

THE PREPARATION AND PROPERTIES OF DI[BIS(TRIFLUOROMETHYL)PHOSPHINO]SELENIDE

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(Received March 30, 1973)

SUMMARY

The selenium-bridged compound $(\text{CF}_3)_2\text{PSeP}(\text{CF}_3)_2$ can be prepared by the reaction of $(\text{CF}_3)_2\text{PI}$ with silver selenide or by heating $(\text{CF}_3)_2\text{PP}(\text{CF}_3)_2$ with selenium. In its reactions with HCl , Cl_2 , I_2 , $(\text{CF}_3)_2\text{P}(\text{S})\text{I}$ and sulphur, no new selenium-containing compounds are formed. Instead, the products are selenium and known $(\text{CF}_3)_2\text{P}$ derivatives. The aqueous hydrolysis of the selenide differs from that of $[(\text{CF}_3)_2\text{P}]_2\text{E}$ ($\text{E} = \text{O}, \text{S}$) as $(\text{CF}_3)_2\text{PH}$ is observed as a volatile product along with CF_3H . Structures have been proposed for the anions present in solution following aqueous or alkaline hydrolysis on the basis of the reaction stoichiometry and NMR spectral measurements.

INTRODUCTION

Following recent interest^{1,2} in the structure of fluorocarbon-phosphorus compounds, a study of the vibrational spectra of the compounds $[(\text{CF}_3)_2\text{P}]_2\text{E}$ ($\text{E} = \text{O}, \text{S}$) was undertaken³ to look for evidence of $d\pi-p\pi$ bonding. To assist in the assignment of the spectra, the selenium analogue was required. This paper describes the preparation and the chemical and physical properties of di[bis(trifluoromethyl)phosphino]selenide, $[(\text{CF}_3)_2\text{P}]_2\text{Se}$.

DISCUSSION

When iodo-bis(trifluoromethyl)phosphine was allowed to stand over silver selenide in a sealed tube at room temperature, there was a rapid and almost quantitative reaction according to the equation:

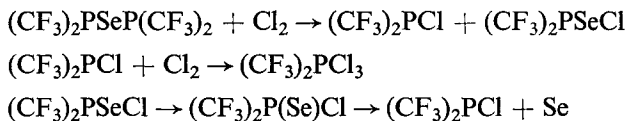


This route follows the preparation^{4,5} of the corresponding sulphide, $(\text{CF}_3)_2\text{PSP}(\text{CF}_3)_2$. An alternative synthesis was to heat the diphosphine, $(\text{CF}_3)_2\text{PP}(\text{CF}_3)_2$, with selenium. The reaction was almost quantitative at 100°. No other stable products could be isolated, although a small quantity (< 2% of starting material) of an unstable compound which decomposed to selenium and $[(\text{CF}_3)_2\text{P}]_2\text{Se}$ at room temperature was recovered from the reaction tube. This is in interesting contrast to the addition of sulphur to $(\text{CF}_3)_2\text{PP}(\text{CF}_3)_2$, which gives $(\text{CF}_3)_2\text{P}(\text{S})\text{SP}(\text{CF}_3)_2$, $[(\text{CF}_3)_2\text{P}(\text{S})]_2$ and several other as yet unidentified products, all stable under ambient conditions⁶.

The selenide is a clear colourless liquid, m.p. -35° , having a most unpleasant and penetrating odour. The IR spectrum of the vapour is similar to that of the oxygen and sulphur analogues^{4,5,7}. A band at 447 cm^{-1} appears to be largely associated with $\nu(\text{P-Se-P})$. Stronger evidence for the symmetrical structure, as opposed to the mixed valence, $\text{P}(\text{Se})\text{P}$, structure, comes from a study of the ^{19}F NMR spectrum. A single complex resonance [$\varphi = 54.2\text{ ppm}$; $^2J(\text{FP}) = 69\text{ Hz}$; $^4J(\text{FP}) = 8.5\text{ Hz}$; $^2J(\text{PP}) = 184\text{ Hz}$] characteristic of the $[\text{AX}_6]_2$ spin system was observed at all temperatures between 30° and -60° . The chemical shift and F-C-P coupling constant ($^2J(\text{FP})$) are characteristic of trivalent rather than pentavalent phosphorus. The parent ion in the mass spectrum of the selenide is more intense than the parent ions of $[(\text{CF}_3)_2\text{P}]_2\text{O}$ and $[(\text{CF}_3)_2\text{P}]_2\text{S}$ ⁸. All three mass spectra show competitive loss of fluorine and CF_3 (established by metastable peaks) from the parent ion. The selenide showed four metastable peaks for the elimination of CF_3 corresponding to the ^{80}Se , ^{78}Se , ^{77}Se and ^{76}Se isotopes.

