Preparation and Properties of Iodo(trifluoromethyl)phosphine and Exchange Reactions of some Simple Trifluoromethylphosphines

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Iodo(trifluoromethyl)phosphine, $F_3CP(H)I$, can be prepared by the reaction of iodine with F_3CPH_2, or by exchange between F_3CPH_2 and F_3CPI_2 with which it is in equilibrium. Chlorine reacts with F_3CPH_2 to give $F_3CP(H)Cl$, $(F_3CPH)_2$, and HCl. Replacement reactions of iodine in $F_3CP(H)I$ with silver(I) and mercury(II) halides lead to the preparation of mixtures containing $F_3CP(H)Cl$ and of pure $F_3CP(H)Br$. With Ag[CN] and $Hg[CN]_2$, $F_3CP(H)I$ gives $(F_3CP)_4$ and $F_3CP(CN)_2$ respectively; in the latter case there is evidence for a mercury–phosphorus intermediate. The diphosphane $(F_3CPH)_2$ can be prepared by reduction of $F_3CP(H)I$ with mercury or by its reaction with SbF_3, CdF_2, or NaF. Reactions between all possible pairs of compounds F_3CPX_2–F_3CPY_2 (X or Y = F, Cl, Br, I, H, or CN) give the mixed species $F_3CP(X)Y$, characterised by n.m.r. spectroscopy, in all cases except when X = F and Y = H, I or CN, although the reaction is often more complex than simple exchange. The vibrational spectra of $F_3CP(H)X$ and $F_3CP(D)X$ (X = Br or I) have been analysed in terms of group vibrations.

In the chemistry of trifluoromethyl-substituted phosphines, many compounds with novel features in structure or reactivity have been prepared and examined. The presence of the strongly electronegative CF_3 groups alters the availability of the lone pair on phosphorus compared to alkyl phosphines and at the same time alters the energy of the phosphorus *d* orbitals which makes for more efficient π overlap with filled orbitals on neighbouring atoms. These effects are exemplified by the weakly basic properties of trifluoromethylphosphines and their reluctance to undergo Arbuzov rearrangements to form phosphorus(V) species.[1] However, little is known about phosphines containing the F_3CPH group. Controlled hydrolysis of the cyclic tetramer, $(PCF_3)_4$, gives $F_3CP(H){\cdot}P(H)CF_3$ in low yield.[2] Although the diphosphane is stable under normal conditions, pyrolysis at 300 °C gives F_3CPH_2 and PCF_3 polymer together with a smaller yield of $(F_3C)_2PH$. The methyl derivative, $F_3CP(H)Me$ has been prepared[3a] by reduction of $F_3CP(I)Me$ and some germanium and tin analogues, $F_3CP(H){\cdot}MMe_3$ (M = Ge or Sn), have been reported.[3b] However, the only easily accessible derivative with a F_3CPH group is the primary phosphine, F_3CPH_2, first prepared by freeze drying of an aqueous hydrolysate of F_3CPI_2,[4] but since made more conveniently using anhydrous HI and mercury as reducing agent.[5]

We were interested in examining the reactivity of hydrogen attached to phosphorus in $F_3CP(H)X$ and also in the ultimate possibility of using such compounds to generate F_3CP, a carbene analogue. In this paper we report the preparation and properties of simple derivatives containing the $F_3CP(H)$ group, and exchange reactions between pairs of compounds F_3CPX_2 and F_3CPY_2(X or Y = halogen, H, or CN).

RESULTS AND DISCUSSION

Preparation of the Compounds $F_3CP(H)X$ (X = I *or* Cl).†—The reaction of iodine with trifluoromethylphosphine gave iodo(trifluoromethyl)phosphine, $F_3CP(H)I$, initially, although further replacement of hydrogen occurred to give di-iodo(trifluoromethyl)phosphine as the final product. At each step hydrogen iodide was liberated. The relative rates of these reactions was such

$$F_3CPH_2 + I_2 \longrightarrow F_3CP(H)I + HI \qquad (1)$$

$$F_3CP(H)I + I_2 \longrightarrow F_3CPI_2 + HI \qquad (2)$$

that use of excess of iodine gave only F_3CPI_2. However, with a deficiency of iodine the yield of $F_3CP(H)I$ was *ca.* 40%. Although pure $F_3CP(H)I$ can be isolated, samples of the neat liquid which are left at room temperature soon show the presence of equimolar amounts of F_3CPH_2 and F_3CPI_2, which together with the spectroscopic data (see below) establishes the formula and structure of $F_3CP(H)I$. Solutions in an inert solvent are markedly more stable towards the redistribution (3).

$$F_3CPH_2 + F_3CPI_2 \rightleftharpoons 2F_3CP(H)I \qquad (3)$$

The equilibrium (*K* 0.7) in (3) was confirmed by heating or irradiating a mixture of F_3CPH_2 and F_3CPI_2. Preparation of $F_3CP(H)I$ from F_3CPH_2 and F_3CPI_2 is more convenient than from F_3CPH_2 and I_2. The deuteriated analogue, F_3CPDI, can be prepared similarly from F_3CPD_2[6] and F_3CPI_2. It is interesting to compare the reaction of $MeAsH_2$ with $MeAsI_2$, recently investigated[7] by Rheingold *et al.* with the F_3CPH_2–F_3CPI_2 mixture. In the case of the arsenic compounds, MeAs(H)I is formed although not apparently by direct exchange. This slowly decomposes to poly(methylarsine), $(MeAs)_n$.

