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The Phosphorus–Phosphorus Bond. II. The Preparation and Characterization of Phosphinodifluorophosphine, H_2PPF_2, Bis(trifluoromethyl)phosphinodifluorophosphine, $(CF_3)_2PPF_2$, and Their Borane Adducts, $H_2PPF_2 \cdot BH_3$ and $(CF_3)_2PPF_2 \cdot BH_3$

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Conditions have been found for a high-yield preparation of phosphinodifluorophosphine, H_2PPF_2, from an excess of PH_3 with F_2PPF_2 in the presence of small amounts of F_2PI. Bis(trifluoromethyl)phosphinodifluorophosphine, $(CF_3)_2PPF_2$, has been prepared with a Wurtz-like coupling of F_2PI and $(CF_3)_2PI$ or by a redistribution reaction involving F_2PPF_2 and $(CF_3)_2PP(CF_3)_2$. Coordination of BH_3 to the PF_2 site in both diphosphines is preferred; neither H_2PPF_2 nor $(CF_3)_2PPF_2$ was found to coordinate two BH_3 groups. The new unsymmetrical diphosphines and their borane adducts have been characterized by nmr (^1H, ^{19}F, ^{31}P, and ^{11}B), ir, Raman, mass spectroscopy, and vapor density. The facile vapor-phase dissociation of the borane adducts precluded determination of their vapor pressure curves but such data are given for the parent diphosphines.

Introduction

Certain symmetrical[1] diphosphines have been reported to form only monoadducts when treated with Lewis acids even though two donor sites are available, *e.g.*, $(C_6H_5)_2PP(C_6H_5)_2 \cdot BF_3$,[2] $(C_6H_5)_2PP(C_6H_5)_2 \cdot Al(C_2H_5)_3$,[3] and $(CH_3)_2PP(CH_3)_2 \cdot B(CH_3)_3$.[4] Obviously such reluctance to form diadducts does not imply that the phosphorus atoms in the parent diphosphine differ in basicity, but the phenomenon can be related to a change in the basicity of one P site after coordination of an acid to the other P site. The basicity change might be related to steric and/or electronic effects. Unsymmetrical diphosphines,[1] on the other hand, have competitive donor sites and can in principle form monoadducts solely on the basis of a difference in the basicity of the P atoms which comprise the homonuclear bond. The Lewis acid BH_3 has previously been found to form a monoadduct with the unsymmetrical diphosphine $(CH_3)_2PP(CF_3)_2$;[5] however, $(C_6H_5)_2PP[N(CH_3)_2]_2$ forms a diadduct.[6] We report here effective synthetic procedures for H_2PPF_2 and $(CF_3)_2PPF_2$ and their interaction with B_2H_6. The structure of H_2PPF_2 and its chemical implications are reported in the succeeding paper.[7]

Results and Discussion

H_2PPF_2.—With careful attention to optimum reaction conditions we have been able to improve the yield of H_2PPF_2 to 72% from the 36% originally reported.[8] Phosphinodifluorophosphine is formed slowly according to

$$PH_3 + F_2PPF_2 \longrightarrow F_2PPH_2 + PF_2H \qquad (1)$$

However, the rate of production of H_2PPF_2 is accelerated when PF_2I is added to the system. It appears that the overall scheme can be represented by

$$PF_2I + PH_3 \rightleftarrows H_2PPF_2 + HI \qquad (2)$$

$$HI + F_2PPF_2 \longrightarrow PF_2H + PF_2I \qquad (3)$$

A large excess of PH_3 and a low $PF_2I:F_2PPF_2$ ratio resulted in a good yield of H_2PPF_2, the optimum being with $PF_2I:F_2PPF_2 \approx 1:6$. In accord with eq 2 and 3, when the $PF_2I:F_2PPF_2$ ratio exceeds 1, F_2PPF_2 is no longer available to "scavenge" the HI. In the absence of other scavengers HI reacts with PF_2H ultimately to yield PF_3H_2.[9] Thus, when $PF_2I:F_2PPF_2$ ratios near 1 were used to prepare F_2PPH_2 or when the F_2PPF_2 was nearly consumed, PF_3H_2, SiF_4, PF_3, and yellow solids were formed in substantial amounts. The PF_3H_2 could not be effiiciently separated from the desired F_2PPH_2. Even when the reaction was "clean," large amounts of H_2PPF_2 could not be obtained free from F_2PI. However, small samples pure enough for characterization were obtained by repeated fractional condensation. Once purified, a gaseous sample of H_2PPF_2 is 26% decomposed over 12 hr at 25° into PF_3, PF_2H, and yellow-orange solids.

The previous physical characterization of H_2PPF_2[8] has been extended to include the mass spectrum of a purified sample (Figure 1) and temperature-dependent nmr studies. The fragmentation pattern is as expected for the compound and is consistent with patterns observed for PF_2H,[10] P_2H_4,[11] and F_2PPF_2.[12] The ^{31}P nmr spectra were found to be essentially independent of temperature from -20 to $-80°$ ($^1J_{PP} = 208 \pm 4$Hz).[13] Other nmr data for H_2PPF_2 are given in Table I.

$(CF_3)_2PPF_2$.—Bis(trifluoromethyl)phosphinodifluorophosphine is reasonably stable and has been handled in the liquid phase in glass tubes at 25° for periods in

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[1] Symmetrical diphosphines have four identical substituents, X_2PPX_2, while the two substituents on each phosphorus atom are different for unsymmetrical diphosphines, X_2PPY_2.

[2] W. Kuchen and H. Buchwald, *Chem. Ber.*, **91**, 2871 (1958).

[3] K. Issleib and F. Krech, *Z. Anorg. Allg. Chem.*, **328**, 21 (1964).

