable. The preparation of PF_2OCH_3, $PF_2OC_2H_5$, and $PF_2OCH_2CF_3$[1] by the reaction of PF_3, pyridine, and the appropriate alcohol was a simpler process involving good to excellent yields of easily purifiable difluorophosphites. Trimethylamine or γ-picoline can be substituted for pyridine depending upon the volatility of the alcohol and the difluorophosphite produced. The generality of this reaction has now been extended to include the preparation of PF_2O-*i*-Pr[8] and the previously unreported PF_2O-*t*-Bu.

Both difluorophosphites are clear volatile liquids at room temperature and both form glasses on freezing. No decomposition at room temperature *in vacuo* is noted by ir and nmr spectra after a period of 400 hr for PF_2O-*i*-Pr. PF_2O-*t*-Bu undergoes no decomposition at 80° for 1 hr. The compounds PF_2O-*i*-Pr[8] and PF_2O-*t*-Bu were characterized by vapor density molecular weights [PF_2O-*i*-Pr (22.1°, $P = 54.3$ mm): found, 129.5; calcd, 128.0. PF_2O-*t*-Bu (24.1°, $P = 71.6$ mm): found, 139.1; calcd, 142.0] and by ir, ^{19}F and ^1H nmr, and mass spectra.[15] Complete mass and nmr spectral data are in the Experimental Section. The gas-phase ir data are listed in Table II.

We attempted to prepare the borane adducts of these difluorophosphites by the direct reaction of B_2H_6 and the ligand.[1,3,5] The adduct of PF_2O-*i*-Pr·BH_3 can be obtained from this reaction in 100% yields. No dissociation is evident from the vapor-phase molecular weight [PF_2O-*i*-Pr·BH_3 (23.0°, $P = 40.4$ mm): found, 143.0; calcd, 141.8] and ir data, and no decomposition is revealed by ir and nmr spectroscopy after 200 hr at room temperature *in vacuo*. The gas-phase ir spectrum is listed in Table II where it may be compared with that of the free ligand. The 1:1 adduct was characterized by the stoichiometry of the reaction from which it was obtained and by ^{11}B, ^{19}F, and ^1H nmr data.

Among difluorophosphites, the reaction of PF_2O-*t*-Bu with B_2H_6 is singularly peculiar.[1,3,5] The phosphite ligands

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(15) Even though PF_2O-*i*-Pr has been prepared (see ref 8), no ir or nmr data have been reported.

Table I

Phosphite (mmol)	Adduct (mmol)	J_{PB}(adduct), Hz	Time, hr	K_{eq}[a] (°0)	% displacement[b]
PF_2O-*i*-Pr[c] (0.895)	$PF_2OEt\cdot BH_3$ (0.895)	70.4[d]	747	2.38	61
PF_2OEt (0.960)	PF_2O-*i*-Pr$\cdot BH_3$ (0.960)	72.5	750	2.22	60

[a] Equilibrium constants are defined by the expression K_{eq} = [weaker base][adduct of stronger base]/[adduct of weaker base][stronger base]. See ref 1 and 5. [b] Per cent displacement is calculated using the expression $100\sqrt{K_{eq}}/\sqrt{K_{eq}} + 1$. See ref 1 and 5. [c] Stronger base of exchanging pairs. [d] See ref 1.

Table II[a]

PF_2O-*t*-Bu	PF_2O-*i*-Pr	PF_2O-*i*-Pr$\cdot BH_3$	Tentative assignment
2996 s	2999 s	2998 m	
2948 m, sh	2957 w, sh	2952 w, sh	CH str
2928 w, sh	2891 vw, sh	2898 w, sh	
2898 vw, sh			
		2438	BH str
		2378 w, sh	
	1736 w, br	1808 vw, br	
1478 w, br	1462 mw, br	1467 w, br	
1403 m, sh	1388 m	1393 m	
1382 ms			
1258 ms			
1183 ms, br	1178 m	1183 m	
	1141 m	1147 m, sh	
	1108 ms	1121 ms, sh	
		1089 s	
1036 vs, br	1019 vvs	1031 vs, br	
1003 s, sh			
992 s, sh	981 vw		
923 w, br			
896 w	893 w	906 vs, br	
858 s	863 m		
818 vs	820 vs		PF str
	793 s	786 m	
	785 s, sh		
738 vs			
728 w, br			
		713 mw	
		637 mw	
570 w, br		595 m	

[a] Vibrational frequencies are given in cm^{-1} followed by a tentative assignment. Notation for intensities: v, very; m, medium; s, strong; sh, shoulder; br, broad; w, weak.