The reaction of chlorine with excess of F_3CPH_2 was in its early stages similar to that with iodine. A mixture of F_3CPH_2, $F_3CP(H)Cl$, and F_3CPCl_2 was obtained together with HCl. After removal of the initially formed hydrogen chloride, chloro(trifluoromethyl)phosphine decomposed to F_3CPH_2 and F_3CPCl_2 slowly at room temperature in an inert solvent, and at the same

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† Professor J. Grobe, University of Darmstadt, has informed us that he has prepared $F_3CP(H)I$ by another route and confirmed its identity.

[1] A. B. Burg, *Accounts Chem. Res.*, 1969, **2**, 353.

[2] W. Mahler and A. B. Burg, *J. Amer. Chem. Soc.*, 1958, **80**, 6161.

[3] (*a*) A. B. Burg, K. K. Joshi, and J. F. Nixon, *J. Amer. Chem. Soc.*, 1966, **88**, 31; (*b*) S. Ansari and J. Grobe, *Z. Naturforsch.*, 1972, **B27**, 1416.

[4] F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1954, 3896.

[5] R. G. Cavell and R. C. Dobbie, *J. Chem. Soc.* (*A*), 1967, 1308.

[6] R. Demuth and J. Grobe, *J. Fluorine Chem.*, 1972, **2**, 263.

[7] A. L. Rheingold, J. E. Lewis, and J. M. Bellama, *Inorg. Chem.*, 1973, **12**, 2845.

time 1,2-bis(trifluoromethyl)diphosphane, $(F_3C)PH{\cdot}PH(CF_3)$,[2] and HCl were formed in equimolar amounts. It is suggested that the diphosphane results from attack of $F_3CP(H)Cl$ on F_3CPH_2 [equation (4)]. Although $F_3CP(H)Cl$ could not be separated completely from F_3CPH_2

$$F_3CP(H)Cl + F_3CPH_2 \longrightarrow (F_3CPH)_2 + HCl \quad (4)$$

and F_3CPCl_2, a pure sample of $F_3CP(H)Br$, prepared as described below, gave the same diphosphane and hydrogen bromide together with F_3CPBr_2, a disproportionation product, when allowed to stand at room temperature with F_3CPH_2. No diphosphane was formed from $F_3CP(H)I$ and F_3CPH_2. The formation of other fluorocarbon P–P bonded compounds by elimination of HCl, usually assisted by the presence of amine, has been reported by Burg and his co-workers.[8]

The contrasting behaviour in the decomposition of $F_3CP(H)I$ and $F_3CP(H)Br$ or $F_3CP(H)Cl$ is consistent with the reaction of the hydrogen halides with 1,2-bis(trifluoromethyl)diphosphane, $(F_3CPH)_2$. Thus excess of anhydrous HI reacted rapidly with the diphosphane, consuming it completely to give a mixture of F_3CPH_2, $F_3CP(H)I$, and F_3CPI_2, the last of which arises from disproportionation of $F_3CP(H)I$. On the other hand, excess of anhydrous HCl reacted slowly and incompletely with the diphosphane giving F_3CPH_2, $F_3CP(H)Cl$, and F_3CPCl_2. Thus reaction (5) is an

$$(F_3CPH)_2 + HCl \rightleftharpoons F_3CP(H)Cl + F_3CPH_2 \quad (5)$$

equilibrium slowly established at room temperature. Eventually, however, the equilibrium should be disturbed by the even slower but thermally irreversible decomposition of $F_3CP(H)Cl$ into F_3CPH_2 and F_3CPCl_2.

Reactions of $F_3CP(H)I$.—In view of the well known usefulness[1] of F_3CPI_2 and $(F_3C)_2PI$ as synthetic intermediates, some reactions of iodo(trifluoromethyl)phosphine were investigated. When liquid $F_3CP(H)I$ was allowed to react with silver(I) chloride for a short time, the products of disproportionation, F_3CPH_2 and F_3CPI_2, were detected together with some F_3CPCl_2, $F_3CP(I)Cl$, $(F_3CPH)_2$, and HCl. In the absence of silver salt, $F_3CP(H)I$ suffered no detectable disproportionation in the time allowed for reaction, suggesting some catalysis by the salt. The new compound $F_3CP(I)Cl$ is presumed to be formed by exchange of F_3CPI_2 with F_3CPCl_2, a reaction shown to occur in a separate experiment. Formation of the diphosphane in the short time allowed for reaction is also remarkable when compared with its much slower formation in the mixture of F_3CPCl_2, $F_3CP(H)Cl$, and F_3CPH_2, and it appears that the halide ion may accelerate reaction by acting as a weak acceptor for HCl. More prolonged contact of $F_3CP(H)I$ with AgCl resulted in complete iodine–chlorine exchange although the products were otherwise little different from the shorter reaction time. When iodine–bromine exchange at phosphorus in $F_3CP(H)I$ was attempted using silver(I) bromide, the products were analogous to those in the AgCl reaction except that no diphosphane was obtained after a short reaction time so that the rate of production of $(F_3CPH)_2$ was slower from $F_3CP(H)Br$ than from $F_3CP(H)Cl$.

