sh 1304 (0.7), 1279 (0.95); and for $CF_3P(S)Cl_2$ at 1384 (0.12), 1334 (0.12), 1313 (0.32), 1283 (0.28), sh 1276 (0.19), sh 1266 (0.12), sh 1151 (1.9), 1132 (0.73), 650 (0.1), 614 (0.1), and sh 590 (2) cm^{-1}. Among these, it is possible to recognize a Fermi-resonance enhanced overtone of CF_3 asymmetric deformation, found for $(CF_3)_2P(S)NH_2$ at 1133 (2.3) cm^{-1}. A peak at 406 (2.1) cm^{-1} for this compound might represent NH_2-group torsion. Not yet assigned are 538 (1.2) cm^{-1} for $(CF_3)_2P(S)SCH_3$, and for $(CF_3)_2P(S)N(CH_3)_2$ 450 (0.9) and 394 (0.23) cm^{-1}. The number of weak and difficultly assignable peaks and shoulders for any of these compounds doubtless could increase indefinitely with increasing pressure and path length. Inflections suggestive of P and R branches were especially noticeable for modes concerning the CF_3 groups, but often were detectable for other fundamental modes as well.

Probably the most significant trend in Table IV is that shown by the P=S frequencies—especially the P=S stretching mode. It is quite clear that these frequencies decrease with increasing π-donor bonding power of the adjacent groups X: least for chloride and most for the amides. It is a reasonable rule that the P=S bond order decreases as the adjacent groups feed π electron density more effectively toward phosphorus, and the present results support such a rule.

Preparation and Properties of Bis(trifluoromethyl)dithiophosphinic Acid and Some Related Pentavalent Trifluoromethylphosphine Sulfides

R. C. Dobbie,[1] L. F. Doty, and R. G. Cavell

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada. *Received September 20, 1967*

Abstract: The aminophosphine sulfides, $(CF_3)_2P(S)NR_2$, where R = H or CH_3, and the halophosphine sulfides, $(CF_3)_2P(S)X$, where X = F, Cl, Br, and I, are prepared by heating the corresponding phosphines with sulfur. The chloro and bromo compounds are best prepared by the action of the appropriate hydrogen halide on $(CF_3)_2P(S)NMe_2$, while the fluoride is conveniently obtained by the action of antimony trifluoride on $(CF_3)_2P(S)Br$. When the iodo compound is shaken with mercury, $(CF_3)_2PSP(CF_3)_2$ is formed, while with mercury and hydrogen iodide the product is $(CF_3)_2PSH$, formed by an anti-Arbuzov rearrangement. Bis(trifluoromethyl)dithiophosphinic acid, $(CF_3)_2P(S)SH$, is formed by heating sulfur with either $(CF_3)_2PH$ or $(CF_3)_2PSH$. Addition of sulfur to CF_3PFNMe_2 and PF_2NMe_2 also gives the corresponding sulfides. The nmr and mass spectra of the new compounds are discussed.

While the chemistry of trifluoromethyl compounds of trivalent phosphorus has been extensively studied,[2] work on the corresponding phosphorus(V) derivatives has been limited to the preparation of halo[3,4] and oxy compounds,[5–10] and of one sulfide, $(CF_3)_3P{=}S$.[11] This paper describes the preparation and properties of some compounds containing the $(CF_3)_2P(S)$ group.

Results and Discussion

Synthesis and Properties of the Phosphine Sulfides. Heating aminobis(trifluoromethyl)phosphine with sulfur in a sealed tube at 180° readily gave the pentavalent phosphine sulfide $(CF_3)_2P(S)NH_2$ in 85% yield based on the aminophosphine consumed. Likewise dimethylaminobis(trifluoromethyl)phosphine, $(CF_3)_2PN(CH_3)_2$, reacted with sulfur at 150° to give the sulfide, $(CF_3)_2P(S)N(CH_3)_2$, although the yields were considerably lower.

Alkaline hydrolysis of $(CF_3)_2P(S)NH_2$ gave only 1 mole of CF_3H. This behavior is readily attributed to the formation of a hydrolytically stable acid containing a CF_3P^V group in solution in common with the behavior of $(CF_3)_3PCl_2$,[5] $(CF_3)_3PO$,[7] and $(CF_3)_3PS$[11] which gave only 2 moles of CF_3H upon alkaline hydrolysis. The evolution of 1 mole of fluoroform less than the total number in the molecule was characteristic of the compounds described in this paper, and the yield of fluoroform upon alkaline hydrolysis was used for analysis.

The chloride and bromide, $(CF_3)_2P(S)X$ (X = Cl, Br), were best prepared by the nearly quantitative reaction of the dimethylamido compound with a large excess of hydrogen halide at high pressure in a sealed tube, *e.g.*

$$(CF_3)_2P(S)N(CH_3)_2 + 2HX \longrightarrow (CF_3)_2P(S)X + (CH_3)_2NH_2^+X^-$$

The reaction was very slow at low pressures of hydrogen halide, suggesting that $(CF_3)_2P(S)N(CH_3)_2$ is only weakly basic. The oxygen analog, $(CF_3)_2P(O)N(CH_3)_2$, exhibits parallel behavior toward acids.[10] The chloride

---

[1] NRC Postdoctoral Fellow (1966–1967). Present address: Department of Inorganic Chemistry, The University, Bristol, England.

[2] H. C. Clark, *Advan. Fluorine Chem.*, 3, 19 (1963).

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

[4] W. Mahler, *Inorg. Chem.*, 2, 230 (1963).

[5] H. J. Emeléus, R. N. Haszeldine, and R. C. Paul, *J. Chem. Soc.*, 563 (1955).

[6] W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, 80, 6161 (1958).

[7] R. C. Paul, *J. Chem. Soc.*, 574 (1955).

[8] A. B. Burg and J. E. Griffiths, *J. Am. Chem. Soc.*, 83, 4333 (1961).

[9] J. E. Griffiths and A. B. Burg, *ibid.*, 84, 3442 (1962).

[10] A. B. Burg and A. J. Sarkis, *ibid.*, 87, 238 (1965).