[4] A. B. Burg, *J. Amer. Chem. Soc.*, **83**, 2226 (1961).

[5] L. R. Grant and A. B. Burg, *ibid.*, **84**, 1834 (1962).

[6] H. J. Vetter and H. Nöth, *Chem. Ber.*, **96**, 1816 (1963).

[7] Part III: R. L. Kuczkowski, H. W. Schiller, and R. W. Rudolph *Inorg. Chem.*, **10**, 2505 (1971).

[8] R. W. Rudolph and H. W. Schiller, *J. Amer. Chem. Soc.*, **90**, 3581 (1968).

[9] The reaction of PF_2H and HI was orginally reported to give a poorly characterized species which was thought to be $PF_2H \cdot HI$ and which decomposed to PF_3, SiF_4, and yellow solids.[10] Subsequent unpublished observations have shown that $PF_2H \cdot HI$ is in fact PF_3H_2.

[10] R. W. Rudolph and R. W. Parry, *Inorg. Chem.*, **4**, 1339 (1965).

[11] Y. Wada and R. W. Kiser, *ibid.*, **3**, 174 (1964).

[12] R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Amer. Chem. Soc.*, **88**, 3729 (1966); M. S. Wei, J. H. Current, and J. Gendell, *J. Chem. Phys.*, **52**, 1592 (1970).

[13] The magnitude and sign of $^1J_{PP}$ for the diphosphines described here have been discussed in a previous publication, part I: C. W. Schultz and R. W. Rudolph, *J. Amer. Chem. Soc.*, **93**, 1898 (1971).

TABLE I

NMR DATA[a] FOR H_2PPF_2 AND $(CF_3)_2PPF_2$. A COMPARISON WITH VALUES FOR P_2F_4, $(CF_3)_2PF$, AND P_2H_4

	$(CF_3)_2PPF_2$		P_2F_4[b]	$(CF_3)_2PF$[c]	P_2H_4[d]	H_2PPF_2		
	^{19}F	^{31}P				^{1}H	^{19}F	^{31}P
J_{PF}	1249	1245	1194.1	1013	...	...	1190	1170
J_{PPF}	87.4	93.9	65.8	...	...	...	83	85
J_{FCPPF}	3.7	...	...	...	...	...	...	...
J_{FCP}	60	63.5	...	89.6	...	...	...	...
J_{FCPP}	14	13.7	...	...	...	...	...	...
J_{PP}	...	234	228.6	...	108.2	...	...	207
J_{FCPF}	...	...	...	3.46	...	...	...	...
J_{PH}	...	...	...	...	186.5	189	...	190
J_{PPH}	...	...	...	...	11.9	17	...	17
J_{HPPF}	...	...	...	...	...	22	22	...

		$(CH_3)_2PPF_2$	H_2PPF_2
δ	^{1}H	...	-2.71[e]
	^{19}F	$+45.9$ (CF_3),[f] $+94.6$ (PF_2)[f]	$+89.8$[g]
	^{31}P	0.0 (CF_3),[h] -236 (PF_2)[h]	-49.8 (PF_2),[i] $+380$ (PH_2)[i]

[a] Coupling Constants are given in Hz and chemical shifts in ppm. [b] R. W. Rudolph and R. A. Newmark, *J. Amer. Chem. Soc.*, **92,** 1195 (1970). [c] K. J. Packer, *J. Chem. Soc.*, 960 (1963). [d] R. Lynden-Bell, *Mol. Phys.*, **6,** 601 (1963). [e] TMS internal (−35°). [f] $CFCl_3$ external (−40°). [g] $CFCl_3$ internal (−20°). [h] H_3PO_4(85%) external (−40°). [i] PF_2I internal (−40°).

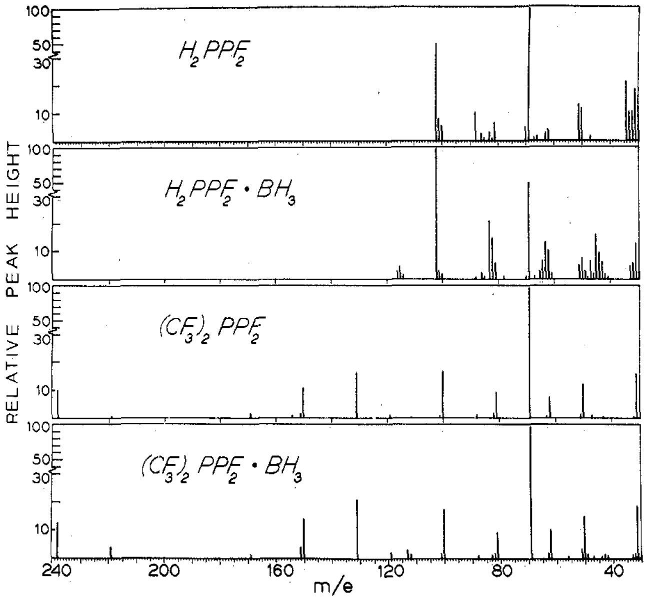

Figure 1.—Mass spectra of the unsymmetrical diphosphines and their BH_3 adducts.

excess of 3 hr without apparent decomposition. The compound was obtained in 62% yield according to

$$(CF_3)_2PI + F_2PI + Hg \longrightarrow (CF_3)_2PPF_2 + Hg_2I_2 \qquad (4)$$

The synthetic method is the same as that used previously for the preparation of $(CF_3)_2PP(CF_3)_2$[14] and F_2PPF_2.[12] Since there is evidence for $\cdot PF_2$ in equilibrium with F_2PPF_2,[12] we were led to ask whether a mixture of F_2PPF_2 and $(CF_3)_2PP(CF_3)_2$ would redistribute to give $(CF_3)_2PPF_2$ (eq 5). Redistribution is favored by entropy and by an increased P–P bond strength due to the polarity of the P–P bond in unsymmetrical diphosphines.

$$F_2PPF_2 + (CF_3)_2PP(CF_3)_2 \rightleftarrows 2(CF_3)_2PPF_2 \qquad (5)$$

Indeed, when equal amounts of F_2PPF_2 and $(CF_3)_2PP(CF_3)_2$ were mixed, the symmetrical diphosphines were 31% converted to $(CF_3)_2PPF_2$ after 18 hr. Thus we believe that the redistribution method will afford an attractive alternative for the formation of a wide variety of unsymmetrical difluorophosphines and that it is worthy of further investigation.

