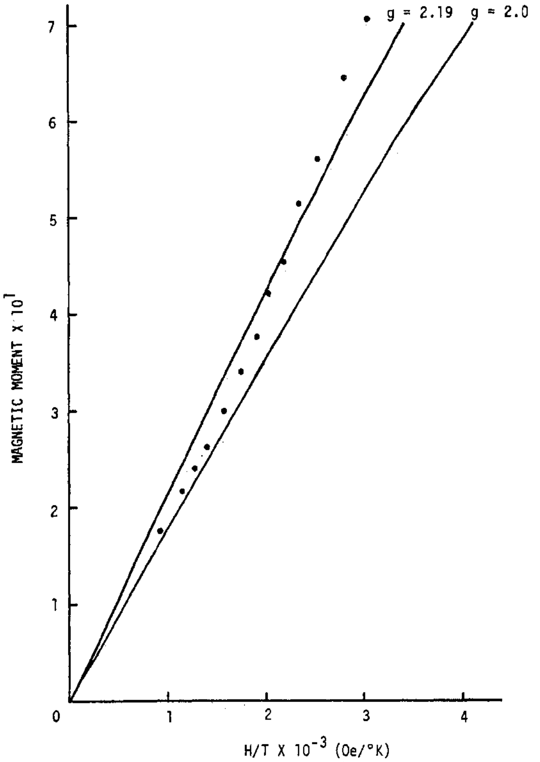

Figure 3. The variation of the experimental magnetic moment $\langle\mu\rangle$ (●) *vs.* H/T for an effective spin equal to 1 (solid lines) system.

A magnetization study was also undertaken in an attempt to understand more clearly the cooperative magnetic phenomenon. The results of the magnetization experiment are shown in Figure 3. Susceptibility measurements were made at multiple temperatures at three different magnetic field strengths. In this antiferromagnetic system it is certain that the excited paramagnetic states are only partially occupied. The susceptibility measured, however, arises from the molecules which populate these states. Thus, using the value of $2J$ found in the dimer fit and Boltzmann's expression for population distributions we are able to normalize approximately the experimental susceptibilities to values that would be expected if all the molecules were in a triplet state. These values can then be compared to the result calculated for a $S = 1$ system by making use of the Brillouin functions.[13] The Brillouin function can be written as

$$B_S(x) = \frac{2S' + 1}{2S'} \coth\left(\frac{2S' + 1}{2S'}x\right) - \frac{1}{2S'} \coth\frac{x}{2S'}$$

where $x = 2S'\beta H/kT$ and S' is the effective spin for the system. The relationship

$$\langle\mu\rangle = \frac{\chi H}{N\beta} = gS'B_S(x)$$

then allows us to calculate the expected magnetic moment for a triplet state. The plot of magnetic moment *vs.* H/T is presented in Figure 3. The solid lines are the moments that would be expected for a system with $S = 1$ having the g values indicated on the plots. It is seen in this plot that the compound is apparently more easily magnetized than would be expected for triplet states alone. Consequently, it appears that the antiferromagnetic interaction may contain contributions from both inter- and intrachain effects, although there is no compelling reason to include interchain effects other than the observation that the Ising model does not provide a satisfying account of the experimental data. The alternate Heisenberg model for intrachain interactions or one of intermediate anisotropy may be more appropriate since the magnetic susceptibilities predicted by such models exhibit more rounded cusps when plotted as a function of temperature.

There are similarities in the behavior observed here and that described by Flippen and Friedberg[14] for $Cu(HCO_2)_2 \cdot 4H_2O$. They pointed out that the anisotropic exchange term $D \cdot S_1 \times S_2$ described by Moriya[15] can lead to weak ferromagnetism. A weak ferromagnet is an antiferromagnet whose sublattice magnetizations are slightly canted.[16] Pairs of copper ions in the chains in $Cu(NH_3)_2CO_3$ are not related by a center of symmetry as required for the Moriya anisotropic exchange, while the pairs of copper ions at 3.5 Å are related by a center of symmetry. Thus, the data are consistent with a model which involves a superexchange interaction along the chains which leads to a short-range antiferromagnetism and weak ferromagnetism. The superexchange mechanism in this model may be more important than the through-space mechanism which has been termed incipient bond formation. The d orbitals of the copper ions are expected to overlap only slightly at 3.5 Å, while the magnetic wave functions may be coupled through the bridging carbonate group by covalent bond formation.