The action of silver(I) cyanide on F_3CPI_2 and $(F_3C)_2PI$ gives $F_3CP(CN)_2$ and $(F_3C)_2P(CN)$ respectively.[9] With $F_3CP(H)I$, the major fluorocarbon product was the cyclotetraphosphane $(F_3CP)_4$, contaminated by a trace of $(F_3CP)_5$, formed together with hydrogen cyanide. A very small quantity of an unidentified phosphine could have been $F_3CPH(CN)$, as it evolved $(F_3CP)_4$, $(F_3CP)_5$, and HCN together with other compounds at room temperature. This suggests that simple exchange occurs to give unstable $F_3CPH(CN)$, which decomposes by loss of HCN.

Reactions of $F_3CP(H)I$ with mercury(II) chloride and bromide resulted in less disproportionation than with the corresponding silver salts, suggesting that the catalytic action may depend on the different acceptor properties of the metals. On brief contact with $HgBr_2$, a pure sample of $F_3CP(H)Br$ was obtained, although the compound decomposed slowly over a period of weeks to F_3CPH_2 and F_3CPBr_2 on standing at room temperature, accompanied by slower formation of $(F_3CPH)_2$ and HBr. The chief volatile product from the action of $F_3CP(H)I$ on mercury(II) cyanide was hydrogen cyanide. The solid remaining in the tube released dicyano(trifluoromethyl)phosphine, $F_3CP(CN)_2$, and a further small quantity of HCN on pyrolysis, forming at the same time globules of free mercury. This suggests the intermediacy of a stable mercury–phosphorus compound. In view of the preparation[10] of $(F_3C)_2P{\cdot}Hg{\cdot}P(CF_3)_2$ by the action of $Hg[CN]_2$ on bis(trifluoromethyl)phosphine, and its thermal decomposition to $(F_3C)_2P{\cdot}P(CF_3)_2$ and free mercury, the mechanism in equations (6)—(8) for the reaction of $F_3CP(H)I$ appears reasonable. This mechanism implies that decomposition of the mercurial is intramolecular, otherwise diphosphanes are likely products.

$$2F_3CP(H)I + Hg[CN]_2 \longrightarrow 2F_3CPH(CN) + HgI_2 \quad (6)$$

$$F_3CPH(CN) + Hg[CN]_2 \longrightarrow F_3CP(CN){\cdot}Hg{\cdot}CN + HCN \quad (7)$$

$$F_3CP(CN){\cdot}Hg{\cdot}CN \xrightarrow{\text{Heat}} F_3CP(CN)_2 + Hg \quad (8)$$

Another route to 1,2-bis(trifluoromethyl)diphosphane was the coupling of two $F_3CP(H)I$ moleules by shaking with mercury, a reaction which is analogous[11] to the preparation of $(F_3C)_2P{\cdot}P(CF_3)_2$ from iodobis(trifluoromethyl)phosphine. Fluorination of $F_3CP(H)I$ with SbF_3, CdF_2, or NaF in acetonitrile also gave $(F_3CPH)_2$

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[8] L. R. Grant and A. B. Burg, *J. Amer. Chem. Soc.*, 1962, **84**, 1834; A. B. Burg and J. F. Nixon, *ibid.*, 1964, **86**, 356; A. B. Burg and K. K. Joshi, *ibid.*, p. 353.

[9] I. H. Sabherwal and A. B. Burg, *Inorg. Chem.*, 1972, **11**, 3138.

[10] J. Grobe and R. Demuth, *Angew. Chem.*, 1972, **11**, 1097.

[11] F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1953, 1565.

as the major fluorocarbon product, together with some tetrafluorosilane in the case of the first two fluorides, suggesting formation of hydrogen fluoride or another reactive fluorine compound. The absence of SiF_4 in the sodium fluoride reaction suggests formation of the former, as alkali-metal fluorides are known to absorb HF. Only trace amounts of an unstable material, whose i.r. spectrum and volatility suggested the formulation $F_3CP(H)F$, were detected. In view of the reaction of F_3CPH_2 with $F_3CP(H)X$ (X = Cl or Br), it is likely that initial formation of $F_3CP(H)F$ is followed by its reaction with F_3CPH_2, produced by disproportionation of $F_3CP(H)X$ (X = I or F), to give $(F_3CPH)_2$ and HF, this further step being encouraged by removal of HF through reaction with glass or through absorption by fluoride ion.