The fragmentation pattern observed in the mass spectrum of $(CF_3)_2PPF_2$ (Figure 1) is consistent with patterns observed for other fluorophosphines and trifluoromethylphosphines, proceeding through elimination of fluorine and CF_3 groups.[12,15]

Both the ^{19}F and ^{31}P nmr spectra of neat liquid $(CF_3)_2PPF_2$ showed the expected first-order splitting patterns. As an example of the spectra, the $(CF_3)_2P$ portion of the ^{31}P spectrum is displayed in Figure 2.

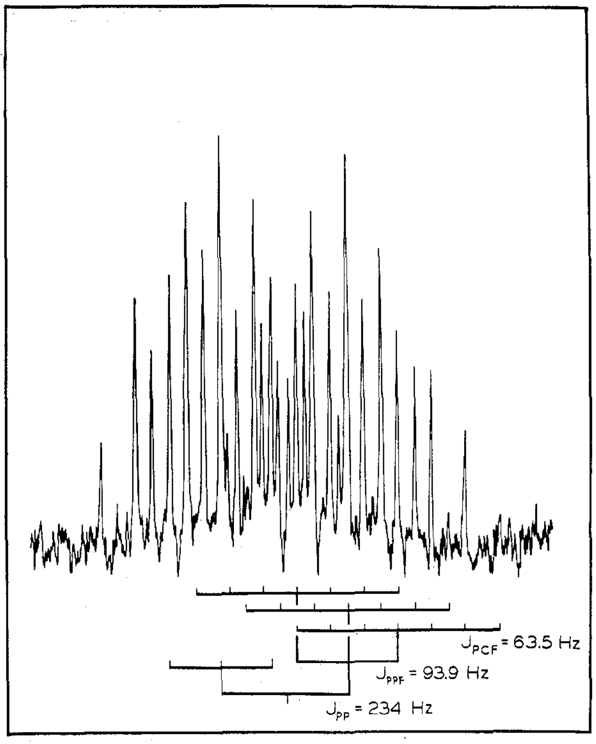

Figure 2.—The ^{31}P nmr spectrum [$(CF_3)_2P$ portion] of $(CF_3)_2PPF_2$. Brackets denote splitting patterns.

The spectrum consists of 1:2:1 triplets of overlapping 1:6:15:20:15:6:1 septets. The F_2P portion of the ^{31}P spectrum gave a 1:2:1 triplet of doublets of 1:6:15:20:15:6:1 septets. The temperature dependence of the ^{31}P spectrum was examined between −20 and −80° with no significant change in the value of

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[14] F. W. Bennet, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).

[15] R. G. Cavell and R. C. Dobbie, *Inorg. Chem.*, **7,** 101, 690 (1968).

${}^1J_{PP}$ (235 ± 2 Hz)[13] or in the appearance of the spectrum. The data derived from the various nmr spectra are summarized in Table I where they can be compared with those for similar phosphines.

Vibrational Spectra.—Even though the P–P stretching frequency for unsymmetrical diphosphines is ir active, the bands for H_2PPF_2 and $(CF_3)_2PPF_2$ are weak. By contrast, as expected, the P–P stretch was the most intense feature of each Raman spectrum. The spectra and tentative assignments are listed in Table II.

TABLE II
IR AND RAMAN DATA[a]

$(CF_3)_2PPF_2$(g) Infrared

2350 vw, b, 2281 w, b, 1670 vw, b, 1389 w, b (overtone or combination); 1194, 1169, 1145 1131 vvs (CF str); 1022, 995, 927 w (?); 844 vs (PF str); 749, 744 m (CF_3 def, PC_2 str); 557 m (CF_3 def); 505 vw (?); 488 m (PP str); 454 s (PF_2 scissors or PC_2 str); 379, 304 m (CF_3 rock, PC_2 scissors)

$(CF_3)_2PPF_2$(l) Raman at −75°

1214, 1155, 1116, vw, b (CF str); 991 vw (?); 836 w (PF str); 744 vs, 735 s (CF_3 def, PC_2 str); 556 s (CF_3 def); 486 vvs (PP str); 453 s, 425, 404 vw (PF_2 scissors or PC_2 str); 380 s, 336 vw, 305 s (CF_3 rock, PC_2 scissors); 282 s, 274 w, 244 m, 215 vvs, 205 w, 158 w, 136 m, 106, 92 s (scissors, wagging, and torsional modes)

H_2PPF_2(g) Infrared

2324 m, 2314 R, 2301 P, m (PH str); 1077 R, 1068 Q, 1060 P, w (PH_2 scissors); 850, 843 w (PF_2I impurity); 839, 828 vs (PF str); 734 R, 728 Q, 722 P, m (PPH_2 wag); 669 R, 657 Q, 649 P, w (PPH_2 rock); 459, 448, 440 w (PP str); 421, 412, 407, vw, 376 w (PF_2I and PF_2 scissors); 279 w, 228 m (PPF_2 wag and rock); 209 m (torsion, PF_2I?)