[11] R. G. Cavell and H. J. Emeléus, *J. Chem. Soc.*, 5896 (1964).

and bromide could also be prepared by heating $(CF_3)_2PCl$ or $(CF_3)_2PBr$ with sulfur. This reaction is not quantitative, but the products can be easily separated and the recovered starting materials can be used to prepare more of the phosphine sulfide.

The fluoride $(CF_3)_2P(S)F$ was best obtained by the slow room-temperature reaction of antimony trifluoride with $(CF_3)_2P(S)Br$. The infrared spectrum of the product showed a strong band at 920 cm^{-1}, in the region expected for the P–F stretching frequency in a pentavalent compound containing trifluoromethyl groups.[4] The fluoride was also produced by the direct addition of sulfur to $(CF_3)_2PF$, although a number of minor products were also formed in this reaction which rendered isolation of the desired fluorophosphine sulfide difficult.

The action of sulfur on the iodophosphine, $(CF_3)_2PI$, at 150° (16 hr) gave $(CF_3)_2P(S)I$ in 64% yield. The compound was a colorless liquid which froze to a crystalline solid with a tendency to sublime under vacuum. In addition to unreacted iodophosphine and the desired iodophosphine sulfide, the reaction products also contained CF_3I, $(CF_3)_3P$, $(CF_3)_3P{=}S$, and an unidentified involatile liquid. Since $(CF_3)_2P(S)I$ was subsequently shown to suffer very little decomposition after 54 hr at 100°, it appeared that the other products must have been formed from the products of the disproportionation of $(CF_3)_2PI$, a reaction which is known[3] to occur at 100°. Addition of sulfur to $(CF_3)_3P$ could have given $(CF_3)_3P{=}S$ and the involatile liquid material could have been $CF_3P(S)I_2$, formed by addition of sulfur to CF_3PI_2. Although $(CF_3)_3P$ has been reported[3] not to react with sulfur at 180° in 3 days, it was found in a separate experiment that about 50% of the phosphine was converted to $(CF_3)_3P{=}S$ after 4 days at 200°.

Similarly, heating sulfur with the fluorophosphines $CF_3PFN(CH_3)_2$ and $PF_2N(CH_3)_2$ gave the sulfides $CF_3PF(S)N(CH_3)_2$ and $PF_2(S)N(CH_3)_2$, respectively. The first of these sulfides would be a useful starting compound in the examination of the chemistry of the $CF_3PF(S)$– group, while the latter is known[12] to be a useful intermediate. The new synthesis of $PF_2(S)N(CH_3)_2$ is the second step in a two-stage preparation from PF_3[13] which is well suited to small-scale work on a vacuum system.

With the exception of $(CF_3)_2P(S)I$, the variation of the vapor pressure with temperature of the new phosphine sulfides was examined in a Pyrex spiral gauge microtensimeter. The results (given in Table V) could be expressed by a linear equation of the form

$$\log P_{\mathrm{mm}} = -A/T + B$$

within the experimental error. The values of A and B together with extrapolated boiling points and other physical constants are shown in Table I. The abnormal Trouton constants of the less volatile amido compounds $(CF_3)_2P(S)N(CH_3)_2$, $CF_3PF(S)N(CH_3)_2$, and $(CF_3)_2P(S)NH_2$ are probably the result of extrapolation of the linear vapor pressure equation over long temperature range rather than hydrogen bonding which is not likely to be of importance for the dimethylamino derivatives. The amidophosphine sulfide $(CF_3)_2P(S)NH_2$, however, may be hydrogen bonded in the liquid in keeping with a similar suggestion proposed to explain the behavior of the amidophosphine $(CF_3)_2PNH_2$.[14] Our results are in reasonable agreement with the more accurate data for $(CF_3)_2P(S)N(CH_3)_2$ reported elsewhere.[15] This data have been fitted to a nonlinear equation which yields a normal Trouton constant.[15] $(CF_3)_2P(O)N(CH_3)_2$ exhibits similar vapor pressure behavior to the sulfur analog,[10] and it appears that the vapor pressures of amidophosphine oxides and sulfides are best expressed by the nonlinear equation.

Table I. Volatility of Seven New Trifluoromethylphosphine Sulfides

Compound	Range studied, °C	A	B	T_b, °C	ΔH_v, kcal mole^{-1}	$\Delta H_v/T_b$
$(CF_3)_2P(S)NH_2$	10–70	2240	8.43	131	10.23	25.4
$(CF_3)_2P(S)N(CH_3)_2$	15–70	2265	8.38	139	10.37	25.2
$(CF_3PF(S)N(CH_3)_2$	10–60	2206	8.43	124	10.10	25.4
$(CF_3)_2P(S)F$	−30–15	1385	7.63	18	6.33	21.8
$(CF_3)_2P(S)Cl$	10–50	1597	7.65	62	7.31	21.8
$(CF_3)_2P(S)Br$	10–55	1840	8.09	80	8.42	23.8
$(CF_3)_2P(S)SH$	10–70	1924	8.015	102	8.80	23.5

Reactions of the Iodophosphine Sulfide. The reactions of bis(trifluoromethyl)iodophosphine sulfide, $(CF_3)_2P(S)I$, with mercury and with mercury and hydrogen iodide were of special interest as the products were derivatives of phosphorus(III), indicating that an anti-Arbuzov rearrangement[16] of the expected phosphorus(V) compounds to phosphorus(III) compounds had occurred in each case. Since the diphosphine, $(CF_3)_2PP(CF_3)_2$, is formed in high yield when iodobis(trifluoromethyl)phosphine is shaken with mercury,[3] the anticipated product from the action of mercury on the iodophosphine sulfide would be the diphosphine disulfide, $(CF_3)_2P(S)P(S)(CF_3)_2$. However, the only volatile product, formed in 96% yield, was the sulfur-bridged diphosphine, $(CF_3)_2PSP(CF_3)_2$.[17] The expected diphosphine disulfide might form, but lose one sulfur (either spontaneously or through the reducing action of the excess mercury), followed by rearrangement to the phosphorus(III) compound.