TABLE 1

N.m.r. parameters and approximate equilibrium constants for some trifluoromethylphosphines

Phosphine	ϕ[a] p.p.m.	^2J(FP) Hz	^3J(FH) or ^3J(FF) Hz	τ	^1J(HP) Hz	K[b]
F_3CPH_2 [c]	42.4	48.5	12.2	6.39	201	
F_3CPF_2 [d]	80.7	87.2	5.8			
F_3CPCl_2 [d]	72.1	79.9				
F_3CPBr_2 [d]	67.8	69.6				
F_3CPI_2 [d]	61.0	52.1				
$F_3CP(CN)_2$ [e]	52.2	89				
$F_3CP(H)Cl$	58.6	68	10.4	4.29	190	
$F_3CP(H)Br$	56.0	65	10.6	5.06	189	
$F_3CP(H)I$	51.6	56	10.2	5.83	186	0.7
$F_3CPH(CN)$	47.8	70	9.7	5.10	234	
$F_3CP(F)Cl$ [f]	76.1	84	0.6			0.1
$F_3CP(F)Br$	73.9	80	1.8			
$F_3CP(Cl)Br$ [g]	70.0	75				2.5
$F_3CP(Cl)I$	66.3	66				0.5
$F_3CP(Br)I$	64.5	62				2.2
$F_3CPCl(CN)$	62.4	85				0.01
$F_3CPBr(CN)$	60.1	81				0.9
$F_3CPI(CN)$	55.9	71				3.2

[a] Resonance of the CF_3 group relative to CCl_3F. [b] Defined as $K = [F_3CP(X)Y]^2/[F_3CPX_2][F_3CPY_2]$ under the conditions described in the Experimental section. [c] Data from J. Dyer and J. Lee, *J. Chem. Soc.* (*B*), 1970, 409. [d] Data from J. F. Nixon, *J. Chem. Soc.*, 1965, 778. [e] ϕ = 52.2 p.p.m. and ^2J(FP) 78.7 Hz (ref. 9). [f] The n.m.r. data were in agreement with ref. 12 with the exception of ^3J(FF) which was not detected in that work. [g] In agreement with ref. 13.

Because of the complexity of the reactions and the instability of the compounds, heavy reliance was placed on n.m.r. measurements (^1H and ^{19}F) for identifying the fluorocarbon phosphines. For $F_3CP(H)I$, the ^{19}F n.m.r. spectrum showed a doublet of doublets with coupling constants close to those for F_3CPH_2, and the ^1H spectrum a doublet of quartets, establishing unambiguously the presence of the F_3CPH unit. The ^{19}F chemical shift was the arithmetic mean of those for F_3CPH_2 and F_3CPI_2. The multiplicity of the n.m.r. signals and the chemical shifts was also confirmatory in the identification of $F_3CP(H)Cl$ and $F_3CP(H)Br$.

Exchange of F_3CPX_2 *with* F_3CPY_2 (X *or* Y = H, *halogen, or* CN).—Assignment of doublets in the ^{19}F n.m.r spectrum to $F_3CP(I)Cl$ and $F_3CP(I)Br$ in some of the reactions of $F_3CP(H)I$ led to examination of the exchange reactions of all 15 possible pairs F_3CPX_2–F_3CPY_2 (X or Y = H, F, Cl, Br, I, or CN). It was hoped to study the influence of the CF_3 group on exchange processes at P^{III} and also to justify the identification by n.m.r. spectroscopy of mixed species such as $F_3CP(H)Cl$ and $F_3CP(I)Br$. Difluoro(trifluoromethyl)phosphine did not undergo detectable exchange with F_3CPH_2, $F_3CP(CN)_2$, or F_3CPI_2 under the thermal or photochemical reaction conditions chosen. Compounds of formula $F_3CP(X)Y$ were detected by n.m.r. spectroscopy in the remaining 12 cases, although in only eight of these was a simple equilibrium set up according to equation (9). The

$$F_3CPX_2 + F_3CPY_2 \rightleftharpoons 2F_3CP(X)Y \qquad (9)$$

presence of the mixed species $F_3CP(X)Y$ was recognised by the appearance of new ^{19}F n.m.r. signals in the expected positions, *i.e.* at the arithmetic mean of the chemical shifts of F_3CPX_2 and F_3CPY_2. It was also noted that the F–P coupling constants for each species $F_3CP(X)Y$ were the arithmetic mean of that for F_3CPX_2 and F_3CPY_2. Compounds containing the F_3CPH grouping were exceptional in that the observed value of ^2J(FP) was higher than the mean. Equilibrium constants for the eight simple cases are given in Table 1 and n.m.r. parameters are listed. The values of K are to be regarded as approximate only, because of the assumptions made and errors involved in the measurements. Exchange of F_3CPF_2–F_3CPCl_2 and F_3CPCl_2–F_3CPBr_2 has been previously reported and the n.m.r. parameters [12,13] and equilibrium constant [13] in the latter case are in agreement with the literature values. The case of F_3CPF_2–F_3CPBr_2 was more complex in that heating to 70 °C gave $F_3CP(F)Br$ which reacted further on standing at room temperature producing PF_3 and $(F_3C)_2PBr$, but no PBr_3, suggesting reactions (10) and (11).

$$F_3CPF_2 + F_3CPBr_2 \rightleftharpoons 2F_3CP(F)Br \qquad (10)$$

$$F_3CP(F)Br + F_3CPF_2 \rightleftharpoons (F_3C)_2PBr + PF_3 \qquad (11)$$

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[12] J. F. Nixon and R. G. Cavell, *J. Chem. Soc.*, 1964, 5983.