H_2PPF_2(l) Raman at −100°

2298 m (PH str); 1059 w (PH_2 scissors); 810, 803 w (PF str); 722 w (PPH_2 wag); 659 vw (PPH_2 rock); 446 vvs (PP str); 407 m, 368 vs (PF_2I? and PF_2 scissors); 257 m (PPF_2 wag); 206 vs (torsion, PF_2I?)

$(CH_3)_2PPF_2 \cdot BH_3$(g) Infrared

2416 m, b (BH str); 2260 w (overtone or combination); 1622, 1601, 1581 w (B_2H_6); 1200 w (?); 1200, 1172, 1141, 1118 vs (CF str); 1036 m (BH_3 def); 910, 895 s (PF str); 836 s [$(CF_3)_2PPF_2$]; 743 w (PC_2 str, CF_3 def); 696 m (BH_3 rock); 671, 621 m, 603 w (PB str); 551 w (CF_3 def); 484 sh, 448 m, 434 sh (PF_2 scissors and PC_2 str); 371, 331 w, 315 sh (CF_3 rock, PC_2 scissors)

$H_2PPF_2 \cdot BH_3$(g) Infrared

2419, 2395 m (BH str); 2310 w, 2298 sh (PH str); 1114 w (BH_3 def); 1060 m, b (PH_2 scissors); 898 s (PF str); 750, 718 m (PPH_2 wag); 664, 593 (PB str, BH_3 rock); 472 sh, 456 w, 442 sh, 370 w, b (PP str, PF_2 scissors)

[a] Vibrational frequencies are given in cm^{-1} followed by a tentative assignment in parentheses. Notation for intensity and band shape: v, very; s, strong; m, medium; w, weak; b, broad; sh, shoulder; P, Q, and R refer to band shapes reminiscent of the corresponding vibration–rotation bands.

The presence of F_2PI as a minor impurity of the H_2PPF_2 was confirmed in both the infrared and Raman spectra by comparison of observed frequencies and intensities with those previously reported.[16] Other frequencies were assigned by comparison to those given for similar phosphines,[16,17] P_2H_4,[18–20] and P_2F_4.[12]

The infrared spectrum of $(CF_3)_2PPF_2$ is almost a composite of the bands reported for P_2F_4[12] and $(CF_3)_4P_2$.[14] The assignments in the region below 400 cm^{-1} are quite uncertain. The strong Raman line at 453 cm^{-1} for liquid $(CF_3)_2PPF_2$, assigned to a PC_2 stretch, is in agreement with the PC_2 stretching frequency of 464 cm^{-1} observed for $CH_3NHP(CF_3)_2$[21,22] and that of 442 cm^{-1} observed in $(CF_3)_4P_2$.[23]

On the basis of two P–P stretching motions and the doubling of other vibrations Durig and Di Yorio[24] estimated that liquid $(CH_3)_2PP(CH_3)_2$ was a 60:40 mixture of the gauche–trans isomers. On the other hand, we have observed no doubling of the P–P motions for either $(CF_3)_2PPF_2$ or H_2PPF_2, perhaps indicative of the presence of single conformers in the condensed states. If the results of a microwave study[7] can be extrapolated to the liquid, the trans conformer of H_2PPF_2 is indicated.

The BH_3 Adducts of H_2PPF_2 and $(CF_3)_2PPF_2$.—The unsymmetrical diphosphine $(CF_3)_2PP(CH_3)_2$ has been reported to form a single BH_3 adduct but the coordination site was not determined.[5] Our results established the existence as well as the coordination site of similar adducts, $H_2PPF_2 \cdot BH_3$ and $(CF_3)_2PPF_2 \cdot BH_3$.

Half of the ${}^{19}F$ nmr spectrum of $H_2PPF_2 \cdot BH_3$ is shown in Figure 3 as a sample of the spectra obtained. The spectrum consists of a doublet (${}^2J_{PF}$ = 29.5 Hz) of 1:3:3:1 quartets (${}^3J_{FPBH}$ = 23.2 Hz) split again into 1:2:1 triplets (${}^3J_{FPPH}$ = 14.5 Hz). The ${}^1H$, ${}^{19}F$, ${}^{11}B$, and ${}^{31}P$ nmr spectra of $H_2PPF_2 \cdot BH_3$ and $(CF_3)_2PPF_2 \cdot BH_3$ were all easily interpretable first-order patterns.[13,25–27] The data are summarized in Table III

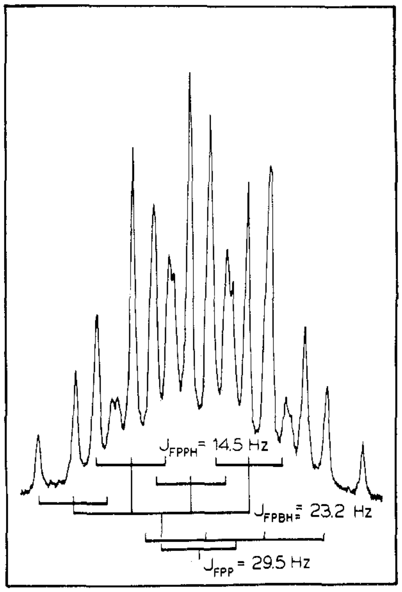

Figure 3.—Half of the ${}^{19}F$ nmr spectrum of $H_2PPF_2 \cdot BH_3$. Brackets denote splitting patterns.

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(16) R. W. Rudolph, J. G. Morse, and R. W. Parry, *Inorg. Chem.*, **5**, 1464 (1966).

(17) D. Corbridge, *Top. Phosphorus Chem.*, **6**, 235 (1969).

