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Methoxytrifluoromethylphosphines and Their Borane(3) Complexes

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New phosphines of the prototype $CH_3O(CF_3)PX$ have been made, starting with $CH_3O(CF_3)PCl$, formed (91%) from $(CH_3O)_2PCF_3$ and CF_3PCl_2, catalyzed by $(CH_3)_3N$. NaI converts $CH_3O(CF_3)PCl$ to $CH_3O(CF_3)PI$, which Hg converts to the diphosphine $(CH_3OPCF_3)_2$. From this comes $CH_3O(CF_3)PH$ by action of CH_3OH; and $CH_3O(CF_3)PF$ is made from $(CH_3O)_2PCF_3$ by action of BF_3 at oxygen. However, BF_3 does not attack the second oxygen; CF_3PF_2 is not formed. The diphosphine $(CH_3OPCF_3)_2$ is cleaved by HCl or BF_3, which seems to attack at oxygen; the major result is disproportionation to $(CH_3O)_2PCF_3$ and $(CF_3P)_n$ or secondary products. A probable CF_3HPCl was a minor product of the HCl reaction. The BH_3 complexes of some of these phosphines were found to be of the relatively volatile, nonpolar type, with too little hydridic character for reaction with HCl to make H_2; and they are far more stable than the classical examples of this type, $BH_3{\cdot}CO$ and $BH_3{\cdot}PF_3$. Both $(CH_3OPCF_3)_2{\cdot}BH_3$ and $(CH_3OPCF_3)_2{\cdot}2BH_3$ equilibrate with diborane and their predecessors; apparently the second BH_3 is bonded no less effectively than the first. Infrared spectra are listed, including evidence that P–H bonding is stronger in $CH_3O(CF_3)PH{\cdot}BH_3$ than in the free phosphine. Characterization by NMR spectra also is extensive.

Fluorocarbon phosphines having alkoxy groups on phosphorus are potentially interesting ligands for the fuller study of complexes in which bases act both as σ donors and as π acceptors. It is now well understood that a CF_3 group enhances the π-acceptor action of phosphorus, while suppressing its σ-donor bonding power, whereas a methoxy group improves the σ-donor action of phosphorus while competing with π return bonding by the Lewis acid or metal atom. There might be situations such that the attachment of both groups to phosphorus would lead to unexpectedly strong ligation. However, very few alkoxyfluorocarbon phosphines have been reported. The present study develops especially the type $CH_3O(CF_3)PX$.

The ligand character of these new phosphines was explored by studying their BH_3 complexes. In general, BH_3 complexes have divided sharply into two classes: the highly polar, rapidly formed, and strongly hydridic base-donor type such as $(CH_3)_3N{\cdot}BH_3$, $(CH_3)_3P{\cdot}BH_3$, or the far less stable $(CH_3)_2O{\cdot}BH_3$; and the virtually nonpolar, slowly formed, and essentially nonhydridic type exemplified by $BH_3{\cdot}CO$, $BH_3{\cdot}PF_3$, or $BH_3{\cdot}P(OCH_3)_3$, wherein the polarity expected from base-donor action is neutralized by a π-type return of B–H bonding electrons in the manner of hyperconjugation. As mentioned in a plenary lecture some years ago,[1] the hydridic character of the base-donor class is demonstrated by rapid reaction with HCl to form hydrogen and place Cl on B, whereas the donor-acceptor class seems to be inert toward HCl except in the sense that HCl attacks the BH_3 group as it is liberated by dissociation of the complex.

The $CH_3O(CF_3)PX{\cdot}BH_3$ complexes conform to the latter class, for they form slowly, are highly volatile relative to their molecular weights, and react with HCl only at rates corresponding to their dissociation. However, they are far more stable than $BH_3{\cdot}CO$ or $BH_3{\cdot}PF_3$, presumably because of the base-enhancement effect of the methoxy group on phosphorus.[2] It seems clear, then, that the study of transition element complexes of the $CH_3O(CF_3)PX$ phosphines would be interesting because both their σ-donor and π-acceptor bonding would be strong.

Experimental Methods

The present studies were performed by means of a Stock-type high-vacuum manifold, with mercury float-valves for quantitative work with volatile compounds or with Apiezon L greased stopcocks where suitable. Infrared spectra were recorded accurately by the Beckman IR7 instrument with NaCl or CsI optics or, for quick identification, by the Beckman IR20A. The frequencies are reported in cm^{-1} with relative intensities in parentheses, calculated by the equation $k = (100/PL) \log (I_0/I)$ for pressure P and path L both in cm.

Preliminary NMR spectra were recorded for ^1H or ^{19}F by the Varian T-60 instrument, but for higher accuracy and sensitivity the Varian XL-100-FT instrument was used. For ^{13}C spectra, each sample was in a 12-mm thin-wall tube with a concentric 5-mm tube containing C_6D_6, which served as the lock and chemical shift standard. For the other nuclei, the samples usually were in 1-mm i.d. microtubes, concentrically placed in 5-mm thin-wall tubes containing the acetone-d_6 or benzene-d_6 lock standard. For the chemical shifts, the standard offsets for TMS, Cl_3CF, H_3PO_4, or $(CH_3O)_3B$ were determined with similar microsamples, minimizing the effects of diamagnetic differences. For all chemical shifts, the positive direction is upfield, including the τ values for protons, defined as the distance upfield from TMS − 10 ppm. The coupling constants J are in s^{-1} ("Hz").