[13] A. D. Jordan and R. G. Cavell, *Inorg. Chem.*, 1972, **11**, 564.

Whatever the reaction mechanism, transfer of a CF_3 group must occur together with transfer of a halogen atom. Although there was no thermal reaction between F_3CPH_2 and F_3CPBr_2, $F_3CP(H)Br$ and $(F_3C)_2PBr$ were detected after irradiation. With F_3CPH_2 and F_3CPCl_2, again no reaction was observed on heating to 70 °C although the behaviour on irradiation is more complex than that found with F_3CPBr_2 as $F_3CP(H)Cl$, $(F_3C)_2PCl$, and $(F_3C)_2PH$ are produced. In the cases involving irradiation, it is likely that the mechanism of the reaction involves free radicals in view of the participation of CF_3 groups in the exchange process. It has been previously suggested[11] that radical intermediates are involved in the exchange between $(F_3C)_3P$, $(F_3C)_2PI$, and F_3CPI_2 in the reaction of CF_3I with phosphorus at 200 °C.

Trifluoromethylphosphine, F_3CPH_2, reacted initially with $F_3CP(CN)_2$ to give, in addition to unchanged reactants, at least two products which were not definitely identified but were believed to be polyphosphanes from the complex ^{19}F and ^{1}H n.m.r. spectra. On allowing the n.m.r. tube containing the mixture to stand at room temperature for several weeks, the complex signals diminished and new signals appeared which could be unambiguously assigned to $F_3CPH(CN)$ (see Table 1 for n.m.r. parameters), $(F_3CPH)_2$, and HCN. When the experiment was repeated on a preparative scale in the absence of solvent, the final products conformed to equation (12). A small amount of $(F_3CPH)_2$ was also

$$F_3CPH_2 + F_3CP(CN)_2 \longrightarrow \tfrac{1}{4}(F_3CP)_4 + 2HCN \quad (12)$$

formed possibly from the intermediate $F_3CPH(CN)$ [equation (13)]. Decomposition of $F_3CPH(CN)$ is the

$$F_3CPH(CN) + F_3CPH_2 \longrightarrow (F_3CPH)_2 + HCN \quad (13)$$

most likely route to the cyclic tetramer. Unlike the F_3CPH_2–F_3CPI_2 system, the reaction of F_3CPH_2 with

$$4F_3CPH(CN) \longrightarrow (F_3CP)_4 + 4HCN \quad (14)$$

$F_3CP(CN)_2$ does not appear to give $F_3CPH(CN)$ by direct exchange. In this respect, and in the final products isolated, the reaction resembles that of $MeAsH_2$ with $MeAsI_2$, where $MeAs(H)X$ probably results from a diarsane intermediate,[7] although in the present case no hydrogen is formed.

The behaviour of the phosphines can be summarised by the series [F] : [Cl, Br] : [I, CN] : [H] where compounds separated by a comma or in adjacent square-bracketed groups will react thermally at 70 °C. The equilibrium constants deviated appreciably from randomness, except in the case of exchange involving the adjacent heavier halogens. There is no uniform correlation between the electronegativity of the substituents at phosphorus and the presence or absence of exchange, although substituents of similar electronegativity tend to undergo exchange, and in general the smaller the difference in electronegativity the more nearly the equilibrium constant approaches the random value.

Vibrational Spectra of $F_3CP(H)X$ *and* $F_3CP(D)X$ ($X = I$ *or* Br). The compounds $F_3CP(D)X$ ($X = I$ or Br) were prepared to assist in assignment of the vibrational spectra of the corresponding hydride. All four compounds possess no elements of symmetry (point group C_1), and so all 15 fundamental modes will be i.r. and Raman active. The lack of symmetry increases the mixing possibilities for the normal modes and so the assignments proposed in Table 2 represent only approximate descriptions of the vibrations. However, it is useful to apply these labels because a comparison can be

TABLE 2

Observed bands (cm^{-1}) and proposed assignments for some $F_3CP(H)X$ and $F_3CP(D)X$ molecules *