When the pentavalent iodophosphine sulfide, $(CF_3)_2P(S)I$, was reduced with mercury and hydrogen iodide, the product was $(CF_3)_2PSH$. Under these conditions, $(CF_3)_2PI$ is known[18] to be reduced to $(CF_3)_2PH$ so that an anti-Arbuzov rearrangement[16] of the expected $(CF_3)_2P(S)H$ to $(CF_3)_2PSH$ appears to have taken place. The intermediate in the reaction might be the diphosphine disulfide $(CF_3)_2P(S)P(S)(CF_3)_2$, which would be cleaved by Hg–HI in the same way as $(CF_3)_2PP(CF_3)_2$[18] to give $(CF_3)_2PSH$, assuming a P(V) to P(III) rearrangement following the cleavage of the P–P bond. This seems more probable than a reaction going through $(CF_3)_2PSP(CF_3)_2$, since cleavage of this compound by HBr[17a] has been shown to give $(CF_3)_2PSH$ and $(CF_3)_2PBr$. Cleavage by HI would therefore be expected to give $(CF_3)_2PSH$ and $(CF_3)_2PI$, the latter being reduced

(12) R. G. Cavell, *Can. J. Chem.*, in press.

(13) R. G. Cavell, *J. Chem. Soc.*, 1992 (1964).

(14) G. S. Harris, *ibid.*, 512 (1958).

(15) K. Gosling and A. B. Burg, *J. Am. Chem. Soc.*, **90**, 2011 (1968). We are indebted to Professor Burg for sending us a copy of the paper prior to publication.

(16) J. E. Griffiths and A. B. Burg, *Proc. Chem. Soc.*, 12 (1961).

(17) (a) R. G. Cavell and H. J. Emeléus, *J. Chem. Soc.*, 5825 (1964); (b) A. B. Burg and K. Gosling, *J. Am. Chem. Soc.*, **87**, 2113 (1965).

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

to $(CF_3)_2PH$,[18] so that equal amounts of the hydride and mercaptophosphine would result.

Synthesis of Bis(trifluoromethyl)dithiophosphinic Acid. The lack of success in preparing the pentavalent hydride, $(CF_3)_2P(S)H$, by the reduction of $(CF_3)_2P(S)I$ prompted an investigation of the reaction of bis(trifluoromethyl)phosphine with sulfur. Two moles of sulfur was consumed to give bis(trifluoromethyl)dithiophosphinic acid, $(CF_3)_2P(S)SH$, contaminated by about 10% of the diphosphine sulfide, $(CF_3)_2PSP(CF_3)_2$, which could not be separated by vacuum fractionation. The formation of the latter may be explained by the abstraction of hydrogen from the phosphine by sulfur, according to the equation

$$2(CF_3)_2PH + 2S \longrightarrow [(CF_3)_2P]_2S + H_2S$$

while the former would arise by addition of sulfur to $(CF_3)_2PSH$, in turn formed from $(CF_3)_2P(S)H$ by an anti-Arbuzov rearrangement. The corresponding arsine, $(CF_3)_2AsH$, has been reported[19] to react with sulfur to give $(CF_3)_2AsSAs(CF_3)_2$ as the sole product. The difference in the behavior of the phosphorus and arsenic compounds toward sulfur may be rationalized by comparing the strengths of the As–H and P–H bonds (59 and 77 kcal mole^{-1} in AsH_3 and PH_3, respectively[20]).

When $(CF_3)_2PSH$ was heated with sulfur, the acid sulfide $(CF_3)_2P(S)SH$ was isolated as a pure compound, free of $(CF_3)_2PSP(CF_3)_2$. The new compound (extrapolated bp 102°) showed a weak absorption in the infrared spectrum at 2580 cm^{-1}, and another of medium intensity at 846 cm^{-1}, assigned to S–H stretching and bending vibrations, respectively.

It is interesting to note that none of the pentavalent phosphorus compounds described above is the isomer of the thiophosphines already reported in the literature.[17] In particular, the apparent instability of the pentavalent hydride, $(CF_3)_2P(S)H$, with respect to the trivalent isomer is surprising in view of the exceptional stability of hydrothiophosphoryl difluoride, $F_2P(S)H$,[21] which shows no tendency to rearrange to F_2PSH. The anti-Arbuzov rearrangements[16] of the trifluoromethyl compounds cannot therefore be attributed *solely* to the effect of strong electron-withdrawing groups on phosphorus.

Nmr Spectra. The ^{19}F and ^{1}H nmr spectral parameters are shown in Table II. The resonance of the CF_3 groups is shifted upfield by 6–12 ppm compared with the trivalent phosphorus compounds[17a,22] lacking the P=S grouping. The F–C–P coupling constants ($^2J_{FP}$) are all larger than the range of values found in CF_3P[23] or $(CF_3)_2P$[22] derivatives of phosphorus(III) but exhibit the same general increase with the electronegativity of the substituent on phosphorus noted by Packer for the trivalent compounds. The directly bonded F–P coupling constants in $(CF_3)_2P(S)F$ and $CF_3PF(S)N(CH_3)_2$ are also in the range expected[24] for pentavalent rather than trivalent phosphorus fluorides. Thus the nmr spectra support the formulation of the new compounds as phosphorus(V) derivatives. No F–H coupling was observed in $(CF_3)_2P(S)NH_2$, and the ^1H resonance spectrum showed a very broad signal whose position could not be determined accurately; both phenomena have also been noted in the nmr spectrum of the phosphine, $(CF_3)_2PNH_2$.[25] The ^1H resonance spectrum of the dithiophosphinic acid, $(CF_3)_2P(S)SH$, was of interest as a single line was observed at the normal operating temperature of the spectrometer (41°), although H–P coupling might be expected to give a doublet of separation similar to that in $(CF_3)_2PSH$ ($^2J_{HP}$ = 22.6 cps).[17a] However, when the sample was cooled to −114°, the lowest operating temperature of the spectrometer, the signal split into a doublet with broad components of equal intensity separated by about 16 cps. Further details of the spectrum and its interpretation will be published elsewhere.