The Monophosphines

Methoxytrifluoromethylphosphine. The compound $CH_3O(CF_3)PH$ was first recognized as a minor product of the methanolysis of $(CF_3P)_4$.[3] A more convenient, virtually quantitative synthesis was performed by methanol cleavage of the diphosphine $(CH_3OPCF_3)_2$ (described later), according to the millimole stoichiometry

$$\underset{0.352}{(CH_3OPCF_3)_2} + \underset{0.352}{CH_3OH} \rightarrow \underset{0.372}{(CH_3O)_2PCF_3} + \underset{0.312}{CH_3O(CF_3)PH} \quad (1)$$

This reaction occurred in a small U-tube between mercury float-valves, during slow warming from −78 to +50 °C. The

deficiency of $CH_3O(CF_3)PH$ and excessive yield of $(CH_3O)_2PCF_3$ were attributable to a trace of $(CF_3P)_4$, which was not easy to remove from the diphosphine. Another effect of this impurity was a slight formation of CF_3PH_2; the high solubility of this in the desired phosphine made it necessary to employ a microcolumn (in vacuo with reflux at −78 °C) for purification.

The vapor-phase molecular weight of $CH_3O(CF_3)PH$ was 132.3 (calcd 132.02). Its equilibrium vapor pressures were correlated by the equation $\log P = 6.4080 + 1.75 \log T - 0.0065T - 1825/T$, from which the normal boiling point is 38 °C and the Trouton constant 21.0 eu. Examples: 0.57 mm at −78.5 °C, 10.7 mm at −45.7 °C, 29.0 mm at −31.0 °C, 165 mm at 0 °C, and 360 mm at 17.75 °C (calcd 0.59, 10.7, 29.5, 164, and 363 mm). The NMR spectra eliminated any doubt of the molecular formula: phosphorus bonded to H, CF_3, and CH_3O. The infrared spectrum also was confirmatory.

The Fluorophosphine. The fluorination process

$$(CH_3O)_2PCF_3 + BF_3 \rightarrow CH_3OBF_2 + CH_3O(CF_3)PF \quad (2)$$

began with the absorption of equimolar BF_3 by $(CH_3O)_2PCF_3$ at −78.5 °C. The 1:1 adduct was not quite completely formed, no doubt because of occlusion of some of the $(CH_3O)_2PCF_3$. The pressure of residual BF_3 reached constancy in 20 min. At this point the complex was dissociated by warming, with the vapors entering a high-vacuum fractional condensation train with U-traps at −120 and −196 °C. One-fourth of the original BF_3 was found in the −196 °C trap, while the rest had either recombined with $(CH_3O)_2PCF_3$ or completed reaction 2. In a second experiment, reaction 2 was completed during a 3-h storage of the adduct at −78.5 °C; then only a minimal part of the original BF_3 could be recovered.

The new fluorophosphine was purified by passing a high-vacuum U-trap at −90 °C and condensing out at −115 °C. Its vapor-phase molecular weight (at 304 mm) was determined as 153 (calcd 150). Its equilibrium vapor pressures determined the equation $\log P = 5.5178 + 1.75 \log T - 0.005T - 1660/T$; bp 37 °C; Trouton constant 21.5 eu. Examples: 16.3 mm at −45.7 °C, 68 mm at −22.8 °C, 218 mm at 0 °C, and 478 mm at 18.3 °C (calcd 16.2, 68, 218, and 476 mm).

A small sample of this phosphine failed to absorb BF_3 at −78.5 °C, and there was no secondary fluoride-transfer reaction, such as would have produced CF_3PF_2. With equimolar BF_3 in a microsize NMR tube, it reacted slowly at 25 °C: after 1 h the reactants had been 25% consumed, and there was a product whose ^{19}F spectrum showed δ 75.0 ppm, with J_1 = 139 and J_2 = 7.9 s^{-1}. After 20 h at 25 °C, there was only a colorless viscous oil, partially volatile under high vacuum at 50 °C—a mixture not readily amenable to further study.

The failure of $CH_3O(CF_3)PF$ to attach BF_3 is consistent with the equally inert behavior of $ROP(CF_3)_2$ compounds toward BF_3. It appears that two CH_3O groups on P compete for the opportunity of π bonding to P, thus permitting either to have enough O→B bonding power to support reaction 2.

The Chlorophosphine. The first sample of $CH_3O(CF_3)PCl$ was a by-product of the synthesis of $(CH_3O)_2PCF_3$ from CF_3PCl_2 with deficient methanol; thus, with millimole quantities

$$\underset{25}{CF_3PCl_2} + \underset{47}{CH_3OH} \rightarrow \underset{46}{HCl} + \underset{20.5}{(CH_3O)_2PCF_3} + \underset{4}{CH_3O(CF_3)PCl} \quad (3)$$

The discrepancies here are due chiefly to the action of HCl on CH_3OH to form CH_3Cl and water, which hydrolyzes CF_3PCl_2 to HCl and CF_3HPOOH.[4] This effect was minimized by frequent removal of the HCl during the 2-day run at 25 °C.

The second reaction for making $CH_3O(CF_3)PCl$ was

$$(CH_3O)_2PCF_3 + CF_3PCl_2 \rightarrow 2CH_3O(CF_3)PCl \quad (4)$$

Like the analogous reaction of $(CH_3O)_3P$ with PCl_3,[5] this process is ineffective at 25 °C but a catalyst makes it feasible. A mixture of 3.76 mmol of each reactant with 0.002 mmol of trimethylamine was 50% converted after 21 h at 25 °C. After brief heating to 100 °C in a 15-ml sealed tube, equilibrium was reached at 91%. There was minor loss in the form of nonvolatiles.