$F_3CP(H)Br$		$F_3CP(D)Br$		$F_3CP(H)I$		$F_3CP(D)I$		Assignment
Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	
117(4)		118(4)		107(4)		106(4)		CF_3 rock
				242(10)		242(10)		CPI def.
260(10)		261(10)						CPBr def.
275(0.5)		270 (sh)		276(0.5)		275(0.5)		PCF_3 def.
				383(10)	394m	381(10)	390m	PI str.
416(10)	425m, br	413(5)	423m, br	414(3)	415m	412(3)	412m	PC str.
429(10)		425(10)						PBr str.
	458vw (sh)			467(0.5)				2 × 242?
			509w				519w	
539(0.5)	522vw		525w	536(0.5)	532w			CF_3 def.
740(6)	741mw	741(5)	740w	739(3)	739mw	741(4)	742w	CF_3 def.
803(0.5)	804m	594(0.5)	596m	748(2)	754 (sh)		557m	I (or Br) PH (or D) def.
853(0.5)	851m	644(0.5)	638m	844(1)	844m	643(0.5)	642m	CPH (or D) def.
	1 010vw		1 010vw		1 022vw		1 022vw	
	1 103 (sh)		1 104 (sh)		1 102w (sh)		1 101w (sh)	
	1 132vs		1 137vs		1 124vs		1 128vs	CF_3 str.
	1 174vs		1 175vs		1 167vs		1 170vs	CF_3 str.
	1 240vw		1 240vw		1 228vw		1 230vw	
	1 278vw		1 278vw		1 278vw		1 279vw	
	2 232vw		2 232vw		2 242w		2 237w	2 × CF_3 str.
	2 300vw (sh)		2 300vw		2 300vw (sh)		2 300vw	2 × CF_3 str.
2 320(4)	2 318m	1 689(4)	1 689m	2 317(1)	2 327m		1 694m	PH (or D) str.

* Relative Raman intensities are given in parentheses. For i.r. bands: v = very, s = strong, w = weak, br = broad, and sh = shoulder.

made between the spectra of $F_3CP(H)X$ and $F_3CP(D)X$ and those of the corresponding F_3CPX_2 compounds.[14,15]

The phosphines under investigation readily disproportionate, the disproportionation being enhanced by irradiation of the samples with laser light. Thus several freshly prepared samples of each compound were examined to ensure that the genuine spectrum of the undecomposed compound had been identified. For the iodophosphines in particular there were always small bands present in both the i.r. and Raman spectra due to traces of F_3CPH_2 (or F_3CPD_2) and F_3CPI_2. Once these small impurity peaks had been accounted for the remaining bands fell into a very regular and recognisable pattern. The comparison with the related F_3CPX_2 compounds [14,15] leaves little doubt that the descriptions given in Table 2 are essentially correct. The assignment of some very weak features arising from overtone and combination bands by numerical fit is not profitable because of substantial anharmonicity effects.

EXPERIMENTAL

All of the reactions were carried out using a Pyrex vacuum system of conventional design. Many reactions gave complex mixtures of products which were only partially resolvable by vacuum fractionation. Accordingly, it was often convenient to measure the total quantity of products by weight, and by pressure where possible, before attempting resolution of mixtures. In identifying products, the i.r. spectra (Perkin-Elmer 457) and molecular weights of fractions were determined before each fraction was distilled into an n.m.r. tube and CCl_3F and $SiMe_4$ added. N.m.r. spectra were then recorded at 90.0 and 84.66 MHz for ^1H and ^{19}F spectra respectively, using a Bruker Spectrospin HFX instrument. In several cases, confirmatory information about the products was obtained from 70 eV mass spectra recorded on an A.E.I. MS9 instrument.* Trifluoromethylphosphines were prepared by the literature methods.[5,6,9,11,16]

The exchange reactions were carried out in the following way. A measured quantity (*ca.* 0.2 mmol) of each phosphine, carefully checked for purity before use, was condensed into an n.m.r. tube together with pure dry CCl_3F as internal standard. Tetramethylsilane was added for mixtures containing F_3CPH_2. The ^{19}F n.m.r. spectrum was recorded within 1 h of warming to room temperature. Little or no reaction was detected at this stage. The tubes were then heated to 70 °C for 10 d and, after cooling to room temperature, the ^{19}F n.m.r. spectrum was recorded again, the results from this occasion being used for the calculation of the equilibrium constant (see Table 1). The integrated n.m.r. signals were used to obtain the mole fraction of each species. The n.m.r. tubes were kept at room temperature for 6 months and then at 70 °C for a further 10 d but no significant shift in the equilibria was noted when the spectra were remeasured at ambient probe temperature (23 °C). The systems F_3CPF_2–F_3CPBr_2 and F_3CPH_2–$F_3CP(CN)_2$ were more complex and are described in more detail below. In the photolysis experiments, the tube was irradiated through a Pyrex filter with a medium-pressure mercury lamp.

Accurate gas-phase i.r. spectra of $F_3CP(H)X$ and $F_3CP(D)X$ (X = Br or I) were obtained in the range 4 000—250 cm^{-1} on a Perkin-Elmer 457 instrument. Raman spectra were recorded for liquid samples in sealed capillaries using a Carey 81 laser-modified spectrometer with a Coherent Radiation model 52 krypton-ion laser for excitation. Lines at 530.8 and 647.1 nm were used to examine the bromo- and iodo-compounds respectively.