(18) M. Baudler and L. Schmidt, *Z. Anorg. Allg. Chem.*, **289**, 219 (1957).

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(21) N. N. Greenwood, B. H. Robinson, and B. P. Straughan, *J. Chem. Soc. A*, 230 (1968).

(22) A. B. Burg, K. K. Joshi, and J. F. Nixon, *J. Amer. Chem. Soc.*, **88**, 31 (1966).

(23) A. B. Burg and J. F. Nixon, *ibid.*, **86**, 356 (1964).

(24) J. R. Durig and J. S. Di Yorio, *Inorg. Chem.*, **8**, 2796 (1969).

(25) It should be noted that the proton and ${}^{11}B$ nmr spectra showed a temperature dependence which has been termed "thermal decoupling."[26] We have noticed the same increased quadrupolar relaxation effect with decreasing temperature for $F_2PPF_2 \cdot BH_3$.[27] The effect makes the detection of P–B spin–spin coupling difficult at low temperatures.

(26) H. Beall, C. H. Bushweller, W. J. Dewkett, and M. Grace, *J. Amer. Chem. Soc.*, **92**, 3489 (1970).

(27) H. L. Hodges and R. W. Rudolph, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 14, 1970, No. INOR 38.

TABLE III
NMR DATA[a] FOR $H_2PPF_2 \cdot BH_3$ AND $(CF_3)_2PPF_2 \cdot BH_3$. A COMPARISON WITH VALUES FOR HPF_2BH_3, PF_3BH_3, AND PH_3BH_3

	$H_2PPF_2 \cdot BH_3$				$(CF_3)_2PPF_2 \cdot BH_3$						
	^1H	^{19}F	^{31}P	^{11}B	^1H	^{19}F	^{31}P	^{11}B	HPF_2BH_3[i]	PF_3BH_3[i]	PH_3BH_3[j]
J_{BH}	102	...	...	100	106	...	...	105	103	107	103
J_{PF}	...	1204	1203	...	...	1267	1264	...	1151	1406	...
J_{PH}	198	...	202	...	...	...	...	...	467	...	372
J_{PB}	...	...	38	35.8	...	...	...	14	49	39	27
J_{FPBH}	23	23.2	...	...	26	27	...	...	26	18	...
J_{HBP}	12	...	...	...	...	...	...	...	17	18	16
J_{HPBH}	...	...	...	...	...	...	...	...	6	...	8
H_{HPP}	4.2	...	...	...	...	...	...	...	...	...	...
J_{HPPF}	14.2	14.4	...	...	...	...	...	...	...	...	...
J_{HPPBH}	1.4	...	...	...	...	...	...	...	...	...	...
J_{FPP}	...	29.5	28	...	...	32	...	...	...	...	...
J_{PP}	...	...	256	...	...	...	316	...	...	...	...
J_{FCP}	...	...	...	...	...	76.3	...	...	...	...	...
J_{FCPP}	...		...	...	...	5.2	...	...	...	...	...

		$H_2PPF_2 \cdot BH_3$	$(CF_3)_2PPF_2 \cdot BH_3$
δ	^1H	-316 (PH_2),[b] -0.92 (BH_3)[b]	$+6.38$[f]
	^{19}F	$+74.0$[c]	$+43.6$ (CF_3),[g] $+77.8$ (PF_2)[g]
	^{31}P	$+217$ (PH_2),[d] -181 (PF_2)[d]	-57 (CH_3),[d] -146 (PF_2)[d]
	^{11}B	$+22.9$[e]	$+125.1$[h]

[a] Coupling constants are given in Hz and chemical shifts in ppm. [b] TMS internal (−40°). [c] $CFCl_3$ internal (−40°). [d] H_3PO_4-(85%) external (−40°). [e] $BF_3 \cdot (C_2H_5)_2O$ external (−30°). [f] $CHCl_3$ external (0°). [g] $CFCl_3$ internal (0°). [h] Trimethylboron external +20°). [i] Reference 24. [j] Reference 28.

where they can be compared with the data for HPF_2BH_3,[28] F_3PBH_3,[28] and H_3PBH_3.[29] Such a comparison shows that BH_3 is coordinated to the F_2P site in both cases. The latter is assured since (1) the magnitude of $^3J_{FPBH}$ is the same as in similar monophosphines, (2) the F_2P portion of the various spectra was broadened by quadrupolar relaxation of the coordinated boron nucleus, (3) the spectra displayed normal line widths for the $(CF_3)_2P$ or H_2P parts of the molecule, (4) $^1J_{PH}$ changed only from 189 to 198 Hz in going from the free ligand to $H_2PPF_2 \cdot BH_3$ (the corresponding change for HPF_2 is from 182 to 467 Hz), and (5) no multiplet patterns consistent with the $(CF_3)_2PBH_3$ group were observed.

The site of BH_3 attachment is also supported by ir evidence. The intensity of PF motions and the "cleanness" of the 800–950-cm^{-1} region makes their assignment trivial and shows shifts (uncoordinated to coordinated) from ν_{PF} 828, 839 to ν_{PF} 898 cm^{-1} and ν_{PF} 836 to ν_{PF} 895, 910 cm^{-1} for H_2PPF_2 and $(CF_3)_2PPF_2$, respectively (Table II). Shifts in the PF stretching motions to higher frequencies upon coordinate bond formation by the phosphine or by increase in oxidation state have been noted previously.[30,31]

The observed reactions of H_2PPF_2 and $(CF_3)_2PPF_2$ with B_2H_6 can be readily explained. The inability of these diphosphines to coordinate more than one BH_3 group and the site of attachment are in accord with expectations based on inductive effects and the relative base strengths of similar phosphines. The H_2P moiety in H_2PPF and the $(CF_3)_2P$ moiety in $(CF_3)_2PPF_2$ reflect the weak donor ability of PH_3[29,32] and $P(CF_3)_3$,[33] respectively. However, since π-bonding arguments also predict the observed trend, $(CF_3)_2PPF_2$ and H_2PPF_2 are not really good "test cases." A good candidate is the unknown species $(CH_3)_2PPF_2$. Extrapolating from the behavior of similar monophosphines the $(CH_3)_2P$ moiety of the latter would be anticipated to be the preferential coordination site for BH_3. However, if there is a strong pπ–dπ component to the P–P bond, the BH_3 would coordinate to the F_2P site.