PF_2OR (R = Me, Et, CH_2CF_3, and *i*-Pr) yield stable 1:1 adducts with borane as do PF_2SCH_3[5] and $PF(OCH_3)_2$.[3] $PF(SCH_3)_2$ also forms an adduct although it is unstable at 0°.[5] The ligand PF_2O-*t*-Bu is apparently reduced to a mixture of butane and/or isobutane (tentatively identified by ir)[12-14] by B_2H_6. A noncondensable species is produced and traces of BF_3, B_2H_6, and PF_3 can be isolated while a bright yellow solid is deposited on the walls of the reaction vessel. If the reaction is frozen at the first appearance of yellow solids and distilled rapidly, the amount of excess B_2H_6 recovered (104% of theory) indicates the PF_2O-*t*-Bu$\cdot BH_3$ has formed but undergoes rapid decomposition. BH stretching is evident in the ir spectrum of the less volatile material.[13]

The free-radical chemistry of $PF_2\cdot$[16a,b] and $(CH_3)_3CO\cdot$[16c] is well established. To determine whether free radicals might be involved in the unusual reaction of PF_2O-*t*-Bu with B_2H_6 we followed the ^1H nmr of a mixture of galvinoxyl,[6] PF_2O-*t*-Bu, and solvent benzene from room temperature to 94°. The color of galvinoxyl in solution did not fade (no free-radical coupling), and no decomposition products of the *t*-butoxy radical (*i.e.*, acetone and ethane) were ever evident in the spectrum. No peaks attributable to any decomposition products were present even after 975 hr at ambient temperature.

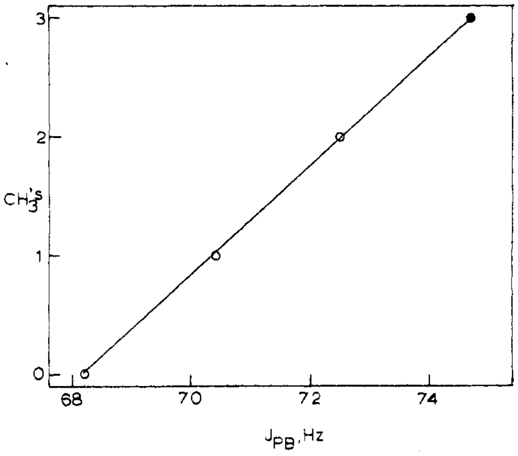

Figure 1. Plot of the number of methyl groups attached to the $PF_2OC\equiv$ skeleton (as opposed to hydrogens) *vs.* J_{PB} for the adducts. A J_{PB} coupling constant of 74.7 Hz is predicted for PF_2O-*t*-Bu$\cdot BH_3$. See Table III.

Since the CO bond was apparently cleaved by B_2H_6, an attempt was made to fluorinate PF_2O-*t*-Bu with SbF_3 at the oxygen-carbon bond. This was unsuccessful, the only volatile products being SiF_4 and PF_3. An attempt to prepare $PF_2OSi(CH_3)_3$[17] by the reaction of PF_2O-*t*-Bu and $(CH_3)_3SiCl$ was also unsuccessful.

2. Basicity Studies. In a continuing effort to determine what effect changes in the R group[1] have upon the Lewis basicity of a series of difluorophosphites we have prepared PF_2O-*i*-Pr$\cdot BH_3$ and attempted the preparation of PF_2O-*t*-Bu$\cdot BH_3$. By displacement equilibria the relative order of base strengths established for the series of phosphites (R = Me, Et, *i*-Pr) is PF_2O-*i*-Pr > PF_2OEt > PF_2OMe. The J_{PB} coupling constants of the adducts decrease in the same order. This agrees with the J_{PB} *vs.* basicity correlation proposed by Cowley and Damasco[3] and Rudolph and Schultz.[4]

Upon considering the stabilizing effect of the R group on the (p-d)π resonance form for methyl, ethyl, and trifluoroethyl difluorophosphites, $F_2P^-{=}O^+{-}R$, we have found a correlation[1] between the basicity toward borane and the classical inductive electron-releasing ability of the R group. The order of the base strengths for PF_2OR (R = Me, Et, CH_2CF_3) predicts the classical electron-releasing order[18-23] for the groups Et > Me > CH_2CF_3.

The series (R = Me, Et, *i*-Pr, *t*-Bu) of difluorophosphite ligands where the number of attached methyls to the

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$PF_2OC\equiv$ skeleton is varied from 0 to 3 is now known, as is the series of adducts, excluding the adduct of PF_2O-*t*-Bu. The basicity order of the series[24] predicts the electron-releasing order *i*-Pr > Et > Me. This order is in agreement with previous work[1] and with the classical electron-releasing ability.[18-23]

The effect of substituting a methyl group for a hydrogen upon the basicity of these difluorophosphites is additive. A plot of the number of attached methyls *vs.* J_{PB} is linear. The relationship of J_{PB} *vs.* the number of attached methyls can be used to predict a J_{PB} coupling constant for PF_2O-*t*-Bu·BH_3 of 74.7 Hz. See Figure 1.