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The Preparation and Characterization of Methylchlorofluorophosphine, CH_3PFCl, and Methylbromofluorophosphine, CH_3PFBr

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The P–N bond in aminodifluorophosphines is subject to facile cleavage by hydrogen halides to give cleanly the appropriate halodifluorophosphine and the amine hydrohalide salt (eq 1).[1] Although the analogous re-

$$R_2NPF_2 + 2HX \longrightarrow PF_2X + [R_2NH_2]X \quad (X = Cl, Br, I) \qquad (1)$$

action between dimethylaminomethylfluorophosphine, $[(CH_3)_2N]PFCH_3$, and hydrogen chloride was reported to give methylchlorofluorophosphine, CH_3PFCl, the product was briefiy characterized.[2] We report here a more complete characterization of CH_3PFCl and the previously unreported CH_3PFBr and attempts to make CH_3PFI.

Discussion

The unsymmetrical phosphines CH_3PFCl and CH_3PFBr were obtained in 65–70% yield according to eq 2.

$$CH_3PF[N(CH_3)_2] + 2HX \longrightarrow CH_3PFX + [(CH_3)_2NH_2]X \quad (X = Cl, Br) \qquad (2)$$

The formulations CH_3PFCl and CH_3PFBr are shown unequivocally by vapor density, mass spectrometry, and the ^1H, ^{19}F, and ^{31}P nmr spectra. The mass spectrum of CH_3PFCl (see Experimental Section) shows two parent ions at *m/e* 100 and 102 ($CH_3P^{35}ClF^+$, $CH_3P^{37}ClF^+$) in the expected 3:1 ratio. Similarly, two peaks of almost identical intensity at *m/e* 144 and 146 ($CH_3P^{79}BrF^+$, $CH_3P^{81}BrF^+$) correspond to the expected isotopic distribution for the CH_3PFBr parent (see Experimental Section). The observed parent ions also correspond well with the vapor density molecular weights of 101 and 145 observed for CH_3PFCl and CH_3PFBr, respectively.

The nmr spectra all showed the expected first-order multiplet patterns; the data are summarized in Table I where they can be compared with those for CH_3PF_2, CH_3PCl_2, and CH_3PBr_2.

Table I

Nmr Spectra of Methylhalophosphines

Compound	Group structure	δ,[a] ppm	*J*, Hz PF	PH	HF	Ref
		^1H Spectra				
CH_3PClF	Doublet of doublets	−1.82	...	14	18	*b*
CH_3PBrF	Doublet of doublets	−2.14	...	15	18	*b*
CH_3PF_2	Doublet of 1:2:1 triplets	−1.41	...	10.0	20.0	*c*
CH_3PCl_2	Doublet	−2.18	...	17.6	...	*d*
CH_3PBr_2	Doublet	−2.66	...	19.9	...	*e*
		^{19}F Spectra				
CH_3PClF	Doublet of 1:3:3:1 quartets	+125	1118	...	18	*b*
CH_3PBrF	Quartets	+133	1098	...	18	*b*
CH_3PF_2	Quartets	+92.9	1157	...	20.0	*c*
		^{31}P Spectra				
CH_3PClF	Doublet of 1:3:3:1 quartets	−237	1110	13	...	*b*
CH_3PBrF	Quartets	−247	1093	14	...	*b*
CH_3PF_2	Triplet of 1:3:3:1 quartets	−251	1157	10.4	...	*c*
CH_3PCl_2	1:3:3:1 quartet	−192	...	16	...	*d*
CH_3PBr_2	Quartet	−184	...	19.6	...	*e*

[a] ^1H reference, TMS internal; ^{19}F reference, $CFCl_3$ external; ^{31}P reference, 85% H_3PO_4 external. [b] This work. [c] Reference 3. [d] L. Maier, *Helv. Chim. Acta*, **46,** 2026 (1963). [e] R. Foester and K. Cohn, *Inorg. Chem.*, **9,** 1571 (1970).