Although the relative basicities of $F_2PP(CF_3)_2$ and F_2PPF_2 toward BH_3 were not established by competitive equilibrium studies, the existence of $F_2PPF_2 \cdot BH_3$[34] and $(CF_3)_2PPF_2 \cdot BH_3$ and the nonexistence of $(CF_3)_2PP(CF_3)_2 \cdot BH_3$[4,5] confirm $(C_3)_2PP(CF_3)_2$ as the weakest base of the three. Also, although the synthesis of H_2PPF_2 completes another interesting triad, H_2PPH_2–H_2PPF_2–F_2PPF_2, relative basicities were not established for the series.

The Nature of the P–P Bond.—Grant and Burg have attributed the intense ultraviolet absorption of diphosphines to the π-acceptor bonding power of the P 3d orbitals.[5] Thus, they noted an increase in the intensity of the uv absorption maximum as the electronegativity of the phosphorus substituents increased in the series $(CH_3)_2PP(CH_3)_2$, $(CH_3)_2PP(CF_3)_2$, $(CF_3)_2PP(CF_3)_2$ (Table IV). The intensity increase was attributed to more delocalization across the P–P bond and correlated nicely with a decrease in the basicity of the diphosphines. Based only on electronegativity, the intensity

TABLE IV
A COMPARISON OF ULTRAVIOLET SPECTRA OF SOME DIPHOSPHINES

Compound	λ_{max}, Å	Molar extinct coeff	Ref
H_2PPF_2	2160	7,100	*a*
$H_2PPF_2 \cdot BH_3$	1920	6,600	*a*
P_2F_4	2606	20,500	*b*
$(CF_3)_2PPF_2$	2190	11,000	*a*
$(CF_3)_4P_2$	2160	7,800	*c*
$(CH_3)_2PP(CF_3)_2$	2330	4,520	*c*
$(CH_3)_4P_2$	2420	4,000	*c*

[a] This work. [b] D. Solan, Ph.D. Thesis, University of California, Berkeley, Calif., 1969. [c] Reference 5.

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data for $(CF_3)_2PPF_2$ and F_2PPF_2 fall nicely in line with those for $(CH_3)_2PP(CH_3)_2$, $(CH_3)_2PP(CF_3)_2$ and $(CF_3)_2PP(CF_3)_2$. However, then an ordering of these diphosphines by the intensity of their uv absorption no longer correlates with their relative base strength toward BH_3 (*vide supra*). Also, two opposite trends in the position of the absorption as a function of substituent electronegativity can be noted. In the triad $(CF_3)_2PP(CF_3)_2$–$(CF_3)_2PP(CH_3)_2$–$(CH_3)_2PP(CH_3)_2$ the maximum shifts to longer wavelengths with decreasing substituent electronegativity, while in the triad $(CF_3)_2PP(CF_3)_2$–$(CF_3)_2PPF_2$–F_2PPF_2 the same trend occurs as the electronegativity of the substituents increases. These difficulties question the validity of an intense uv absorption as evidence for p_π–d_π bonding in diphosphines.[5,35] In fact, the absorption features are not exclusively characteristic of P–P bonded diphosphines since the monophosphine PHF_2 shows uv spectra similar to those just described.[36]

Structural data are not available for $(CF_3)_2PPF_2$ but the structure of H_2PPF_2 gives no evidence of a p_π–d_π component to the P–P bond.[7]

Experimental Section

The compounds investigated were handled in a high-vacuum system using standard high-vacuum techniques.[37] Stopcocks and standard-taper joints were greased with Apiezon N. Manometers were isolated from the system with stopcocks to minimize the contact of reactive materials with mercury.

Materials.—PF_2I,[38] PH_3,[39] P_2F_4,[12] $(CF_3)_2PI$,[40] B_2H_6,[41] and $P_2(CF_3)_4$[13] were prepared by published procedures. All materials were checked for purity by ir and vapor pressure prior to use.

Preparation of H_2PPF_2.—In a typical experiment, a 2.81-mmol sample of P_2F_4, 0.56 mmol of PF_2I, and 6.15 mmol of PH_3 were condensed at −196° into a 10-ml thick-walled tube equipped with a 10/30 standard-taper joint. The tube was sealed above the joint and placed in a −78° bath. The liquid in the bottom of the tube was still colorless after 24 hr. After 10 hr at −23° the liquid began to turn yellow. After an additional 4 hr at −23°, the tube was frozen at −196° and broken into the vacuum system; the products separated by fractional condensation at −111, −130, −160, and −196°. Yellow-brown solids remained in the reaction tube. The −111° trap contained 2.49 mmol of a mixture of PF_2I and the desired H_2PPF_2. The H_2PPF_2 was found to be 81% pure as demonstrated by a vapor density molecular weight of 120. This corresponds to a 72% yield of H_2PPF_2 based on the amount of P_2F_4 used. The −130° trap contained 0.24 mmol of a mixture of P_2F_4 with a trace of H_2PPF_2. The −160° trap contained 2.14 mmol of PF_2H, while the −196° trap contained 4.65 mmol of a mixture of PF_3 and PH_3. The reaction was also carried out successfully in a 500-ml reaction flask, the tip of which was held at −78° until yellow solids formed in the flask (periods ranging from 1 to 3 days).