The product was purified by high-vacuum fractional condensation (through −60 °C; trapped at −78 °C) and then showed 52-mm equilibrium vapor pressure at 0 °C, unchanged after 6 days at 25 °C. Its vapor-phase molecular weight (168.7 or 167.3) approached the calculated 166.5 as the pressure was lowered. Even though it seemed to be permanently stable at 25 °C, it could be catalytically disproportionated by a trace of either HCl or $(CH_3)_3N$, approaching equilibrium at 9% (in agreement with the results of the forward reaction 4) within a few hours at 25 °C. It appears that the equilibrium constant for formation by reaction 4 is close to 100 and not highly variable with temperature.

An attempt to cause the Arbuzov reaction, whereby this methoxyphosphine would be converted to CH_3CF_3POCl, did not succeed. The 0.444-mmol sample, with 0.0027 mmol of CH_3I in a 2-ml sealed tube, after 14 h at 100 °C showed 9% disproportionation to $(CH_3O)_2PCF_3$ and CF_3PCl_2, with 91% recovery of the original $CH_3O(CF_3)PCl$. Methyl iodide may have been catalytic for this disproportionation but not for a rearrangement.

The Iodophosphine. For the synthesis of $CH_3O(CF_3)PI$, neither the methanolysis of CF_3PI_2 nor an exchange like reaction 4 could be used, for both attempts gave major yields of methyl iodide. One might consider converting the chlorophosphine to the yet unknown $CH_3O(CF_3)PN(CH_3)_2$ for a low-temperature reaction with HI to make $CH_3O(CF_3)PI$, but it was convenient enough to use reaction 5. This is

$$CH_3O(CF_3)PCl + NaI \rightarrow NaCl + CH_3O(CF_3)PI \quad (5)$$

analogous to the earlier conversion of CH_3CF_3PCl to CH_3CF_3PI.[6]

For this purpose, NaI in large excess was vacuum-dried and baked out with the temperature rising slowly to 250 °C. The very porous product converted $CH_3O(CF_3)PCl$ to $CH_3O(CF_3)PI$ almost completely in 15 min at 25 °C. A remaining trace of the chlorophosphine could be removed easily through a high-vacuum U-tube at −50 °C. A greater difficulty arose from the formation of traces of $(CH_3O)_2PCF_3$ and CF_3PI_2, for the latter could not easily be eliminated by the usual high-vacuum distillation methods. The light yellow, nearly pure $CH_3O(CF_3)PI$ showed 4-mm vapor pressure at 0 °C and seemed conveniently stable. Its NMR spectra left no doubt of its identity.

NMR Spectra. The NMR data shown in Table I were obtained as described in "Experimental Methods". It is curious that J_{COP} was not observable for either the chloro- or iodophosphine; the J_{CH} quartets were sharp and clean. The reason might have some relation to the blurred character of the ^{31}P spectrum of the chlorophosphine, which may be ascribed to the coupling of P to the chlorine quadrupoles. If P_{3s} contact to Cl occurs at the expense of P_{3s} character in the P–O bond, the contact term for J_{COP} may be small enough to be canceled out by at least one other component of the coupling Hamiltonian, opposite in sign. The same argument would apply to the iodophosphine, although the ^{127}I quadrupole would be too deeply buried for any appreciable blurring effect upon the ^{31}P spectrum.

For the longer range couplings (POCH = HCOP and even FCPOCH = HCOPCF), which are clearly observable, it would appear that the terms do not balance out. Such skip-over effects are fairly common for phosphorus–oxygen compounds: a short-range J may be smaller than a longer range J.

Table I. NMR Parameters of the Monophosphines $CH_3O(CF_3)PX$

	X			
	H	F	Cl	I
$^1H\ \tau$	6.84 CH_3 4.5 HP	6.32	6.47	6.4
J_{HCOP}	9.2	10.66	11.0	11.5
J_{HCOPCF}	1.1	0.79	0.9	0.8
J_{other}	199 HP 12 HPCF	1.88 HCOPF		
$^{19}F\ \delta$	61.4	78.1 CF_3 119.4 FP	72.3	65.5
J_{FCP}	60.3	82.6	73.3	61.9
J_{FCPOCH}	1.1	0.76	1	0.9
J_{other}	12.0 FCPH	5.17 FCPF 1.9 FPOCH 1138 FP		
$^{31}P\ \delta$	−82	−150	−133	−139
J_{PCF}	59.5	82.5	75	61.8
J_{POCH}	9.15	10.74	"10.3"	11.3
J_{other}	201 PH	1138 PF		
$^{13}C\ \delta$	*a*	*a*	1.15 CF_3 72.2 CH_3	2.80 CF_3 67.2 CH_3
J_{CF}			325.6	326
J_{CP}			66.0	79.3
J_{CH}			148.7	148.0

[a] Sample size inadequate.

The Diphosphine

Synthesis and Characterization. The conversion of the iodophosphine to the diphosphine can be nearly quantitative

$$2CH_3O(CF_3)PI + 2Hg \rightarrow Hg_2I_2 + (CH_3OPCF_3)_2 \quad (6)$$

The iodophosphine is shaken with a plentiful excess of mercury in a stopcocked tube (conveniently by slow end-for-end rotation of the tube on a horizontal motor-driven clamp) for 15 min; then the volatiles are distilled under high vacuum to another reaction tube for repetition of the process with fresh mercury. A further repetition usually proves completion of the process.