For both CH_3PFCl and CH_3PFBr the infrared spectra are similar to that reported for CH_3PF_2[3] except for the P–Cl and P–Br stretching frequencies at 512 and 413 cm^{-1}, respectively. Other tentative assignments are listed with the observed frequencies and those for similar molecules in Table II.

Table II

A Comparison of the Infrared Spectra of CH_3PClF, CH_3PBrF, CH_3PF_2, CH_3PCl_2, and CH_3PBr_2[a]

CH_3PClF	CH_3PBrF	Assignment	CH_3-PF_2[b]	CH_3-PCl_2[c]	CH_3-PBr_2[d]
2979 w	2980 w		2987	3008	2962
2899 w	2910 w	CH str	2910	2991	2880
2800 vw	2811 vw		...	2922	...
	2399 vw	?			
1411 m	1409 m	CH_3 def	1410	1416	1400
1283 m	1284 m		1287	1288	1278
987 w, br				987	
890 sh	888 s				
884 s	866 s	CH_3 rock and	885	885	875
869 s	860 s	CH_3PF_2	867	867	860
861 s					
845 sh			864		
797 vs	796 vs	PF str	806		
701 sh	700 sh	PC str	700	699	682
696 s	692 s				
512 vs		PCl str		495	
	413 vs	PBr str			*e*
		PF_2 scissors	483		
			402		

[a] Absorption position given in reciprocal centimeters. Intensity: w, weak; m, medium; s, strong; v, very; sh, shoulder; br, broad. [b] Reference 3. [c] J. Dirig, F. Block, and I. W. Levin, *Spectrochim. Acta*, **21,** 1105 (1965). [d] L. Maier, *Helv. Chim. Acta*, **46,** 2026 (1963). [e] Not reported.

We have found that with an initial pressure of 630 mm, CH_3PFCl disproportionates completely within 12 hr. Disproportionation is much more rapid for CH_3PFBr, especially in the liquid, and occurs rapidly enough above −31° to prevent the measurement of accurate vapor pressure values. In both cases the initial disproportionation is to the less volatile dihalophosphine and the more volatile difluorophosphine (eq 3). Sub-

$$2CH_3PFX \longrightarrow CH_3PF_2 + CH_3PX_2 \quad (X = Cl, Br) \qquad (3)$$

sequently CH_3PF_2 undergoes oxidation–reduction as previously described (eq 4).[3,4] Although such a mode

$$10CH_3PF_2 \longrightarrow 5CH_3PF_4 + (CH_3P)_5 \qquad (4)$$

of decomposition has been noted for CH_3PFCl,[2] no mention was made of the effect of hydrogen halides on the reaction products. We have found that if the hydrogen halide is taken in even slight stoichiometric excess (eq 2), disproportionation of CH_3PFX is accelerated. In the latter case small amounts of CH_3PF_3H,[5,6] methylhydridotrifluorophosphorane, can also be recovered from the reaction mixture. Since CH_3PF_2 is a known constituent in these mixtures (*vide supra*), CH_3PF_3H probably results from the combination of CH_3PF_2 and HF. Indeed, the latter reaction is in agreement with previous studies.[6] The requisite HF is probably formed *via* an exchange reaction between the excess hydrogen halide and one of the fluorophosphines.

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Experimental Section

General Data.—Standard high-vacuum techniques[7] were used for the manipulation of all compounds. Starting materials and previously known reaction products were identified and checked for purity by vapor pressure, ir, and nmr. Hydrogen chloride and hydrogen iodide were obtained from the Matheson Co., but hydrogen bromide was prepared by the hydrolysis of PBr_3. Dimethylaminomethylfluorophosphine was prepared as described by Schmutzler.[8]

The ^1H, ^{19}F, and ^{31}P nmr spectra were determined with a Varian HR-100 operating at 100, 94.1, and 40.4 MHz, respectively. Mass spectra were determined at 70 eV with a Consolidated Electrodynamics Model 21-103B instrument. The infrared spectra were obtained on a Beckman IR-10 with an 87-mm gas cell equipped with KBr windows.