Preparation of Iodo(trifluoromethyl)phosphine, $F_3CP(H)I$.—In a typical reaction I_2 (AnalaR, 5.95 mmol) was weighed into an ampoule and surface water removed by pumping. Trifluoromethylphosphine (10.0 mmol) was distilled onto the iodine and the mixture shaken at 0 °C (1.5 h), by which time all traces of iodine had dissolved. Vacuum fractionation gave F_3CPI_2 (2.17 mmol), $F_3CP(H)I$, a clear yellow liquid [1.50 mmol; *M* 226 (calc. 228)] (41% yield based on F_3CPH_2 consumed), and a mixture of HI and F_3CPH_2 (12.1 mmol). It was convenient to combine the products other than $F_3CP(H)I$ with mercury to produce F_3CPH_2 from F_3CPI_2. The compound $F_3CP(H)I$ was also prepared by warming (40 °C) an equimolar mixture of F_3CPI_2 and F_3CPH_2 in CCl_3F solution. After 2 h, the yield of $F_3CP(H)I$ was 23%. Alternatively, photolysis (8 h) of excess of F_3CPH_2 with F_3CPI_2 in the liquid phase through a Pyrex filter gave $F_3CP(H)I$ in 32% yield. The analogue $F_3CP(D)I$ [*M* 226 (calc. 229)] was prepared similarly from F_3CPD_2 and F_3CPI_2.

Pure samples of $F_3CP(H)I$ underwent slow partial decomposition (23% in 6 months) at 20 °C in a 10% solution in CCl_3F to an equimolar mixture of F_3CPH_2 and F_3CPI_2. The decomposition of the neat liquid was more rapid, although an equilibrium concentration of $F_3CP(H)I$ remained.

Reactions.—F_3CPH_2 *with chlorine*. The phosphine (0.56 mmol) and Cl_2 (0.56 mmol) reacted in 7 d at room temperature in an ampoule (12 cm^3) to give HCl (0.57 mmol, *M* 36.9) and a mixture of F_3CPH_2 (0.32 mmol), $F_3CP(H)Cl$ (0.20 mmol), and F_3CPCl_2 (0.16 mmol). Further reaction occurred in the mixture of phosphines from which HCl had been removed, the concentration of $F_3CP(H)Cl$ decreasing at the expense of F_3CPH_2 and F_3CPCl_2 over a period of several weeks. After 10 months at room temperature, $(F_3CPH)_2$ (0.05 mmol) was present in the sample together with F_3CPH_2 (0.30 mmol), $F_3CP(H)Cl$ (0.06 mmol), and F_3CPCl_2 (0.21 mmol). Vacuum fractionation of the products resulted in separation of HCl (0.05 mmol), not present in the original mixture.

$F_3CP(H)I$ *with* $HgBr_2$. The iodophosphine (0.72 mmol) and dry $HgBr_2$ (1.5 g) were shaken at 20 °C (45 min), giving pure $F_3CP(H)Br$, a colourless liquid (0.685 mmol) [*M* 179 (calc. 181)] as the only volatile product, formed in 96% yield. The analogue $F_3CP(D)Br$ [*M* 180 (calc. 182)] was prepared similarly from $F_3CP(D)I$.

$F_3CP(H)I$ *with* Hg. The phosphine (0.67 mmol) was totally consumed when shaken with clean dry mercury (2 cm^3) for 20 min, giving $(F_3CPH)_2$ (0.32 mmol; 96% yield) (*M* 203), also identified by i.r. and n.m.r. spectroscopy.

$F_3CP(H)I$ *with* $HgCl_2$. The phosphine (0.45 mmol) and

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* 1 eV ≈ 1.60×10^{-19} J.

[14] J. D. Brown, R. C. Dobbie, and B. P. Straughan, *J.C.S. Dalton*, 1973, 1691.

[15] H. Bürger, J. Cichon, R. Demuth, and J. Grobe, *Spectrochim. Acta*, 1973, **A29**, 943.

[16] V. N. Kulakova, Yu. M. Zinovev, and L. Z. Soborovskii, *Zhur. obshchei Khim.*, 1959, **29**, 3957.

$HgCl_2$ (*ca.* 3 g) were shaken at room temperature (2 h) in an evacuated tube. The products were HCl, identified by i.r. spectroscopy, F_3CPH_2 (0.16 mmol), $F_3CP(H)Cl$ (0.06 mmol), F_3CPCl_2 (0.11 mmol), and $(F_3CPH)_2$ (0.05 mmol), all identified by i.r. and n.m.r. spectroscopy. The solid residue in the tube released a further small quantity of F_3CPCl_2 (0.01 mmol) on pyrolysis at 90 °C (2 h).

$F_3CP(H)I$ *with* AgCl. The phosphine (0.75 mmol) partially reacted (10 min) with excess of dry AgCl to give HCl, $F_3CP(I)Cl$ (0.04 mmol), F_3CPCl_2 (0.01 mmol), $(F_3CPH)_2$ (0.08 mmol), in addition to $F_3CP(H)I$ (0.22 mmol), F_3CPH_2 (0.20 mmol), and F_3CPI_2 (0.13 mmol). In another reaction, prolonged shaking (16 h) of $F_3CP(H)I$ (0.47 mmol) with AgCl gave HCl (0.05 mmol), F_3CPH_2 (0.18 mmol), $F_3CP(H)Cl$ (0.05 mmol), F_3CPCl_2 (0.19 mmol), and $(F_3CPH)_2$ (0.03 mmol), the products being identified by i.r., n.m.r., and mass spectroscopy.

