Volatile Fluoro- and Trifluoro-methyl Diphosphorus Compounds containing Phosphorus in Two Valencies

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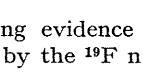
RECENTLY reported attempts to prepare quinquevalent diphosphorus compounds from bis(trifluoromethyl)iodophosphine sulphide, $(CF_3)_2P(S)I$,[1] and iodothiophosphoryl difluoride, SPF_2I,[2] were unsuccessful. We have now found that the reaction of the above iodophosphorus compounds with *stoicheiometric* quantities of metallic mercury at room temperature gives the desired diphosphorus disulphide compounds

$$2X_2P(S)I + Hg \rightarrow X_4P_2S_2 + HgI_2 \ (X = F,CF_3) \qquad (1)$$

The reactions are slow and require vigorous agitation to renew the reactive metal surface. In the case of the trifluoromethyl compound the product contained appreciable amounts of $(CF_3)_2P{\cdot}S{\cdot}P(CF_3)_2$ and other impurities.

The new compounds are volatile liquids with moderate stability at normal temperatures. Spectroscopic evidence suggests that the compounds do not have the expected phosphorus–phosphorus bonded structure but rather the isomeric structure with a sulphur bridge linking quinquevalent and tervalent phosphorus atoms:



$$X_2\overset{\overset{\displaystyle S}{\|}}{P}{-}S{-}PX_2$$

The most compelling evidence for the mixed valence structure is provided by the ^{19}F n.m.r. spectra. At room temperature the spectrum of $F_4P_2S_2$ has the appearance of a doublet of doublets with parameters: ϕ_a 60·5 p.p.m. (*vs.* CCl_3F), ^1J_a (FP^{III}) 1320 Hz.; ϕ_b 14·0 p.p.m., ^1J_b (FP^V) 1218 Hz. At −80°, further spin–spin splitting transforms *each* doublet into a doublet of doublets of triplets yielding the following additional coupling constants: ^3J_a (FPP^V) 22·0 Hz., ^3J_b (FPP^{III}) 15·0 Hz., and ^4J(FF) 5·9 Hz.). The trifluoromethyl compound $(CF_3)_4P_2S_2$ shows a doublet [ϕ_a 53·8 p.p.m., ^2J_a (FP^{III}) 82·5 Hz.] and a doublet of doublets [ϕ_b 58·9 p.p.m., ^2J_b(FP^V) 111·7 Hz., ^4J(FPP^{III}) 5·0 Hz.] at room temperature. Both regions of chemical shift in each compound exhibited equal total intensity, and the observed parameters are in good agreement with those of similar compounds[1-3].

I.r. spectra, particularly that of $F_4P_2S_2$, also support the structures with both P^{III} and P^V, showing bands which are readily associated with P^{III}–F stretching (847 and 834 cm.$^{-1}$) and with P^V–F stretching (925 and 898 cm.$^{-1}$). The CF region of $(CF_3)_4P_2S_2$ is complex, and suggests that CF_3 absorptions arising from two different CF_3–P environments are overlapped.

Both compounds react with hydrogen chloride to form the quinquevalent thioacid and tervalent chlorophosphine in nearly quantitative yields:

$$X_2P{\cdot}S{\cdot}P(S)X_2 + HCl \rightarrow X_2PCl + X_2P(S)SH \qquad (2)$$

providing chemical evidence in support of the structure. Reaction 2 proceeds well with stoicheiometric quantities of HCl in the case of the fluoro-compound, but a large excess of HCl is required to consume the trifluoromethyl compound completely.

Additional chemical evidence in support of the structure is provided by the synthesis of the mixed-valence compounds in good yields from quinquevalent thioacid and aminophosphine:

$$2X_2P(S)SH + X_2PNMe_2 \rightarrow X_2P(S){\cdot}S{\cdot}PX_2 + Me_2NH_2{}^+S_2PX_2{}^- \qquad (3)$$

and, in the case of the trifluoromethyl compound, the reaction:

$$(CF_3)_2P(S)SH + (CF_3)_2PCl \rightarrow (CF_3)_2P(S){\cdot}S{\cdot}P(CF_3)_2 + HCl \qquad (4)$$

the latter using an excess of chlorophosphine.

Reaction of difluorophosphoric acid with dimethylaminodifluorophosphine proceeds analogously to equation 3 to give fair yields of the diphosphorus dioxide compound. Again, according to the ^{19}F n.m.r. spectrum which shows a doublet of doublets at room temperature [ϕ_a 38·3 p.p.m., ^1J_a(FP^{III}) 1396 Hz.; ϕ_b 68·9 p.pm., ^1J_b(FP^{III}) 1032·5 Hz.), the compound has the mixed valence structure, $F_2P(O){\cdot}O{\cdot}PF_2$.

Since all diphosphine disulphides and dioxides known at present have structures containing a direct phosphorus–phosphorus bond,[4] the adoption of mixed valence structures in this case is somewhat unexpected. While it is tempting to suggest that a stabilization of the tervalent state relative to the quinquevalent state by electronegative substituents such as CF_3 or F is responsible for the observed structure, it is apparent that the choice of the most stable structure must involve many different factors.

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