The diphosphoxane, $[(\text{CF}_3)_2\text{P}]_2\text{O}$, is quantitatively cleaved⁷ by hydrogen chloride at 80° to give the phosphinous acid, $(\text{CF}_3)_2\text{POH}$, together with $(\text{CF}_3)_2\text{PCl}$. When the selenide was allowed to react with hydrogen chloride at room temperature, red selenium was deposited and equimolar amounts of bis(trifluoromethyl)phosphine and chlorobis(trifluoromethyl)phosphine were formed. It was thought likely that initial attack of HCl would give $(\text{CF}_3)_2\text{PH}$ and $(\text{CF}_3)_2\text{PSeCl}$; the latter could then decompose to $(\text{CF}_3)_2\text{PCl}$ *via* an Arbuzov rearrangement to $(\text{CF}_3)_2\text{P}(\text{Se})\text{Cl}$. In an independent experiment, it was shown that chloro-bis(trifluoromethyl)phosphine did not add on selenium. The alternative possibility of initial cleavage by HCl to give $(\text{CF}_3)_2\text{PCl}$ and $(\text{CF}_3)_2\text{PSeH}$ seems less probable as the selenophosphinous acid would decompose at least partially to $[(\text{CF}_3)_2\text{P}]_2\text{Se}$ and hydrogen selenide, in a similar manner⁵ to $(\text{CF}_3)_2\text{PSH}$. No hydrogen selenide or hydrogen was detected among the reaction products.

The reaction of the sulphide, $[(\text{CF}_3)_2\text{P}]_2\text{S}$, with chlorine below room temperature gives the chlorophosphine sulphide, $(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}$, and the phosphorane $(\text{CF}_3)_2\text{PCl}_3$ ⁹. Under similar conditions, an excess of the selenide reacts with chlorine to give equimolar amounts of $(\text{CF}_3)_2\text{PCl}_3$ and $(\text{CF}_3)_2\text{PCl}$, as well as selenium. The stoichiometry of the reaction suggests the following steps:



where the intermediate $(\text{CF}_3)_2\text{PSeCl}$ or $(\text{CF}_3)_2\text{P}(\text{Se})\text{Cl}$ is stable under the reaction conditions but loses selenium on warming towards room temperature. The reaction with iodine to give $(\text{CF}_3)_2\text{PI}$ and selenium was less vigorous, even when the reaction vessel was irradiated. The action of $(\text{CF}_3)_2\text{P}(\text{S})\text{I}$ upon the selenide gave selenium, $(\text{CF}_3)_2\text{PI}$ and $[(\text{CF}_3)_2\text{P}]_2\text{S}$. Again the observed products may be rationalised in terms of the initial cleavage of the P-Se-P bridge, giving $(\text{CF}_3)_2\text{PSeI}$ and $(\text{CF}_3)_2\text{P}(\text{S})\text{P}(\text{CF}_3)_2$, followed by the rearrangement of both intermediates and loss of selenium from $(\text{CF}_3)_2\text{P}(\text{Se})\text{I}$. The selenide consumes sulphur at 100° to yield $[(\text{CF}_3)_2\text{P}]_2\text{S}$, presumably by a similar mechanism; at 150° , the final product is $(\text{CF}_3)_2\text{P}(\text{S})\text{SP}(\text{CF}_3)_2$ ¹⁰, formed by further addition of sulphur to $[(\text{CF}_3)_2\text{P}]_2\text{S}$.

Although the alkaline hydrolysis of $[(\text{CF}_3)_2\text{P}]_2\text{O}$ ⁷ or $[(\text{CF}_3)_2\text{P}]_2\text{S}$ ^{4,5} gives 4 mol of fluoroform, that of $[(\text{CF}_3)_2\text{P}]_2\text{Se}$ gives only 2.69 mol. It has now been shown that the plain water hydrolysis of the oxygen and sulphur compounds yields 2 mol of fluoroform, along with 1 mol of hydrogen sulphide in the case of the sulphur compound, leaving the $\text{CF}_3\text{PHO}_2^-$ ion in solution. On the other hand, the reaction of the selenide with water is complex, giving fluoroform and bis-(trifluoromethyl)phosphine, and leaving a mixture of three fluorocarbon-containing ions in solution. Although the presence of hydrogen selenide could not be detected spectroscopically, the volatile fraction deposited traces of red selenium on standing at room temperature, suggesting the presence of small amounts of an unstable selenium compound, possibly hydrogen selenide. Aqueous lead acetate solution gave a slight black precipitate with the volatile fraction, presumably of lead selenide. No selenium was deposited from the solution during hydrolysis, but if the hydrolysate was cooled before distilling off the volatile products, some selenium was precipitated. In most cases, the cooling effect produced by the evaporation of solvent was sufficient to deposit selenium. Nevertheless, it was shown by NMR studies before and after the removal of fluoroform and $(\text{CF}_3)_2\text{PH}$ that the relative proportions of the anions present in solution were not much changed.