A 0.39-mmol sample of H_2PPF_2 was condensed into a 30-ml tube at −196°. The −196° bath was removed, and the tube was allowed to stand for 12 hr at 25°. The volatile products were then fractionated through traps at −130 and −196°. The −130° trap contained 0.29 mmol of H_2PPF_2. This corresponds to 26% decomposition. The −196° trap contained 0.09 mmol of a mixture of PF_3 and PF_2H. Yellow-orange solids remained in the tube.

A well-purified sample of H_2PPF_2 gave the following temperatures (°C) and vapor pressures (mm): −63.6, 11.4; −45.8, 36.1; −30.6, 80.6; −22.9, 118.0; −16.3, 151.2. The equation $\log[p(\text{mm})] = -1288/T + 7.211$ gives an extrapolated boiling point of 24.4° and a Trouton constant of 19.81 cal/deg mol.

Preparation of $(CF_3)_2PPF_2$.—When $(CF_3)_2PPF_2$ was prepared by the coupling reaction, a 3-ml quantity of mercury was placed in a 500-ml reaction bulb equipped with a stopcock. The bulb was evacuated and 5.22 mmol of PF_2I and 5.03 mmol of $(CF_3)_2PI$ were condensed into the bulb at −196°. The mixture was then shaken for 8 hr at 25°. Evidence for the reaction was the formation of gray solids. The tip of the bulb was cooled to −196° and then allowed to warm to 25° while passing the volatile products through traps at −78, −111, and −196°. A 3.12-mol sample of $(CF_3)_2PPF_2$ (62% yield based on $(CF_3)_2PI$) was recovered from the −111° trap. The −78° trap contained 0.52 mmol of $(CF_3)_4P_2$ while the −196° trap held 1.35 mmol of PF_3 and a product tentatively identified as $(CF_3)_3P$. The products were identified by their infrared spectra.[14] The $(CF_3)_4P_2$ was additionally identified by its vapor pressure at 0.0° (observed 21.2 mm; reported[14] 20.5 mm).

To prepare $(CF_3)_2PPF_2$ by redistribution, 0.36 mmol of $(CF_3)_4P_2$ and 0.35 mmol of P_2F_4 were condensed at −196° into a 300-ml reaction flask. The flask was closed off from the vacuum system and allowed to warm slowly to 25°. After 5 hr the volatile products were separated by fractional condensation at −78, −111, and −196°. Yellow solids remained in the bulb. The −78° trap contained 0.26 mmol of $(CF_3)_4P_2$, while the −196° trap held 0.34 mmol of a mixture of PF_3, P_2F_4, and a trace of a compound tentatively identified as $(CF_3)_3P$. A 0.11-mmol sample of $(CF_3)_2PPF_2$ was held at −111°. After measurements were made, the volatile products were condensed back into the reaction bulb and held for an additional 13 hr at 25°. Fractional condensation through traps at −78, −111, −126, and −196° yielded 0.16 mmol of $(CF_3)_4P_2$ in the −78° trap, 0.19 mmol of P_2F_4 in the −126° trap, and 0.08 mmol of PF_3 in the −196° trap. The −111° trap held 0.22 mmol of $(CF_3)_2PPF_2$.

The vapor pressure data for $(CF_3)_2PPF_2$ [temperature (°C), vapor pressure (mm): −47.4, 9.7; −36.1, 22.2; −24.8, 41.8; −16.8, 66.0; 0.0, 147.2] are summarized by the equation $\log[p(\text{mm})] = -1532/T + 7.788$. The extrapolated boiling point is 39.1° and the Trouton constant is 22.45 cal/deg mol. The vapor density gave a molecular weight of 237.

Preparation of $H_2PPF_2 \cdot BH_3$.—In a typical experiment a 0.52-mmol sample of H_2PPF_2 and a 1.19-mmol quantity of B_2H_6 were condensed at −196° into a 150-ml reaction bulb connected to a manometer. The −196° bath was replaced with a −78° bath and an initial pressure of 90 mm was attained. The pressure decreased until 0.5 hr had elapsed. During this time a small amount of yellow solid formed in the reaction tube. The products were then fractionated through traps held at −95, −130, and −196°. The desired $H_2PPF_2 \cdot BH_3$ was retained in the −95° trap (0.46 mmol, 88% yield). The −130° trap contained a trace amount of $PF_3 \cdot BH_3$ while the −196° trap held 0.94 mmol of unreacted B_2H_6. The mass balance indicates that formation of 0.46 mmol of $H_2PPF_2 \cdot BH_3$ consumed 0.25 mmol of B_2H_6. This stoichiometry was also confirmed by a tensimetric titration at −78° and a vapor density molecular weight of 116.

In order to test for stability a 0.46-mmol sample of $H_2PPF_2 \cdot BH_3$ was condensed at −196° into a 30-ml tube. The −196° bath was removed, and the contents of the tube were allowed to warm to 25°. After 1 hr, yellow-orange solids appeared in the bottom of the tube. After 24 hr, the volatiles were distilled through traps at −130, −160, and −196°. The −130° trap contained 0.28 mmol of $H_2PFF_2 \cdot BH_3$ (39% decomposition). The −160° trap held a trace amount of PF_2H, while the −196° trap contained a 0.11-mmole mixture of PF_3 and B_2H_6.