Preparation of CH_3PFX (X = Cl, Br).—The reaction was carried out in the gas phase in an apparatus consisting of two bulbs (2-l. capacity and 300-ml. capacity, respectively) separated by a stopcock. A similar apparatus has been previously described.[9] In a typical experiment for the preparation of CH_3PFCl, 4.32 mmol of HCl was condensed into the smaller bulb and the stopcock between the two bulbs closed. A 2.40-mmol sample of $CH_3PFN(CH_3)_2$ was condensed into the larger bulb. Both reactants were allowed to warm to 25°, and the stopcock between the two bulbs was opened, allowing the higher pressure HCl to expand into the larger bulb. An immediate reaction was observed by the formation of white clouds. The bulb was allowed to stand at 25° for 3 min and then the volatile products were condensed at −196°. Purification was effected by fractional condensation with traps held at −78, −111, and −196°. The −78° fraction contained 0.31 mmol of CH_3PCl_2 and a trace of $CH_3PFN(CH_3)_2$. The −196° trap contained 0.35 mmol of CH_3PF_2. The desired CH_3PFCl (1.42 mmol) was retained at −111°.

In a typical reaction for the preparation of CH_3PFBr a 5.75:2.99 mmol ratio of $HBr{:}CH_3PF[N(CH_3)_2]$ was treated in the manner described above. The volatile products were separated by traps held at −63, −111, and −196°. The −63° fraction contained 0.51 mmol of CH_3PBr_2 and a small amount of CH_3PFBr. The −196° fraction contained 0.24 mmol of CH_3PF_2 and CH_3PF_3H. The −111° fraction contained 2.03 mmol of the desired CH_3PFBr.

Attempts to prepare CH_3PFI in the manner described for CH_3PFCl and CH_3PFBr yielded only CH_3PF_2, CH_3PF_4, some unreacted $CH_3PF[N(CH_3)_2]$, and intractable yellow-brown solids.

In all cases it is desirable to use a slight excess of $CH_3PF[N(CH_3)_2]$. An excess of HX promotes the disproportionation of CH_3PFX and typically results in the formation of larger amounts of CH_3PX_2 and CH_3PF_2 plus the formation of CH_3PF_3H.[5]

The vapor pressures (mm) observed for CH_3PFCl [−63.5° (7.2), −45.9° (25.6), −31.1° (61.8), −15.6° (145.5), 0.0° (290.6)] are described by the equation $\log p(\text{mm}) = -1451/T + 7.786$ which gives an extrapolated boiling point 22.6° and a Trouton constant of 22.45 cal/deg mol. The compound compound melts in the range −121.6 to −120.9°.

Vapor pressure data (mm) for CH_3PFBr below −31° are as follows: −45.5° (6.0), −35.8° (14.5), −31.2° (23.6). At higher temperatures disproportionation was too rapid to obobserve reliable pressures.

The mass spectrum of CH_3PFCl displayed the following fragmentation pattern (*m/e*, relative peak height, and assignment, respectively): 103, 0.6, $P^{35}Cl^{37}Cl^+$; 102, 16.0, $CH_3P^{37}ClF^+$; 101, 1.1, $CH_2P^{37}ClF^+$, $P^{35}Cl_2^+$; 100, 49.0, $CH_3P^{35}ClF^+$; 99, 0.8, $CH_2P^{35}ClF^+$; 87, 33.0, $P^{37}ClF^+$; 85, 100.0, $P^{35}ClF^+$; 81, 1.6, $CH_3P^{35}Cl^+$, $CHP^{37}Cl^+$; 80, 0.6, $CH_2P^{35}Cl^+$, $CP^{37}Cl^+$; 79, 3.2, $CHP^{35}Cl^+$; 78, 0.7, $CP^{35}Cl^+$; 69, 1.1, PF_2^+; 68, 0.8, $P^{37}Cl^+$; 66, 3.1, $P^{35}Cl^+$, $C^{35}ClF^+$; 65, 42.0, CH_3PF^+; 64, 9.2, CH_2PF^+; 63, 4.2, CHP^+; 62, 2.8, CPF^+; 51, 0.8, HPF^+; 50, 10.0, PF^+; 46, 1.1, CH_3P^+; 45, 29.0, CH_2P^+; 44, 13.0, CHP^+; 43, 3.3, CP^+; 37, 0.8, $^{37}Cl^+$; 36, 0.9, $H^{35}Cl^+$; 35, 2.7, $^{35}Cl^+$; 32, 0.8, PH^+; 31, 6.0, P^+.