The individual species in solution have not been separated and identified unambiguously. However, the application of ¹⁹F NMR spectroscopy and a detailed study of the reaction stoichiometry leaves little doubt as to their nature. Within each of the series of anions investigated by Pinkerton and Cavell¹¹, regular changes in ²J(FP) and φ clearly depend upon the electronegativity of the attached groups. Allowing for the reduced electronegativity of selenium compared to that of sulphur, formulae have been assigned to the species in the hydrolysate responsible for the observed NMR signals (Table 1). The hydrolysate was strongly acid and so the results are directly comparable with those obtained under the limiting conditions described in the literature¹¹. The assignment of the formulae is sup-

ported by the observed stoichiometry of the reaction, shown for typical examples in Table 2. It is interesting to note that the ratio of fluoroform to bis(trifluoromethyl)phosphine formed varied with the molar proportions of the selenide and water, suggesting that the acidity of the medium, which must increase as the selenide hydrolyses, affects the reaction.

TABLE 1

NMR DATA FOR IONS IN AQUEOUS SOLUTION

Ion	ϕ (ppm) ^a	2J (FP) (Hz)
(CF ₃) ₂ PO ₂ ^{-b}	72.8	103.6
(CF ₃) ₂ POS ^{-b}	73.1	97.0
(CF ₃) ₂ POSe ^{-c}	73.0	94
(CF ₃) ₂ PS ₂ ^{-b}	72.9	92.0
(CF ₃) ₂ PSe ₂ ^{-c}	71.8	88
CF ₃ PO ₃ ^{2--b}	72.0	93.0
CF ₃ PO ₂ S ^{2--b}	74.6	89.9
CF ₃ PO ₂ Se ^{2--c}	75.4	88
CF ₃ POS ₂ ^{2--b}	76.1	86.6
CF ₃ POSe ₂ ^{2--c}	77.0	80

^a Relative to external CCl₃F.

^b From ref. 11.

^c Proposed formula based on observed NMR parameters (see text).

Within experimental error, equal quantities of CF₃H and CF₃PHO₂⁻ were formed, suggesting that these products have a common source. This is almost certainly (CF₃)₂POH which is known^{11,12} to hydrolyse as follows:



Hydrogen selenide would be expected to be formed along with (CF₃)₂POH, following the hydrolysis of [(CF₃)₂P]₂S. The formation of (CF₃)₂PSe₂⁻ could then be explained by attack of hydrogen selenide on the starting compound, made more likely than in the analogous sulphur compound by the polarity of the P-Se bond. The remaining selenium anion present in the aqueous hydrolysate, to which the formula (CF₃)₂POSe⁻ has been assigned, may be formed by direct attack of water on the selenide, without cleavage of both P-Se bonds, according to the equation:



In alkaline hydrolyses, (CF₃)₂PSe₂⁻, (CF₃)₂POSe⁻ and CF₃PHO₂⁻ were not observed but the expected products of their decomposition by alkali, namely CF₃PSe₂O²⁻⁻, CF₃PO₂Se²⁻⁻ and HPO₃²⁻⁻, were detected by NMR spectroscopy and the fluorine-containing anions identified by comparison with known CF₃P anions, as shown in Table 1. From the assumed formulae of the ions found in the aqueous

hydrolysis experiment, and their quantities as measured by NMR spectroscopy, the amount of CF_3H liberated on alkaline hydrolysis of 1 mol of the selenide was calculated to be 2.56 mol, in fair agreement with that observed and supporting the formulae assigned. Traces of other anions were occasionally observed in solution. These may be partly protonated species such as $\text{CF}_3\text{PSeO}_2\text{H}^-$.