Preparation of $(CF_3)_2PPF_2 \cdot BH_3$.—In order to prepare the adduct a 0.62-mmol sample of $(CF_3)_2PPF_2$ and a 0.97-mmol sample of B_2H_6 were condensed at −196° into a 150-ml reaction bulb attached to a manometer. The −196° bath was replaced with a −78° bath, and the initial pressure was found to be 65 mm. After 10 hr, the pressure did not decrease, the −78° bath was removed, and the mixture was allowed to stand at 25° for 24 hr at which time the pressure reached a minimum. The volatile products were separated by fractional condensation through traps at −95, −126, and −196°. A small amount of white solid remained in the tube. The −95° trap contained 0.34 mmol of $(CF_3)_2PPF_2 \cdot BH_3$ (55% yield); 0.27 mmol of unreacted $(CF_3)_2PPF_2$ was recovered from the −126° trap, while 0.79 mmol of B_2H_6 was held at −196°. The B_2H_6 mass balance shows that 0.18 mmol was consumed in forming 0.34 mmol of product. The most efficient separation of $(CF_3)_2PPF_2$ from

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$(CF_3)_2PPF_2 \cdot BH_3$ was effected when distillation through the $-95°$ trap was slow.

The vapor density of $(CF_3)_2PPF_2 \cdot BH_3$ also corresponds well with theory (mol wt: calcd, 251.8; found, 253). However, the molecule dissociates easily as evidenced by the observation of appreciable amounts of B_2H_6 and $(CF_3)_2PPF_2$ in the infrared spectra and the lack of a molecular ion in the mass spectrum of $(CF_3)_2PPF_2$ (Figure 1). Other easily dissociated species such as $B_4H_8 \cdot CO$ also show only fragment ions by conventional mass spectrometry.[42]

Instrumentation.—Infrared spectra were obtained with an 87-mm gas cell equipped with CsI windows on either a Beckman IR-10 or a Beckman IR-12. The Raman samples were sealed in capillary tubes and the spectra determined on a SPEX Ramalog 1401 using an argon ion laser. A Consolidated Electrodynamics Model 21-103B operating at 70 eV was used to obtain the mass spectra. The ^1H, ^{19}F, ^{31}P, and ^{11}B nmr spectra were determined with a Varian HR-100 operating at 100.0, 94.1, 40.5, and 32.1 MHz, respectively. A Cary 14 was used to obtain the uv spectra of samples in a 103-mm quartz gas cell.

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The Phosphorus–Phosphorus Bond. III. The Microwave Spectrum, Conformation, and Dipole Moment of Phosphinodifluorophosphine[1]

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The rotational spectrum of phosphinodifluorophosphine was assigned with the following rotational constants (MHz): $A = 6916.53$, $B = 3372.94$, $C = 2648.59$ for H_2PPF_2; $A = 6625.56$, $B = 3192.44$, $C = 2522.37$ for D_2PPF_2. The dipole moment was measured as 1.71 ± 0.01 D, with principal axes components $\mu_a = 1.25$ D and $\mu_c = 1.16$ D. From the rotational constants and dipole moment data, the conformation was determined as trans. With the assumption that $d(PH) = 1.42 \pm 0.01$ Å, the following structural parameters were derived: $d(PP) = 2.218 \mp 0.038$ Å, $d(PF) = 1.587 \pm 0.013$ Å, $\angle HPH = 93.2 \mp 1.0°$, $\angle HPP = 90.3 \mp 0.4°$, $\angle FPF = 98.2 \mp 1.2°$, and $\angle FPP = 97.2 \pm 1.6°$.

Introduction

Structure investigations of diphosphines are of interest because of the possibility of conformational isomerism. Although no precise structural data are available, the infrared and Raman spectra have been interpreted in terms of a gauche configuration for P_2H_4[2,3] and a trans configuration for P_2F_4[4] and P_2Cl_4.[5] Vibrational spectra and X-ray data also confirm the trans symmetry for P_2I_4.[6,7] Vibrational spectra for $(CH_3)_4P_2$ indicated a gauche–trans rotameric mixture in the liquid phase but only the trans form in the solid.[8] A recent electron-diffraction study of gaseous $(CH_3)_4P_2$ indicated that the dihedral angle (ϕ) was $164 \pm 23°$, measured from the cis configuration[9] ($\phi = 0°$ for cis, $180°$ for trans). Finally, semiempirical SCF and extended Hückel MO calculations for P_2H_4 and P_2F_4 suggested that the stability of the various conformations decreases in the order gauche > cis > trans.[10]

In the related compounds $F_2PN(CH_3)_2$ and F_2PNH_2, a pyramidal arrangement of neighboring atoms about phosphorus was found; however, the arrangement about the nitrogen was planar and the NX_2 plane bisected the FPF angle.[11,12] PF_2PH_2 has been recently synthesized;[1,13] in view of the above data it was of interest to determine its conformation.

Experimental Section

Apparatus.—The spectra were obtained with a Stark modulated spectrometer which has been described previously.[14] The transitions were measured with a precision of about 0.2 MHz. The absorption cell was cooled with Dry Ice ($-78°$) for all observations.

Materials.—The H_2PPF_2 was prepared by the reaction of PF_2I and PH_3 and identified by comparison with the reported infrared, nmr, and mass spectra.[1,13] The D_2PPF_2 was made by substituting PD_3 obtained by hydrolysis of calcium phosphide. The synthesis of D_2PPF_2 was confirmed by infrared spectroscopy.

Spectra.—The transitions which were assigned for the two isotopic species are listed in Table I. The rotational constants listed in Table II were obtained by a least-squares fit of the observed transitions. The assignment was based on the Stark effect and the rigid-rotor fit for both species.

In addition to the transitions from H_2PPF_2, absorptions from the decomposition products PF_2H and PF_3 were also noted. A weaker satellite line was found accompanying many of the ground-state lines. This was attributed to a vibrational satellite since the lowest fundamental has been assigned at 209

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