$F_3CP(H)I$ *with* AgBr. Shaking $F_3CP(H)I$ (0.71 mmol) with dry silver bromide (3 g) for 1 h gave a trace of HBr together with a pale yellow liquid, found by spectroscopic methods to consist of $F_3CP(H)I$ (0.11 mmol), F_3CPH_2 (0.32 mmol), F_3CPI_2 (0.19 mmol), F_3CPBr_2 (0.02 mmol), and $F_3CP(I)Br$ (0.06 mmol). The products, dissolved in CCl_3F, were shaken (3 h) with a fresh batch of AgBr, giving a colourless solution containing a further trace of HBr (unmeasured), F_3CPH_2 (0.35 mmol), $F_3CP(H)Br$ (0.10 mmol), and F_3CPBr_2 (0.25 mmol).

$F_3CP(H)I$ *with* AgCN. When $F_3CP(H)I$ (0.57 mmol) was shaken (2 h, 20 °C) with AgCN (0.25 g) the solid became yellow-green and the volatile products were HCN (0.54 mmol), contaminated by a small quantity of an unknown phosphine, F_3CPH_2 (0.07 mmol), and a mixture of $(F_3CP)_4$ and $(F_3CP)_5$ (0.31 mmol of 'F_3CP'). The unknown phosphine was thermally unstable, evolving more F_3CP tetramer and pentamer at room temperature.

$F_3CP(H)I$ *with* $Hg[CN]_2$. Mercury(II) cyanide (2.32 g) and $F_3CP(H)I$ (0.86 mmol) reacted at 20 °C to give HCN (0.77 mmol), identified by i.r. spectroscopy and molecular-weight measurements, and a trace amount (0.01 mmol) of an unknown trifluoromethylphosphorus compound. Heating the residue at 110—120 °C for 24 h gave a further quantity of HCN (0.05 mmol), $F_3CP(CN)_2$ (0.67 mmol), and small amounts of unidentified material. Globules of free mercury were observed in the tube after pyrolysis.

$F_3CP(H)I$ *with some fluorinating agents.* Antimony trifluoride was sublimed directly into the reaction tube and shaken for 30 min with $F_3CP(H)I$ (0.55 mmol) at 0 °C. The major volatile products were SiF_4 and F_3CPH_2, while a less volatile liquid was identified as $(F_3CPH)_2$ (*ca.* 0.15 mmol). There was some evidence from i.r. spectroscopy for the presence of a small amount of an unstable phosphine, possibly $F_3CP(H)F$, characterised by a band with a distinctive fine structure centred at 860 cm^{-1}. The reaction of $F_3CP(H)I$ with CdF_2 also gave SiF_4, $(F_3CPH)_2$, and the same unstable phosphine. With NaF in acetonitrile, $F_3CP(H)I$ again gave $(F_3CPH)_2$ as the major product. No SiF_4 was produced.

$(F_3CPH)_2$ *with* HI *and with* HCl. The diphosphane (0.46 mmol) and pure anhydrous HI (1.10 mmol) reacted at room temperature (24 h) to give F_3CPH_2 (0.60 mmol), $F_3CP(H)I$ (0.06 mmol), and F_3CPI_2 (0.17 mmol), in addition to excess of HI. With HCl (1.18 mmol) the diphosphane (0.34 mmol) reacted to a small extent (5% in 24 h at 20 °C), giving a mixture of F_3CPH_2, $F_3CP(H)Cl$, and F_3CPCl_2 (0.02 mmol together).

F_3CPF_2 *with* F_3CPBr_2. A mixture of F_3CPF_2 (0.20 mmol; 52% of phosphorus present) and F_3CPBr_2 (0.19 mmol; 48%) showed the presence of $F_3CP(F)Br$ (*ca.* 7%) after 10 d at 70 °C. On standing at room temperature for a further 40 d the products were PF_3 (2%), $(F_3C)_2PBr$ (3%), $F_3CP(F)Br$ (3%), F_3CPF_2 (45%), and F_3CPBr_2 (47%).

F_3CPH_2 *with* $F_3CP(CN)_2$. The phosphine (3.73 mmol) and $F_3CP(CN)_2$ (2.50 mmol) were warmed (50 °C, 14 d) in a tube (25 cm^3). The products, separated completely by vacuum fractionation, were F_3CPH_2 (1.03 mmol), $(F_3CP)_4$ (1.25 mmol), HCN (4.90 mmol), and $(F_3CPH)_2$ (0.15 mmol).

Photolysis of F_3CPH_2 *with* F_3CPCl_2. A mixture of the phosphines, prepared as described above for the thermal-exchange experiments, showed F_3CPH_2 (49.6% of CF_3 groups present), F_3CPCl_2 (43.0%), $F_3CP(H)Cl$ (4.8%), $(F_3C)_2PCl$ (0.9%), and $(F_3C)_2PH$ (1.7%) after 2 h irradiation.

Photolysis of F_3CPH_2 *with* F_3CPBr_2.—A mixture of F_3CPH_2 and F_3CPBr_2 likewise consisted of F_3CPH_2 (29.5% of CF_3), F_3CPBr_2 (59.0%), $F_3CP(H)Br$ (11.1%), and $(F_3C)_2PBr$ (0.5%) after 2 h irradiation.

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