Foester and Cohn[5] have reported that a 1:1 correlation between displacement base strength and J_{PB} is not possible in a series of the type PF_2X (X = Me, MeO, Me_2N, MeS). However, Rudolph and Schultz[4] indicated that for a series of smoothly varying phosphine ligands [*i.e.*, PF_2X (X = F, Cl, Br) or $PF_{3-n}H_n$] the relationship between the magnitude of J_{PB} and the dative bond strength is a general one. The relationship between J_{PB} and the displacement base strength of the smooth series $PF_2OC(CH_3)_{3-n}H_n$ is essentially quantitative. See Table III.

Verkade and White[5] have recently correlated the relative stability of borane adducts with BH stretching frequencies. Coyle and Stone[26] originally suggested that BH ir stretching frequencies could be related to boron-ligand bond strength in boron adducts, but Cohn[5] found no simple relationships in a series of similar fluorophosphine-boranes. Although the differences in frequencies (cm^{-1}) are small in the series PF_2OR [R = *i*-Pr (2438, 2378), Et (2448, 2382),[1] Me (2452, 2383),[1] Tfet (2456, 2382)[1]], a trend similar to that suggested by Coyle and Stone and demonstrated by Verkade and White is evident.

Table III

Ligand	Adduct J_{PB}, Hz	ΔJ_{PB}, Hz	Av % displacement[a]	Δ(av % displacement)[b]
PF_2O-*i*-Pr	72.5			
		2.1	60.5	10.5
PF_2OEt	70.4[c]			
		2.2	60.5[c]	10.5
PF_2OMe	68.2[d]			

[a] See Table I. Average per cent displacement is calculated by averaging the two per cent displacements obtained from the pairs of exchange reactions. [b] Change in per cent displacement is calculated by subtracting 50% from the average per cent displacement. Per cent displacement for the reaction $PF_2OEt + PF_2OEt\cdot BH_3 \rightleftarrows PF_2OEt + PF_2OEt\cdot BH_3$ is 50% ($K_{eq} = 1$). See Table I. [c] See ref 1. [d] See ref 3.

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Registry No. PF_2O-*t*-Bu, 41380-08-9; PF_2O-*i*-Pr, 1737-83-3; PF_2O-*i*-Pr·BH_3, 41380-10-3; B_2H_6, 19287-45-7.

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(24) Steric effects on the basicity are assumed to be small in relation to (p-d)π electron drift from the oxygen system since the order of basicity is not that expected for steric requirements, PF_2OMe > PF_2OEt > PF_2O-*i*-Pr. See ref 1, 3, and 5. See also H. C. Brown, *J. Amer. Chem. Soc.*, **75**, 16 (1953).

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Characterization of the Thermal Dehydration of Zirconium Oxide Halide Octahydrates

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The compounds $ZrOX_2\cdot 8H_2O$ (X = Cl, Br) dehydrate thermally in a stepwise manner to the respective hexahydrates, tetrahydrates, and finally ZrO_2. Dehydration is complete at 700°. The intermediate hydrates have been isolated and characterized. Several regions of the infrared spectra of the various hydrates have been assigned with the aid of analogous deuterated compounds. The experimental evidence may be interpreted in terms of the structural formulations $[Zr_4(OH)_8(H_2O)_{16}]X_8\cdot 12H_2O$, $[Zr_4(OH)_8(H_2O)_{16}]X_8\cdot 4H_2O$, and $[Zr_4(OH)_8(H_2O)_{12}]X_8$, for the octahydrates, hexahydrates, and tetrahydrates, respectively. The last tetrameric cation is proposed to contain seven-coordinate Zr(IV).

Constant-temperature dehydration of zirconium oxide chloride octahydrate, $ZrOCl_2\cdot 8H_2O$, at varying humidities has been investigated previously.[1,2] The inconsistencies among the results reported in these studies are indicative of the difficulty of establishing equilibrium in the experimental system. Furthermore, dynamic thermal dehydration studies have employed rapid heating rates on bulk samples in stagnant atmospheres and have produced varying results.[3,4] We undertook the present investigation with the principal objective of clarifying the thermal behavior of the octahydrates of both $ZrOCl_2$ and $ZrOBr_2$.

X-Ray crystallographic studies have shown[5,6] that the correct structural formulation of $ZrOCl_2\cdot 8H_2O$ is $[Zr_4(OH)_8$-

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