The mass spectrum of CH_3PFBr gave the following pattern (*m/e*, relative peak height, and assignment, respectively): 146, 76.8, $CH_3P^{81}BrF^+$; 144, 77.6, $CH_3P^{79}BrF^+$; 131, 45.2, $P^{81}BrF^+$; 129, 45.6, $P^{79}BrF^+$; 125, 3.6, $CH_3P^{79}Br^+$, $CHP^{81}Br^+$; 123, 2.9, $CHP^{79}Br^+$; 112, 2.7, $P^{81}Br^+$; 110, 2.8, $P^{79}Br^+$; 107, 2.1, PF_4^+; 103, 2.6, $CH_3PF_3^+$; 102, 2.7, $CH_2PF_3^+$; 100, 8.2, CPF_3^+; 89, 5.5, PF_3H^+; 87, 5.0, ?; 85, 16.6, $CH_3PF_2H^+$; 84, 4.4, $CH_3PF_2^+$; 82, 2.0, $H^{81}Br^+$; 81, 6.8, $^{81}Br^+$; 80, 2.0, $H^{79}Br^+$; 79, 6.8, $^{79}Br^+$; 69, 12.4, PF_2^+; 66, 1.8, CH_3PFH^+; 65, 100.0, CH_3PF^+; 64, 16.9, CH_2PF^+; 63, 7.8, $CHPF^+$; 62, 4.4, CPF^+; 51, 1.7, PFH^+; 50, 22.1, PF^+; 46, 3.4, CH_3P^+; 45, 64.8, CH_2P^+; 44, 27.0, CHP^+; 43, 6.4, CP^+; 32, 5.0, PH^+; 31, 12.2, P^+.

Vapor densities in agreement with the mass spectral results were obtained by minimizing the time which CH_3PBr and CH_3PFCl remained liquid as they were vaporized to make the pressure–volume measurements

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Evidence for an Axial Methyl Group in the Photolysis Product of $(-)_{5461}$-Rhodium(III) D-(−)-1,2-Propylenediaminetetraacetate[1]

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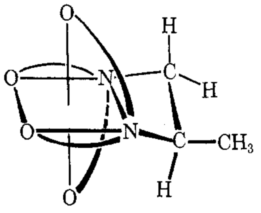
Dwyer and Garvan, soon after demonstrating the stereoselectivity of the 1,2-propylenediaminetetraacetate (PDTA) ligand, observed that $(-)_{5461}$-Rh^{III}-D-(−)-PDTA, **1**, suffered a loss of optical activity when exposed to ultraviolet radiation. The fully mutarotated sample was observed to regain its initial rotational strength completely upon storage in the dark for about 3 days.[2] This phenomenon, which is capable of many repetitions, was attributed to a photoaquation reaction in which a water molecule is substituted for a carboxylate ligand.



1

We have investigated the systems involving optically active $Rh^{III}PDTA$ and $Rh^{III}EDTA$ complexes by proton magnetic resonance (pmr) and circular dichroism (CD) in neutral solution (pH ∼6.5, the ligands being hexadentate[3]) and have reached a different conclusion as to the nature of the photolysis product.[4]

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[4] We have reproduced Dwyer and Garvan's results in all respects under these conditions. For $(-)_{5461}$-Rh^{III}-D-(−)-PDTA $[\alpha]_{5461}$ is −159.7°; after photolysis $[\alpha]_{5461}$ is −49.5°.