Impurities inherent in this synthesis arise from a slight disproportionation of the iodophosphine. The resulting $(CH_3O)_2PCF_3$ is not difficult to remove, but CF_3PI_2 (coming also possibly as an original impurity in the iodophosphine) converts to $(CF_3P)_4$ and $(CF_3P)_5$. These less volatile impurities can be removed by means of a small high-vacuum fractionating column with reflux at 0 °C.

The equilibrium vapor pressures of the purified $(CH_3OPCF_3)_2$ (examples: 1.81 mm at 0 °C, 5.76 mm at 16.9 °C, and 6.45 mm at 18.6 °C) determined the equation $\log P = 7.536 + 1.75 \log T - 0.0065T - 2668/T$; bp 132 °C; Trouton constant 21.5 eu; calcd 1.81, 5.79, and 6.43 mm. Its vapor-phase molecular weight was determined as 263.6 (calcd 262.04). Stored in a sealed NMR tube for 2 months, it showed no evidence of decomposition. With CH_3I at 90 °C (15 h) it failed to produce any recognizable Arbuzov rearrangement product; 80% of the original diphosphine was recovered.

Cleavage Reactions. The cleavage of $(CH_3OPCF_3)_2$ by CH_3OH has been mentioned (reaction 1); it probably occurs through a basic attack by the methanol oxygen upon the electron acceptor P. With a stronger protic acid, however, such as HCl, one cannot expect such a process; for example, $P_2(CF_3)_4$ is cleaved by methanol but is inert to both HCl and BF_3. But both HCl and BF_3 rapidly attack $(CH_3OPCF_3)_2$ and we can only assume that they attach at O, which these "hard" acids prefer over P. The results are complicated but consistent with such a first step.

For example, 0.674 mmol of $(CH_3OPCF_3)_2$ with 0.800 mmol of HCl (5 min, 25 °C) gave only 0.180 mmol of $CH_3O(CF_3)PCl$ and far less $CH_3O(CF_3)PH$; these would be the expected products of P–P bond cleavage. If $CH_3O(CF_3)PH$ were catalytically disproportionated, one would expect more CF_3PH_2 than the observed 0.047 mmol. Meanwhile, a 0.625-mmol yield of $(CH_3O)_2PCF_3$ would suggest a catalytic disproportionation of $(CH_3OPCF_3)_2$, with the other product expected to be the equivalent amount of CF_3P as the tetramer and pentamer. However, the observable yield of these volatiles was only 0.096 mmol of CF_3P, and one does not expect higher polymers of this unit to be formed at 25 °C. Indeed, in another experiment, 17% of the expected CF_3P units came as what seemed to be the new compound CF_3HPCl. Its infrared spectrum included P–H peaks at 2334, 875, 869, 844, and 834 cm^{-1}, CF_3 peaks at 1164, 1141, 745, and 550, and P–CF_3 stretching at 422. P–Cl stretching seemed clear enough at 522. This compound could be expected if there were a catalytic transfer of CH_3O from one P to the other, allowing HCl to attach itself to the broken-off CF_3P unit.

The BF_3 reaction was even more distinctly a catalytic disproportionation, for 42% of the CF_3P units appeared as the tetramer and pentamer, while an equivalent yield of $(CH_3O)_2PCF_3$ was partly destroyed by reaction 2. The original BF_3 amounted to only 0.65 per diphosphine, and 0.21 was recovered. Both the HCl and BF_3 reactions seem worthy of more detailed study, each under a wider variety of experimental conditions.

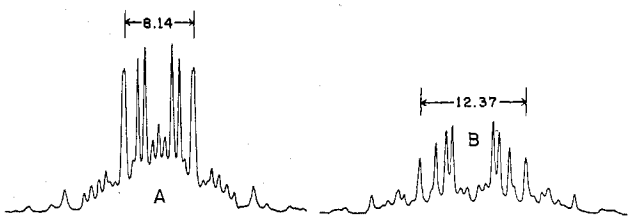

Figure 1. Central portions of the ^{19}F spectra of the $(CH_3OPCF_3)_2$ isomers, taken from the same proton-decoupled run. For the observed high resolution, the cylindrical sample had 1-mm diameter. The acquisition time was 10 s and the pulse width 50. The number of transients was 100 and the time constant zero.

NMR Spectra. Like other diphosphines of the $(RR'P)_2$ type, or similar P–X–P connected bis(phosphines), the diphosphine $(CH_3OPCF_3)_2$ exists as an equilibrium mixture of meso and optical isomers having slightly different NMR parameters, so that their complex spectra overlap. Since there is no obvious way to decide which is the meso form vs. the spectrally alike optical isomers, the more intense spectra will be assigned to isomer A and the less intense to isomer B.

The ^{13}C, ^{19}F, and ^1H spectra all were of the complex type wherein two high sharp peaks enclose a characteristic internal pattern, such that the overall width is the sum of two J values. The ^{13}C spectrum of each isomer showed a quartet of such patterns, for CF_3 as well as for CH_3. For the CF_3 aspect, δ_A is −2.14 with $J_{CF} = 321.9$, while δ_B is −2.51 with $J_{CF} = 324.7$; the different J_{CF} values meant different overlap patterns for different members of the quartet. For A, $J_{CP} + J_{CPP}$ (the distance between the high end peaks) could be estimated fairly well as 24; for B it was completely uncertain. For the CH_3 aspect, δ_A is 67.64 with $J_{CH} = 147.2$ and $J_{COP} + J_{COPP} = 17.3$ and δ_B is 67.33 with $J_{CH} = 147.1$ and $J_{COP} + J_{COPP} = 16.1$.