Table II. ^1H and ^{19}F Nmr Spectra of Some Trifluoromethylphosphine Sulfides

Compound	ϕ ppm	J_{FP}, cps	τ
$(CF_3)_2P(S)NH_2$	73.5	111.0	
$(CF_3)_2P(S)N(CH_3)_2$[a]	68.3	102.9	7.20
$CF_3PF(S)N(CH_3)_2$[b]	72.3	121.5	7.22
	76.8[d]	1084[d]	
$(CF_3)_2P(S)F$[c]	72.3	128.6	
	94.5[d]	1174.6[d]	
$(CF_3)_2P(S)Cl$	70.5	123.1	
$(CF_3)_2P(S)Br$	70.1	119.7	
$(CF_3)_2P(S)I$	70.1	111.4	
$(CF_3)_2P(S)SH$	71.0	110.0	7.33

[a] $^2J_{HP}$ = 10.7 cps, $^5J_{FH}$ = 0.7 cps. [b] $^3J_{FF}$ = 5.8 cps, $^5J_{FH}$ = 0.8 cps, $^4J_{FH}$ = 2.5 cps, $^2J_{HP}$ = 10.9 cps. [c] $^3J_{FF}$ = 1.6 cps. [d] These values refer to the P–F group. All other fluorine parameters refer to the CF_3 group.

Mass Spectra. It is now known[26] that trifluoromethyl derivatives of trivalent phosphorus and arsenic undergo rearrangement in the mass spectrometer to give ions with P–F and As–F bonds. The mass spectra of the pentavalent phosphorus sulfides also showed rearrangement under electron impact, the rearranged ions contributing between 19 and 35% to the total ionization. The principal ions in the spectra are shown in Table III, while Table IV lists some metastable ions. The parent ion was intense in all of the spectra, as in $F_2P(S)$–derivatives[21] and $(C_6F_5)_3P{=}S$[27] but in contrast to fluorocarbon phosphorus(V) halides[25,27] such as CF_3PCl_4 and $(C_6F_5)_3PCl_2$ which do not show a parent ion. The breakdown pattern of all of the compounds examined was remarkably similar. Initial fragmentation was by loss of CF_3 followed either by elimination of CF_2S, probably as thiocarbonyl fluoride, $S{=}CF_2$, or by loss of CF_2, as follows. The fragmentation pattern was

$$(CF_3)_2P(S)X^+ \longrightarrow CF_3P(S)X^+ + CF_3$$

$$CF_3P(S)X^+ \longrightarrow FPX^+ + SCF_2$$

$$\searrow FP(S)X^+ + CF_2$$

demonstrated by observation of the appropriate metastable ions in several spectra, and by precise mass

---

(19) W. R. Cullen, *Can. J. Chem.*, **41**, 2424 (1963).

(20) T. L. Cottrell, "Strengths of Chemical Bonds," Butterworth & Co., Ltd., London, 1958.

(21) T. L. Charlton and R. G. Cavell, *Chem. Commun.*, 763 (1966); *Inorg. Chem.*, **6**, 2204 (1967).

(22) K. J. Packer, *J. Chem. Soc.*, 960 (1963).

(23) J. F. Nixon, *ibid.*, 777 (1965).

(24) E. L. Muetterties and W. D. Phillips, *Advan. Inorg. Chem. Radiochem.*, **4**, 231 (1962).

(25) R. G. Cavell and R. C. Dobbie, unpublished work.

(26) R. C. Dobbie and R. G. Cavell, *Inorg. Chem.*, **6**, 1450 (1967); R. G. Cavell and R. C. Dobbie, *ibid.*, **7**, 101, 690 (1968).

(27) J. M. Miller, *J. Chem. Soc., A*, 828 (1967).

Table III. Mass Spectra of the Compounds $(CF_3)_2P(S)X$

Ion	X = NH_2[b]	NMe_2[c]	F[d]	Cl[e]	Br	SH[f]	CF_3[g]
	Intensity[a]						
$(CF_3)_2P(S)X$	23.6[h]	4.2[h]	30.9[h]	33.2[h]	26.0[h]	6.6[h]	27.5[h]
$CF_3P(S)X$	18.0	24.9	5.4	7.7	18.0	3.7[h]	2.1[h]
CF_3PX	2.3	2.9	10.8	4.3	3.2	8.0[h]	
CF_3PF				5.4	2.4	1.4[h]	
$FP(S)X$	18.3[h]	15.7[h]		2.2	2.0	1.6[h]	
FPX	15.6	9.2[h]		15.5[h]	9.6[h]	10.1[h]	10.6[h]
$P(S)X$	2.1	0.9	3.4	1.8	1.4		
CF_3	4.4[h]	2.2[h]	14.7[h]	2.7[h]	4.4[h]	6.9[h]	16.9[h]
PF_2	0.9[h]	1.1[h]	15.4[h]	1.5[h]	9.8[h]	6.8[h]	16.3[h]
PS	5.4	5.5	10.6	17.5	16.6	14.5	14.0
CF	0.7[h]		5.0[h]	3.3[h]	3.4[h]	2.5	4.5[h]

[a] Expressed as per cent of total ionization, defined as Σ_n (intensity) for all ions with m/e >30 having intensity >2% of the strongest peak. [b] PNH^+, 6.5%. [c] $P(S)NC_2H_5^+$, 1.7%; $CF_2NC_2H_6^+$, 3.1%;[h] $PNCH_3^+$, 2.3%; $NC_2H_6^+$, 7.2%; $NC_2H_5^+$, 7.0%; $NC_2H_4^+$, 11.3%. [d] CF_2^+, 2.1%. [e] $(CF_3)_2P(S)^+$, 3.2%. [f] $(CF_3)_2PSH^+$, 8.9%;[h] $F_2PS_2H^+$, 2.8%;[h] CF_3PH^+, 1.0%;[h] CF_3P^+, 1.4%;[h] CF_2PS^+, 1.1%;[h] PS_2^+, 1.2%; CF_2SH^+, 1.0%;[h] PSH^+, 2.5%; CF_2H^+, 2.0%;[h] CF_2^+, 0.6%.[h] [g] $(CF_3)_2P(S)^+$, 2.1%; $(CF_3)_2P^+$, 2.2%. [h] Composition established by exact mass measurement.