The ^{19}F spectra also overlapped, but not so closely, permitting a clear view of the shape of each complex pattern. The very different central regions of the two spectra could be resolved by ^1H decoupling, but the peaks (Figure 1) do not seem interpretable in terms of present theory: δ_A 58.9 with $J_{FCP} + J_{FCPP} = 91.0$ and δ_B 59.7 with $J_{FCP} + J_{FCPP} = 83.9$.

The ^1H spectra were more severely superposed, but by the use of both the T-60 and XL-100 instruments, the values τ_A 6.34 and τ_B 6.40 could be recognized, with respective widths 12.8 and 12.7 s^{-1}. Sharp peaks in each central portion suggest that these spectra might be analyzable if they could be recorded with a higher frequency instrument.

Table II. Infrared Spectra (cm^{-1}) of Monophosphines and Their BH_3 Complexes

Expected mode	H CH_3OPCF_3	H CH_3OPCF_3 BH_3	D CH_3OPCF_3	D CH_3OPCF_3 BH_3	F CH_3OPCF_3	F CH_3OPCF_3 BH_3	Cl CH_3OPCF_3
CH_3, ν	3010 (0.9)	3020 (0.7)	3004 (1.4)	3020 (0.7)	3030 (0.6)	3030 (0.4)	3023 (0.8)
	2954 (1.4)	2970 (1.8)	2954 (2.1)	2970 (2.1)	2976 (1.2)	2975 (2.0)	2970 (1.8)
	2852 (0.9)	2920 (0.2)	2888 (0.7)	2920 (0.2)	2860 (0.6)	2920 (0.2)	2923 (0.3)
		2866 (0.8)	2853 (1.3)	2865 (0.9)		2873 (0.7)	2854 (0.6)
BH_3, ν		2438 (6.2)		2436 (5.6)		2443 (6.2)	
		2411 (6.0)		2411 (5.4)		2419 (4.7)	
Overtones	2322 (0.7)	2371 (1.3)	2320?	2374 (1.2)		2375 (1.0)	
					2280 (0.1)	2225 (0.2)	
P-H, P-D, ν	2258 (2.4)	(2413?)	1643 (1.9)	1756 (0.8)			
CH_3, δ	1457 (0.5)	1462 (0.8)	1490 (1.8)	1464 (0.6)	1470 (0.5)	1459 (0.7)	1460 (0.5)
	1400 (0.1)	1385 (0.4)	1363 (3.5!)	1385 (0.6)	1385 (0.1)	1385 (0.3)	1300 (0.2)
CF_3, ν	1189 (10)	1215 (14)	1190 (1.8)	1212 (10)	1207 (10)	1227 (11)	1200 sh (8)
	1137 (24)	1172 (39)	1138 (43)	1165 (25)	1144 (33)	1176 (47)	1189 (13)
		1140 (6)		1137 (8)		1153 sh (14)	1142 (30)
						1140 sh (13)	1136 sh (25)
C-O, ν	R 1060 (8.6)	1074 (9)	R 1062 (1.8)	1053 (10)	1057 (20)	1062-1080 (14)	R 1057 (13)
	Q 1055 (9.5)	1050 sh (5)	Q 1055 (2.0)				Q 1052 (19)
	P 1051 (8.3)		P 1050 (1.8)				P 1045 (15)
P-O, ν	965 sh (1.0)	946 (10)	927 (0.3)	947 (1.2)		904 (8)	952 (0.9)
P-H, P-D bend	963 sh (1.1)						
CH_3, ρ etc.	960 sh (1.2)		R 725 (1.2)				
	957 (1.3)		Q 720 (1.7)				
	953 sh (1.1)		P 715 (1.25)				
	928 (1.5)						
	919 (1.5)	917 (8)		917 (1.1)	R 821 (8.2)		
	869 (2.6)	845 (0.2)	865 (0.5)		Q 812 (11)	835 (8)	
			817 (0.4)	821 (3.3)	P 804 (6.6)		
Uncertain		795 (4)	775 sh (2.4)				780 (1.7)
CF_3, δ-e	R 757 (3.5)		762 sh (2.6)				
	Q 752 (3.8)	745 (0.2)	755 (4)	770 (1.3)	765 (2.2)	771 (2.3)	751 (3.0)
	P 745 (3.1)						
BH_3, ρ		708 (1.8)		716 (1.4)		703 (5.1)	
BH_3, ω		682 (1.0)		676 (0.6)		622 (3.2)	
CF_3, δ-a		570 (1.4)	570 (0.2)	555 (0.26)	565 (1.1)	540 (0.5)	553 (2.4)
							539 (1.0)
P-F bend					480 (1.7)	516 (0.7)	P-Cl 512 (4.6)
P-CF_3, ν	441 (1.8)	417 (1.7)	435 (2.0)	417 (0.85)	415 (1.5)	438 (2.2)	463 (3)
Uncertain	380 (0.3)	388 (1.3)			380 (0.3)	388 (1.3)	375 (0.5)