Table IV. Some Metastable Ions in the Mass Spectra of the Compounds $(CF_3)_2P(S)X$

	Obsd	Calcd	Transition
$(CF_3)_2P(S)NH_2$	100.9	100.9	$(CF_3)_2P(S)NH_2^+ \longrightarrow CF_3P(S)NH_2^+ + CF_3$
$(CF_3)_2P(S)NMe_2$	126.6	126.2	$(CF_3)_2P(S)NMe_2^+ \longrightarrow CF_3P(S)NMe_2^+ + CF_3$
	61.4	61.3	$CF_3PNMe_2^+ \longrightarrow FPNMe_2^+ + CF_2$
$(CF_3)_2P(S)F$	103.7	103.6	$(CF_3)_2P(S)F^+ \longrightarrow CF_3P(S)F^+ + CF_3$
$(CF_3)_2P(S)Cl$	120.1	120.0	$(CF_3)_2P(S)^{37}Cl^+ \longrightarrow CF_3P(S)^{37}Cl^+ + CF_3$
	118.2	118.2	$(CF_3)_2P(S)^{35}Cl^+ \longrightarrow CF_3P(S)^{35}Cl^+ + CF_3$
	44.8	44.9	$CF_3P(S)^{37}Cl^+ \longrightarrow FP^{37}Cl^+ + CF_2S$
	43.3	43.2	$CF_3P(S)^{35}Cl^+ \longrightarrow FP^{35}Cl^+ + CF_2S$
$(CF_3)_2P(S)Br$	161.0	160.9	$(CF_3)_2P(S)^{81}Br^+ \longrightarrow CF_3P(S)^{81}Br^+ + CF_3$
	159.2	159.0	$(CF_3)_2P(S)^{79}Br^+ \longrightarrow CF_3P(S)^{79}Br^+ + CF_3$
	80.7	80.6	$CF_3P(S)^{81}Br^+ \longrightarrow FP^{81}Br^+ + CF_2S$
	79.0	78.9	$CF_3P(S)^{79}Br^+ \longrightarrow FP^{79}Br^+ + CF_2S$
$(CF_3)_3PS$	149.7	149.6	$(CF_3)_3PS^+ \longrightarrow (CF_3)_2PS^+ + CF_3$
	70.5	70.5	$(CF_3)_2PS^+ \longrightarrow CF_3PF^+ + CF_2S$
$(CF_3)_2P(S)SH$	116.4	116.5	$(CF_3)_2P(S)SH^+ \longrightarrow CF_3P(S)SH^+ + CF_3$
	87.6	87.6	$(CF_3)_2PSH^+ \longrightarrow CF_3PSH^+ + CF_3$

measurement of ambiguous peaks, necessary since CF and P are nearly equal in mass.

Experimental Section

All of the manipulations were carried out in a conventional Pyrex vacuum system. Reactions were done in sealed Pyrex tubes and the products separated by fractional condensation through appropriate series of cold baths. Molecular weights were determined by Regnault's method. Hydrolysis was done by condensing a weighed quantity of the compound into a Pyrex tube containing 2 ml of 1 *N* sodium hydroxide solution. The tube and contents were kept at room temperature for several hours, and then the evolved CF_3H was removed, purified by vacuum fractionation, and weighed. Infrared spectra were recorded on a Perkin-Elmer 337 grating spectrometer, and nmr spectra on a Varian A56/60A. For ^{19}F spectra, recorded at 56.4 Mcps, the compound was made up as a 10% solution in CCl_3F, the reference compound, while for ^1H spectra, recorded at 60.0 Mcps, a capillary containing 5% TMS was added to the tube as an external standard. Mass spectra were recorded on an AEI MS 9 operating at an ionizing voltage of 70 ev, samples being introduced as vapors through a heated inlet system at 185°. Mass measurement was carried out by peak matching against perfluorotri-*n*-butylamine.

Preparation of $(CF_3)_2P(S)NH_2$. Aminobis(trifluoromethyl)phosphine (0.195 g, 10.5 mmoles), prepared from $(CF_3)_2PCl$ and ammonia,[14] was combined with sulfur and heated in a sealed tube at 180° (4 days). Vacuum fractionation gave $(CF_3)_2PNH_2$ (0.072 g, 0.39 mmole), identified by its infrared spectrum, and aminobis(trifluoromethyl)phosphine sulfide, $(CF_3)_2P(S)NH_2$ (0.122 g, 0.56 mmole), which was trapped at −63°. *Anal.* Calcd for $C_2H_2F_6NPS$: CF_3 liberated on alkaline hydrolysis, 31.8%; *m/e* (mass spectrometer), 216.9550; mol wt, 217. Found: CF_3, 31.2%; *m/e*, 216.9550; mol wt, 219. A trace of an involatile solid which distilled slowly in the vacuum system was discarded. The aminophosphine sulfide had bands in the infrared spectrum at 3520 m, 3415 m, 1540 s, 1300 w, 1221 vs, 1192 vs, 1170 vs, 960 s, 928 s, 758 m, 704 s, 543 m, 488 m cm^{-1}.

Preparation of $(CF_3)_2P(S)N(CH_3)_2$. In a typical experiment, $(CF_3)_2PN(CH_3)_2$ (0.243 g, 0.99 mmole), prepared from $(CF_3)_2PCl$ and $(CH_3)_2NH$,[14] and sulfur were heated in a sealed tube at 150° for 3 days. The products were unreacted $(CF_3)_2PN(CH_3)_2$ (0.171 g, 0.70 mmole), identified by its infrared spectrum, and dimethylaminobis(trifluoromethyl)phosphine sulfide, $(CF_3)_2P(S)N(CH_3)_2$ (0.068 g, 0.28 mmole). The desired product was trapped at −63°. *Anal.* Calcd for $C_4H_6F_6NPS$: CF_3 liberated on alkaline hydrolysis, 28.2%; *m/e* (mass spectrometer), 244.9863; mol wt, 245 Found: CF_3, 27.9%; *m/e*, 244.9866; mol wt, 246.5. The infrared spectrum showed absorption at 2950 w, 2922 w, 2870 w-2840 and 2815 (doublet) w, 1465 w, 1300 w, 1207 vs, 1178 vs, 1164 vs, 1122 w, 1070 w, 993 s, 787 s, 749 w, 673 m, 548 w, 487 m cm^{-1}.

Preparation of $(CF_3)_2P(S)Cl$. (a) From the Aminophosphine Sulfide and Hydrogen Chloride. $(CF_3)_2P(S)N(CH_3)_2$ (0.101 g, 0.41 mmole) and HCl (0.150 g, 4.11 mmoles) were allowed to react in a sealed tube (volume ~10 cc) at room temperature (16 hr). Excess HCl (0.119 g, 3.27 mmoles) was recovered and identified spectroscopically, leaving as the other volatile product the chlorophosphine sulfide, $(CF_3)_2P(S)Cl$ (0.089 g, 0.38 mmole), trapped at −96°. *Anal.* Calcd for C_2ClF_6PS: CF_3 liberated on alkaline hydrolysis, 29.2%; *m/e* (mass spectrometer, ^{35}Cl isotope), 235.9052; mol wt, 236.5. Found: CF_3, 28.8%; *m/e*, 235.9054; mol wt, 236.7. The principal bands in the infrared spectrum were at 1288 w, 1270 w, 1207 vs, 1176 vs, 1149 m, 796 s, 741 s, 576 s, 530 m, 481 m cm^{-1}.

(b) From the Chlorophosphine and Sulfur. $(CF_3)_2PCl$ (0.311 g, 1.52 mmoles) and sulfur (~1 g), heated in a sealed tube at 180° for 4 days, gave unreacted chloro compound (0.053 g, 0.26 mmole), and $(CF_3)_2P(S)Cl$ (0.288 g, 1.22 mmoles), identified by its infrared and nmr spectrum and molecular weight (found: mol wt, 235).

Preparation of $(CF_3)_2P(S)Br$. (a) From the Aminophosphine Sulfide and Hydrogen Bromide. $(CF_3)_2P(S)N(CH_3)_2$ (0.178 g, 0.73 mmole) was allowed to warm to room temperature in a small sealed tube with a large excess of HBr (0.406 g, 5.02 mmoles). Vacuum fractionation gave HBr (0.208 g, 2.57 mmoles) and $(CF_3)_2P(S)Br$ (0.194 g, 0.69 mmole), the latter being trapped at −63°. *Anal.* Calcd for C_2BrF_6PS: CF_3 liberated on alkaline hydrolysis, 24.6%; *m/e* (mass spectrometer, ^{79}Br isotope), 279.8547; mol wt, 281. Found: CF_3, 24.1, 25.6%; *m/e*, 279.8543; mol wt, 281. The infrared spectrum showed bands at 1301 w, 1270 w, 1243 (sh) w, 1203 (br) vs, 1175 vs, 1146 s, 788 s, 733 s, 555 m, 480 s cm^{-1}.

(b) From the Bromophosphine and Sulfur. $(CF_3)_2PBr$ (0.206 g, 0.83 mmole) reacted with sulfur (1 g) at 160° for 3 days to give $(CF_3)_2P(S)Br$ (0.129 g, 0.46 mmole), identified by its infrared and nmr spectrum and molecular weight (found: mol wt, 277). A more volatile fraction of the products was a mixture of $(CF_3)_2PBr$ and $(CF_3)_2P(S)Br$.

Table V. Vapor Pressure Data for Some Trifluoromethylphosphine Sulfides

$(CF_3)_2P(S)NH_2$								
t, °C		10.9	29.7	35.5	41.9	49.0	61.8	67.0
P, mm (obsd)		3.7	10.6	14.6	19.8	29.6	55.0	70.4
P, mm (calcd)[a]		3.5	10.9	15.0	20.9	30.0	55.5	70.4
$(CF_3)_2P(S)N(CH_3)_2$								
t, °C		29.5[b]	31.0	38.3	46.9	47.0[b]	48.1	54.0
P, mm (obsd)		8.0	8.7	12.9	20.5	20.9	22.0	28.3
P, mm (calcd)[a]		8.0	8.6	12.9	20.2	20.7	21.5	28.3
t, °C		56.1	60.2	63.0[b]	64.1	65.4	67.0	
P, mm (obsd)		33.1	38.7	44.1	46.1	48.5	53.2	
P, mm (calcd)[a]		31.8	38.6	44.8	46.1	49.7	53.1	
$CF_3PF(S)N(CH_3)_2$								
t, °C		11.0	20.9	38.0[b]	40.6	43.9[b]	54.0	59.8
P, mm (obsd)		4.2	8.5	22.0	26.6	29.5	47.8	64.5
P, mm (calcd)[a]		4.6	8.5	21.8	25.7	29.5	47.9	64.6
$(CF_3)_2P(S)F$								
t, °C		−31.3	−26.8	−19.6	−12.0	−4.4	3.7	9.4
P, mm (obsd)		79.2	100.5	148.8	216	304	422	530
P, mm (calcd)[a]		80.2	102.1	147.6	213	300	425	535
$(CF_3)_2P(S)Cl$								
t, °C	10.3[b]	16.4	22.2	24.1[b]	29.4	35.9[b]	39.0	45.1
P, mm (obsd)	103.8	135.3	177.0	186.5	237.6	307.4	342.5	426.0
P, mm (calcd)[a]	103.2	136.1	175.0	188.8	234.0	303.0	341.0	426.6
$(CF_3)_2P(S)Br$								
t, °C	7.1	11.5	18.8	25.5	30.0	36.0	39.0	45.9
P, mm (obsd)	33.0	41.8	61.0	88.0	106	137	157	218
P, mm (calcd)[a]	33.7	42.5	61.4	85.0	105	138	158	210
$(CF_3)_2P(S)SH$								
t, °C	11.1	11.6[b]	18.1	26.9	38.4[b]	44.8	51.8	70.8
P, mm (obsd)	17.5	18.1	24.2	40.0	69.3	91.2	124.2	262
P, mm (calcd)[a]	17.6	18.1	25.5	40.0	68.9	91.6	123.6	263

[a] Pressures are calculated using the coefficients given in Table I. [b] Measured with temperature descending from the maximum value attained.

Preparation of $(CF_3)_2P(S)F$. (a) Fluorination of the Bromophosphine Sulfide. $(CF_3)_2P(S)Br$ (0.316 g, 1.12 mmoles) was condensed onto resublimed SbF_3 (1.5 g) and kept at room temperature for 16 hr, and then at 100° for 4 hr. Vacuum fractionation of the products gave $(CF_3)_2P(S)F$ (0.129 g, 0.59 mmole) which was trapped at −116°. *Anal.* Calcd for C_2F_7PS: CF_3 liberated on alkaline hydrolysis, 31.3%; *m/e* (mass spectrometer), 219.9347; mol wt, 220. Found: CF_3, 30.0%; *m/e*, 219.9347; mol wt, 221.