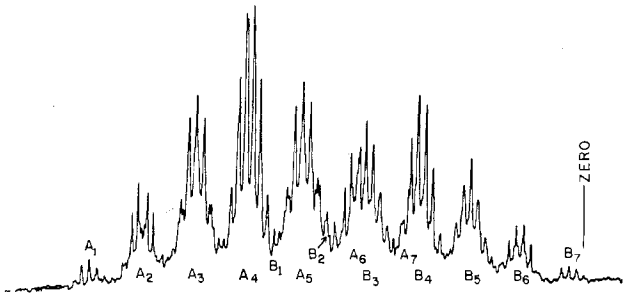

Figure 2. Phosphorus NMR spectra of the A and B isomers of $(CH_3OPCF_3)_2$. The relative frequencies of the peaks, measured in s^{-1} ("Hz") from the indicated arbitrary zero point (with weak or uncertain peaks in parentheses) are as follows. A_1: (434.6), 428.10, 421.64, 415.22, (408.75). A_2: 385.00, 380.03, (376.68), (377.75), (377.03), (375.43), (374.71), (373.78), 372.11, 367.15. A_3: (345.62), (343.61), (341.75), 337.06, 330.61, 324.17, (319.47), (317.61), (315.53). A_4: 300.80, 295.9 sh, 293.96, 288.98, 288.04, 282.54, 281.60, 276.22, 274.3 sh, 269.78. $A_7 = A_1$; $A_6 = A_2$; $A_5 = A_3$. B_4: (153.7), 146.63, 140.59, 134.14, 127.84, (121.5). B_5: 107.44, 101.52, 95.21, 89.37, 82.72. B_6: 62.43, 57.8 sh, 56.38, 54.9 sh, 51.3 sh, 49.81, 48.4 sh, 43.63. B_7: (25.64), 18.90, 12.82, 6.21, (0).

The ^{31}P spectra are remarkably complex with interesting regularities; full analysis seems tantalizingly difficult. At low resolution one sees two partially superposed septets of broad peaks: δ_A −121.3 with J_A = 45.5; δ_B −117.7 with J_B = 42.1. At high resolution the broad peaks become complex patterns, as shown in Figure 2. Even with the protons decoupled (Figure 3), the interpretation seems to be both difficult and uncertain.

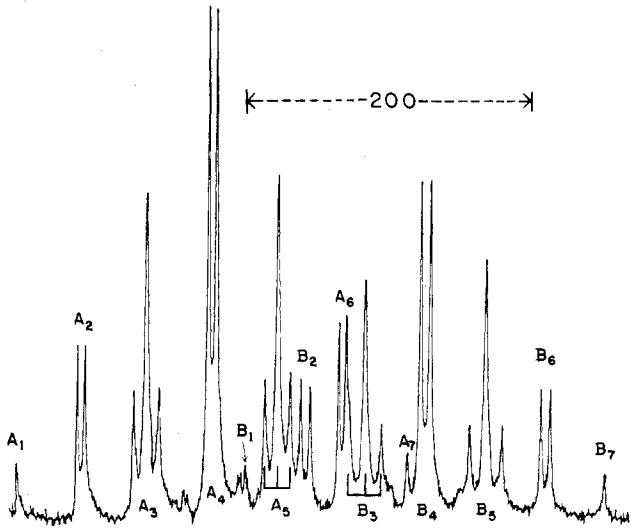

Figure 3. Phosphorus NMR spectra of the A and B isomers of $(CH_3OPCF_3)_2$, with protons decoupled. The A_3, A_5 pseudotriplets have "J" = 8.7; for B_3, B_5, "J" = 11.5. The apparently similar doublets for A_2, A_4, A_6 ("J" = 5.2) or for B_2, B_4, B_6("J" = 6.3) become different second-order patterns when protons are not decoupled; see Figure 2.

The Borane(3) Complexes

Methoxytrifluoromethylphosphine–Borane(3). The compound $CH_3O(CF_3)PH{\cdot}BH_3$ was formed from a 2:1 mixture of the free phosphine and diborane during a 17-h warm-up from −78 to +25 °C. The liquid phase seemed advantageous,

Table III. ^{19}F NMR Parameters for $(CH_3OPCF_3)_2 \cdot BH_3$

	Isomer A			Isomer B		
	Free	BH_3 adduct		Free	BH_3 adduct	
δ	60.71	58.02	66.85	61.43	59.19	66.75
$J_1 + J_2$	90.7	89.4	80.7	84.0	90.3	79.7
J_1(FCP)		76.1	65.4		78.4	65.5
J_2(FCPP)		13.3	15.3		11.9	14.2
J_3(FCPPCF)			1.7			2.75

but conversion beyond 80% was slow; however, the remaining reactants could be removed easily by passage through a U-trap in vacuo at −78 °C, for further action. The purified product was 10% decomposed during 17 h at 25 °C; then the fraction passing a −78 °C trap showed only the infrared spectra of the components B_2H_6 and $CH_3O(CF_3)PH$.

The equilibrium vapor pressures of the repurified complex were measured quickly to avoid incipient dissociation: 1.25 mm at −26.5 °C, 6.5 mm at 0 °C, and 30.4 mm at 26.0 °C, determining the equation $\log P = 7.1210 + 1.75 \log T - 0.0064T - 2410/T$; bp 108.5 °C; Trouton constant 21.04 eu. The high curvature and low volatility, relative to the free phosphine, as compared to the similar relation of $CH_3O(CF_3)PF \cdot BH_3$ to $CH_3O(CF_3)PF$, would suggest somewhat greater polarity, as hinted also by a 5% too high value (153) for the vapor-phase molecular weight not far from the saturation pressure.