(b) From the Fluorophosphine and Sulfur. When $(CF_3)_2PF$ (0.183 g, 0.98 mmole) was heated with sulfur (1 g) at 200° for 16 hr, a cursory examination of the products by infrared spectroscopy showed that a small amount of $(CF_3)_2P(S)F$ had been formed. After a further 2 days at 200°, the fluorophosphine was largely converted to $(CF_3)_2P(S)F$, which was identified by infrared and nmr spectroscopy. Small amounts of $(CF_3)_2PF$, $(CF_3)_3P$, $(CF_3)_3P{=}S$, $(CF_3)_2PSCF_3$, and possibly $CF_3PF_2(S)$, all identified by infrared and nmr spectroscopy, were also found among the products. Some of these compounds could not be separated from $(CF_3)_2P(S)F$.

Preparation of $(CF_3)_2P(S)I$. Iodobis(trifluoromethyl)phosphine (0.798 g, 2.70 mmoles) and sulfur (1 g), when heated together at 150° (16 hr), gave a volatile fraction containing CF_3I, $(CF_3)_3P$, $(CF_3)_2PI$, and $(CF_3)_3P{=}S$ and a less volatile fraction which was shown to be the iodophosphine sulfide, $(CF_3)_2P(S)I$ (0.567 g, 1.73 mmoles). The desired iodophosphine sulfide was trapped at −63°. *Anal.* Calcd for C_2F_6IPS, CF_3 liberated on alkaline hydrolysis, 21.0%, *m/e* (mass spectrometer), 327.8409; mol wt, 328. Found: CF_3, 20.7%; *m/e*, 327.8410; mol wt, 325. A small amount of involatile material in another fraction was not examined. $(CF_3)_2P(S)I$ showed bands in the infrared spectrum at 1290 w, 1208, 1196 (doublet) vs, 1171 vs, 1140 m, 775 s, 731 s, 553 m, 497 w, 465 s cm^{-1}.

Reactions of $(CF_3)_2P(S)I$. (1) With Mercury. The iodo compound (0.267 g, 0.815 mmole) and mercury (2 ml) reacted at room temperature (3 days) to give, as the only volatile product, $(CF_3)_2PSP(CF_3)_2$ (0.144 g, 0.39 mmole), identified by its characteristic infrared[17a] and nmr spectrum,[25] and by molecular weight (found: mol wt, 362) and vapor-pressure measurements[17a] (p = 0.53 cm at 3°).

(2) With Mercury and HI. The iodide (0.0608 g, 0.21 mmole), hydrogen iodide (0.102 g, 0.80 mmole), and mercury (2 ml) reacted immediately on warming to room temperature. When the reaction tube was opened after 4 days at 29°, the products were noncondensable gas, a trace of $(CF_3)_2PH$, identified spectroscopically, and $(CF_3)_2PSH$ (0.0364 g, 0.18 mmole), identified by its infrared and nmr spectrum[17a] and molecular weight (found: mol wt, 206). No peaks were found in the infrared spectrum which could be assigned to $(CF_3)_2P(S)H$, and signals in the region expected for CF_3P^V compounds were absent from the nmr spectrum.

Reaction of $(CF_3)_3P$ with Sulfur. When $(CF_3)_3P$ (0.472 g, 1.98 mmoles) and sulfur (1 g) were kept at 200° (4 days), it was shown by nmr spectroscopy that about 50% of the trisphosphine had been converted to $(CF_3)_3P{=}S$.[11] Although the two compounds could not be completely separated by vacuum fractionation, the presence of the sulfide was confirmed by infrared spectroscopy.

Preparation of $(CF_3)_2P(S)SH$. (a) Reaction of $(CF_3)_2PH$ with Sulfur. Bis(trifluoromethyl)phosphine (0.435 g, 2.56 mmoles) and sulfur (1 g) were heated together in a sealed tube at 160° for 4 days. A trace of a mixture of CF_3P tetramer and pentamer[6] was found in the least volatile fraction of the products. Bis(trifluoromethyl)dithiophosphinic acid, $(CF_3)_2P(S)SH$ (0.246 g), contaminated by about 10% $(CF_3)_2PSP(CF_3)_2$, was shown to be present in another fraction by molecular weight measurement (found: mol wt, 238) and by infrared and nmr spectroscopy.

Other products were $(CF_3)_2PSH$ (0.022 g, 0.11 mmole), excess $(CF_3)_2PH$ (0.209 g, 1.23 mmoles), both identified by their infrared spectra, and a small amount of H_2S, identified by mass spectrometry and the characteristic reaction with lead acetate.

(b) Reaction of $(CF_3)_2PSH$ with Sulfur. The mercaptophosphine (0.311 g, 1.54 mmoles) reacted with sulfur (1 g) after 36 hr at 160° to give a small amount (0.06 mmole) of a volatile material (shown not to be H_2S), unreacted $(CF_3)_2PSH$ (0.012 g, 0.06 mmole), and the phosphinic acid, $(CF_3)_2P(S)SH$ (0.313 g, 1.34 mmoles), which was trapped at −63°. *Anal.* Calcd for $C_2HF_6PS_2$: *m/e* (mass spectrometer), 233.9161; CF_3 liberated on alkaline hydrolysis, 29.5%; mol wt, 234. Found: *m/e*, 233.9159; CF_3, 29.6%; mol wt, 237. The main bands in the infrared spectrum were at 2580 w, 2565 (sh) w, 1280 w, 1208 vs, 1178 vs, 846 m, 760 m, 730 s, 573 m, 519 m, 472 m cm^{-1}. Samples of the dithiophosphinic acid prepared from the reaction of $(CF_3)_2PSH$ and sulfur were examined by fluorine nmr for $(CF_3)_2PSP(CF_3)_2$ which is readily identified by its strong and characteristic spectrum.[25] At the highest gain only resonances due to the phosphinic acid were observed indicating that there was certainly less than 0.25% of the bis(phosphino) sulfide impurity present.