However, the bonded BH_3 group seems not to have developed much hydridic character, for the rate of reaction of the complex with HCl to produce hydrogen is close to the rate of dissociation; thus the reaction must be ascribed to the free BH_3 group. The same effect has been noticed for the case of $BH_3 \cdot CO$: the $HCl \rightarrow H_2$ reaction is exactly parallel to the dissociation and is inhibited in the same manner by CO.[1]

Of special interest here is the increase in the stretching frequency of the P–H bond by the formation of the complex. The same principle has been recognized for $(CH_3)_2PH \cdot BH_3$[7] and can be attributed to an increase in the base strength of phosphorus; the effect of BH_3 on P here is like that of CH_3.[8] In the present case the effect was demonstrated most conveniently by means of the deuterated phosphine, because the P–H frequency at 2258 cm^{-1} was increased enough to be covered by the more intense B–H stretching band at 2411 cm^{-1}. The pertinent full spectra, along with those of related compounds, are shown in Table II. The increase of P–D stretching frequency from 1643 to 1756 cm^{-1} (6.9%) is indeed greater than observed for $(CH_3)_2PD \cdot BH_3$ (3.8%).[7] The effect is more difficult to see for the P–D or P–H bending modes, because coupling effects are not the same in the BH_3 complexes. The effect of transition element complexing upon P–H stretching deserves exploration.

The Fluorophosphine–Borane(3). With 0.196 mmol of B_2H_6, 0.328 mmol of $CH_3O(CF_3)PF$ was only 95% combined after 2 h in a microsize NMR tube; the spectra proved the BH_3 complex. The purified product, left for 17 h at 25 °C in a 2-ml tube, was only 0.3% decomposed; repetition with the same result suggested an approach to equilibrium.

The equilibrium vapor pressures, 4.8 mm at −30.7 °C, 34.0 mm at 0 °C, and 93.6 mm at 19.8 °C, determined the equation $\log P = 5.8200 + 1.75 \log T - 0.005T - 1963/T$; bp 72 °C; Trouton constant 21.4 eu.

Exposure of 0.301 mmol of the complex to 0.390 mmol of HCl at −78 to +25 °C (20 ml tube) was ineffective: both components were recovered intact. An exactly similar experiment with BF_3 was equally negative. It is clear that the BH_3 group here lacks hydridic character and that the CH_3O group is not attached by either HCl or BF_3. Since the BH_3 group usually is weaker than BF_3 for attachment to oxygen bases and stronger toward phosphines, it was expected to attach to P in such complexes as these, and indeed the NMR spectra confirm the prediction.

The Dimethoxyphosphine Complex. The reaction of 0.378 mmol of $(CH_3O)_2PCF_3$ with diborane (0.225 mmol) was 80% complete after 11 h at −78 °C but still incomplete after 30 min at 25 °C; there may have been inadequate mixing in the 22-ml reaction tube. After 10 h in a microsize NMR tube, the spectra for the complex were clean, with no trace of the

Table IV. NMR Parameters of BH_3 Complexes

	^{11}B	^{31}P	^{19}F	^1H
$(CH_3O)_2PCF_3 \cdot BH_3$	δ 64.2 $J_{BH} = 101$ $J_{BP} = 60$	δ −125.5 $J_{PB} = 60$ $J_{PCF} = 90$	δ 75.0 $J_{FCP} = 91$	CH_3 τ 6.18 $J_{HCOP} = 11.2$ HB τ 9.78 $J_{HB} = 100$ $J_{HBP} = 17$
$CH_3O(CF_3)PH \cdot BH_3$	δ 62.1 $J_{BH} = 103$ $J_{BP} = 37$	δ −98.9 $J_{PH} = 428$ ($J_{PB} = 36$) blurred	δ 68.3 $J_{FCP} = 72.7$ $J_{FCPH} = 6.2$	HP τ 3.50 $J_{HP} = 425$ CH_3 τ 6.45 $J_{HCOP} = 11.9$ $J_{HCOPH} = 0.6$ HB τ 9.64 $J_{HB} = 102$
$CH_3O(CF_3)PF \cdot BH_3$	δ 64.7 $J_{BH} = 103.5$ $J_{BP} = 44.3$	δ −140 $J_{PF} = 1165$ ($J_{PB} = 43$)[a] ($J_{PCF} = 100$)[a]	CF_3 δ 76.7 $J_{FCP} = 102.3$ $J_{FCPF} = ?$ $J_{F\cdots H} = ?$ FP δ 101.3 $J_{FP} = 1165$ $J_{FPCF} = 22$	CH_3 τ 6.15 $J_{HCOP} = 11.2$ HB τ 9.52 $J_{HB} = 103.4$
$(CH_3OPCF_3)_2 \cdot BH_3$	δ 61.2 J_{BH} 104	δ −126 blurred	(Table III)	CH_3 τ 6.22 complex HB τ 9.20 ($J_{HB} = 105$)
$(CH_3OPCF_3)_2 \cdot 2BH_3$	δ 61.6 $J_{BH} = 104$	(Complex)	A δ 64.40 $J_1 + J_2 = 83.4$ B δ 64.87 $J_1 + J_2 = 85.7$	A τ 6.22 (complex) B τ 6.29 (complex) HB τ 8.41 $J_{HB} = 104$

[a] Rough interpretation.

^{19}F spectrum of $(CH_3O)_2PCF_3$. The volatility of the complex was high enough to indicate no very high polarity: 1.6 mm at 0 °C and 7.5 mm at 26 °C (cf. free ligand, 16 mm at 0 °C[4]). For a normal Trouton constant (21.3 eu), these data would develop the equaton $\log P = 6.3305 + 1.75 \log T - 0.005T - 2465/T$; bp 140 °C.

The Diphosphine–Borane(3) Adducts. The ^{19}F spectra of $(CH_3OPCF_3)_2$ and its mono- and diadducts of BH_3 proved to be well enough resolved for clear demonstration that both complexes exist only in equilibrium mixtures:

$$2(CH_3OPCF_3)_2 + B_2H_6 \rightleftarrows 2(CH_3OPCF_3)_2{\cdot}BH_3 \quad (7)$$

$$2(CH_3OPCF_3)_2{\cdot}BH_3 + B_2H_6 \rightleftarrows 2(CH_3OPCF_3)_2{\cdot}2BH_3 \quad (8)$$

Reaction 7 was performed with 0.335 mmol of diphosphine and 0.143 mmol of diborane (85% of the calculated proportion) in a microsize NMR tube. The ^{19}F spectrum then showed 25% presence of the free diphosphine. This result indicated a formation–dissociation equilibrium which was confirmed by means of a stoichiometrically exact sample (derived from the dissociation of the $2BH_3$ adduct); this showed 15% presence of the free diphosphine.

The equilibrium of reaction 8 was established by equimolar diphosphine and diborane, showing 30% presence of $(CH_3OPCF_3)_2{\cdot}BH_3$ but no observable free diphosphine. The mixture included a viscous component, probably related to a small side reaction producing nonvolatile material.

When a diphosphine forms a polar-type BH_3 complex, it is the usual expectation that attachment of BH_3 to the second P atom is either inhibited or prevented altogether. For example, $(CH_3PCF_3)_2{\cdot}BH_3$ is slightly dissociable and forms no two-BH_3 complex.[6] If the present case were like that, we should expect no addition of the second BH_3 group. However, with the dative-bond polarity neutralized by B–H to P π bonding, the successive BH_3 attachments seem to occur with nearly equal bond energy.

For $(CH_3OPCF_3)_2{\cdot}BH_3$, the ^{19}F NMR spectra of the two very different CF_3 groups were of the simple type, with a large difference of chemical shift, as shown in Table III. There are two main reasons for assigning the low-field patterns to the CF_3 group belonging to the BH_3-attached P atom in each isomer: (1) the change of chemical shift from the free diphosphine is small, just as for the monophosphines and their BH_3 adducts; (2) the peaks are somewhat blurred, so that the quartets for FCPPCF coupling could not be seen—an effect ascribed to the proximity of boron. It is also not surprising that these downfield doublets of doublets for the two isomers are entirely separated, indicating that the effect of BH_3 upon each isomer is greater for the nearer CF_3 group. In contrast, the upfield patterns for the two isomers are closely interlaced, but the peaks are sharp enough for resolution of the FCPPCF quartets. The reason for the large change of chemical shift of these upfield patterns, relative to the free diphosphine, may be fairly subtle. It could be suggested that a B–H to P π bond would suppress P–P π bonding from the noncomplexed P atom, so that its lone-pair electrons would bear inductively upon the CF_3 group.

The identity of $(CH_3OPCF_3)_2{\cdot}2BH_3$ was apparent from its second-order ^1H and ^{19}F spectra, somewhat like those for the free diphosphine but with different parameters; cf. Table IV. The ^{11}B spectrum was like that for $(CH_3OCF_3P)_2{\cdot}BH_3$ but appreciably more blurred; neither showed the resolution of B–P coupling which was so apparent for the monophosphine–borane(3) complexes. The complex ^{31}P spectrum of the BH_3 diadduct seemed to be superposed upon that of the BH_3 monoadduct, so that the chemical shift was uncertain and the coupling constants were not available.

Decomposition was about two-thirds complete after a 75-day storage of $(CH_3OPCF_3)_2{\cdot}BH_3$ in the microsize NMR tube at 25 °C. The new ^{19}F spectrum now showed roughly one-third of the CF_3 groups in the form of $(CH_3O)_2PCF_3{\cdot}BH_3$, one-third in a broad, complex, and unintelligible spectrum in the region δ 63 ppm, and one-third as the mixture of $(CH_3OPCF_3)_2$ (36%) and its one-BH_3 complex (64%). Apparently there was a cleavage like that caused by HCl or BF_3, to form mainly $(CH_3O)_2PCF_3$ as the BH_3 complex, along with the successors of the CF_3P unit; but this process was far slower than with HCl or BF_3 because an attack by BH_3 at oxygen would be energetically unfavorable. The expected CF_3P unit did not appear as $(CF_3P)_4$ and $(CF_3P)_5$—possibly on account of some yet unknown combination with the BH_3 group.

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Registry No. $CH_3O(CF_3)PF$, 61104-38-9; $CH_3O(CF_3)PCl$, 61104-39-0; $CH_3O(CF_3)PI$, 61104-40-3; $CH_3O(CF_3)PH$, 6395-71-7; $CH_3O(CF_3)PH{\cdot}BH_3$, 61118-12-5; $CH_3O(CF_3)PD$, 61104-41-4; $CH_3O(CF_3)PD{\cdot}BH_3$, 61118-07-8; $CH_3O(CF_3)PF{\cdot}BH_3$, 61118-11-4; $(CH_3OPCF_3)_2{\cdot}BH_3$, 61118-10-3; $(CH_3O)_2PCF_3{\cdot}BH_3$, 61118-09-0; $(CH_3OPCF_3)_2{\cdot}2BH_3$, 61118-08-9; $(CH_3OPCF_3)_2$, 61104-42-5; CH_3OH, 67-56-1; $(CH_3O)_2PCF_3$, 684-56-0; BF_3, 7637-07-2; CF_3PCl_2, 421-58-9; ^{31}P, 7723-14-0.

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