Preparation of $CF_3PF(S)N(CH_3)_2$. The dimethylaminophosphine, $CF_3PFN(CH_3)_2$ (0.460 g, 2.82 mmoles), prepared from CF_3PF_2 and $(CH_3)_2NH$,[28] was sealed in an evacuated tube with sulfur (1 g) and heated at 180° (6 days). The phosphine sulfide, $CF_3PF(S)N(CH_3)_2$ (0.235 g, 1.21 mmoles), was isolated by vacuum fractionation. *Anal.* Calcd for $C_3H_6F_4NPS$: *m/e* (mass spectrometer), 194.9895; mol wt, 195. Found: *m/e*, 194.9891; mol wt, 192. No CF_3H was liberated on alkaline hydrolysis, as expected. The infrared spectrum showed absorption at 3020 w, 2950 m, 2915 (sh) w, 2870 w, 2825 w, 1455 w, 1318 m, 1212 vs, 1166 vs, 1149 vs, 1078 w, 1010 vs, 890 vs, 786 s, 750 (sh) w, 653 s, 474 m cm^{-1}.

Preparation of $F_2P(S)N(CH_3)_2$. $PF_2N(CH_3)_2$ (0.116 g, 1.03 mmoles) and sulfur (1 g) were allowed to react for 5 days at 150°. Vacuum fractionation gave $F_2P(S)N(CH_3)_2$ (0.131 g, 0.90 mmole), identified by its infrared, nmr, and mass spectra.[12] A more volatile fraction was shown by infrared spectroscopy to contain PF_3, $F_3P{=}S$, and a trace of SiF_4.

Acknowledgment. We thank Dr. A. Hogg and Mr. A. Budd for assistance with the mass spectral measurements and The National Research Council of Canada and The Defence Research Board of Canada for financial support.

(28) J. F. Nixon and R. G. Cavell, *J. Chem. Soc.*, 5893 (1964).

High-Pressure–High-Temperature Syntheses. III. Direct Syntheses of New High-Pressure Forms of $LiAlO_2$ and $LiGaO_2$ and Polymorphism in $LiMO_2$ Compounds (M = B, Al, Ga)[1a]

C. H. Chang and J. L. Margrave

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001. *Received July 21, 1967*

Abstract: New high-pressure polymorphs, β-$LiAlO_2$ and β-$LiGaO_2$, have been synthesized in an opposed-anvil press at 18 kbars, 370° and 18 kbars, 420°, respectively. These new high-pressure forms are isostructural. Debye–Scherrer powder patterns have been indexed on the basis of monoclinic structures and indicate the lattice parameters a = 8.147 Å, b = 7.941 Å, c = 6.303 Å, β = 93.18° for β-$LiAlO_2$ and a = 8.110 Å, b = 8.065 Å, c = 6.422 Å, β = 94.56° for β-$LiGaO_2$. Infrared absorption spectra suggest that aluminum and gallium in these new phases have both coordination numbers four and six. A consistent nomenclature for the system $LiMO_2$ (M = B, Al, Ga) is proposed and used.[1b] The polymorphs of $LiMO_2$ include three phase types: (1) the α phases, prepared at normal pressures (M^{3+} exhibits a low coordination number: three for boron or four for aluminum); (2) the γ forms synthesized at high pressures and temperatures (M^{3+} has a high coordination number: four for boron and six for aluminum); and (3) the β forms, prepared at intermediate pressures and temperatures (M^{3+} exhibits both coordination numbers).

Two crystalline forms of $LiAlO_2$ have been reported. The first form (α-$LiAlO_2$) was prepared at normal pressure,[2] and it is tetragonal with a = 5.169 Å and c = 6.268 Å with all cations tetrahedrally coordinated.[3–5] The second crystalline form of $LiAlO_2$ was obtained first by Lehmann and Hesselbarth[6] at 600°, and recently by Marezio and Remeika,[7] at 35 kbars and 850°. This hexagonal form, γ-$LiAlO_2$, has a = 2.801 Å and c = 14.214 Å and all cations are octahedrally bonded.[8]

There are also two crystalline forms of $LiGaO_2$ which have been synthesized at normal pressure and temperature; α-$LiGaO_2$ crystallizes in an orthorhombic structure with a = 5.402 Å, b = 6.372 Å, and c = 5.007 Å.[9,10] By subjecting the low-pressure form to a pressure of 30 kbars and a temperature of 850°, Marezio and Remeika[11] obtained a high-pressure phase, γ-$LiGaO_2$, with a hexagonal unit cell of a = 2.9113 Å and c = 14.466 Å. The most important difference between these two phases is that, in the low-pressure form, the coordination number of Ga, paralleling that of Al in

---

(1) (a) Extracted, in part, from the Ph.D. thesis of C. H. Chang, submitted to the faculty of Rice University, May 1967. (b) The new nomenclature described in the abstract is used throughout the paper.

(2) (a) R. A. Hatch, *Am. Mineralogist*, **28**, 471 (1953); (b) F. A. Hummel, *J. Am. Ceram. Soc.*, **34**, 235 (1951).

(3) J. Thery, A. M. Lejus, D. Bariancon, and R. Collonges, *Bull. Soc. Chim. France*, 973 (1961).

(4) E. F. Bertaut, A. Delapalme, G. Bassi, A. Durif-Varambon, and J. C. Joubert, *Bull. Soc. Franc. Mineral. Crist.*, **88**, 103 (1965).

(5) M. Marezio, *Acta Cryst.*, **59**, 396 (1965).

(6) H. A. Lehmann and H. Hesselbarth, *Z. Anorg. Allgem. Chem.*, **313**, 117 (1961).

(7) M. Marezio and J. P. Remeika, *J. Chem. Phys.*, **44**, 3143 (1966).

(8) A. M. Lejus and R. Collongues, *Compt. Rend.*, **254**, 2005 (1962).

(9) R. Hoppe, *Angew. Chem.*, **71**, 457 (1959).

(10) M. Marezio, *Acta Cryst.*, **18**, 481 (1965).

(11) M. Marezio and J. P. Remeika, *J. Phys. Chem. Solids*, **26**, 1277 (1965).