CONCLUSION

Although the physical properties of the new compound $[(\text{CF}_3)_2\text{P}]_2\text{Se}$ are comparable with those of $[(\text{CF}_3)_2\text{P}]_2\text{O}$ and $[(\text{CF}_3)_2\text{P}]_2\text{S}$, the chemical properties are different, in that the reactions of the selenide generally lead to the elimination of elemental selenium. However, hydrolysis of the selenide appears to give stable selenium-containing anions.

EXPERIMENTAL

Volatile compounds were handled in a Pyrex vacuum system using standard techniques. IR spectra were recorded on a Perkin-Elmer 457 spectrometer and mass spectra on an A.E.I. MS9 instrument operating at an ionising energy of 70 eV. NMR spectra were recorded on a Brüker Spectrospin operating at 84.66 MHz for ^{19}F nuclei, with CCl_3F as internal reference for non-aqueous solutions and as external reference for aqueous solutions. Bis(trifluoromethyl)iodophosphine sulphide was prepared according to the literature method¹³.

Preparation of $[(\text{CF}_3)_2\text{P}]_2\text{Se}$

(a) Reaction of $(\text{CF}_3)_2\text{PI}$ with silver selenide

Freshly prepared, dry silver selenide (2.297 g, 8.11 mmol) and iodo-bis(trifluoromethyl)phosphine (2.808 g, 9.50 mmol) reacted in the dark at room temperature (12 h) to give di[bis(trifluoromethyl)phosphino]selenide (1.751 g, 4.20 mmol; 88% yield based on phosphine used) [Found: C, 11.4%; *m/e*, 417.8436. $\text{C}_4\text{F}_{12}\text{P}_2\text{Se}$ requires C, 11.5%; *m/e*, 417.8448]. The mass measurements are based on the ^{80}Se isotope. A sample of the selenide was unchanged after heating at 150° (10 days).

(b) Reaction of tetrakis(trifluoromethyl)diphosphine with selenium

The diphosphine (0.448 g, 1.32 mmol) was heated at 100° (4 days) with excess selenium. The major volatile product was $[(\text{CF}_3)_2\text{P}]_2\text{Se}$ (0.537 g, 1.29 mmol; 98% yield based on diphosphine used.) A small amount (*ca.* 0.01 g; < 2% yield) of a less volatile compound was found to decompose rapidly to $[(\text{CF}_3)_2\text{P}]_2\text{Se}$ and selenium at room temperature. The selenide was unchanged after heating with excess of selenium at 150° (6 days).

*Reactions of di[bis(trifluoromethyl)phosphino]selenide**(a) With HCl*

The selenide (0.179 g, 0.43 mmol) and HCl (0.111 g, 3.05 mmol), sealed in a small tube, reacted at room temperature (26 days) in the dark. The volatile products were $(\text{CF}_3)_2\text{PH}$ (0.054 g, 0.32 mmol) and $(\text{CF}_3)_2\text{PCI}$ (0.062 g, 0.30 mmol) with some of the selenide (0.052 g, 0.12 mmol) and HCl (0.100 g, 2.73 mmol) being recovered. The remaining solid was red selenium (0.025 g, 0.32 mmol).

(b) With chlorine

The selenide (0.402 g, 0.96 mmol) and chlorine (0.062 g, 0.87 mmol) were allowed to warm up slowly from -82° . The volatile products were removed from the tube leaving a brown-black solid identified as selenium (0.036 g, 0.46 mmol). The volatile products were fractionated at -96° , the more volatile fraction being $(\text{CF}_3)_2\text{PCI}$ (0.087 g, 0.42 mmol). The less volatile fraction was shown by IR and NMR spectroscopy to be a mixture of $(\text{CF}_3)_2\text{PCL}_3$ (46 mol%, 0.43 mmol) and the selenide (54 mol%, 0.50 mmol).

(c) With iodine

The selenide (0.360 g, 0.86 mmol) and excess of iodine, in a Pyrex reaction tube, were irradiated with a medium-pressure mercury arc lamp (6 h). The volatile products were identified by NMR spectroscopy as $(\text{CF}_3)_2\text{PSeP}(\text{CF}_3)_2$ (78 mol%, 0.74 mmol) and $(\text{CF}_3)_2\text{PI}$ (22 mol%, 0.21 mmol). The solid residue from the reaction was selenium.

(d) With $(\text{CF}_3)_2\text{P(S)I}$

The selenide (0.144 g, 0.35 mmol) and $(\text{CF}_3)_2\text{P(S)I}$ (0.167 g, 0.51 mmol) were left at room temperature in the dark (1 day). A red-black deposit left in the tube when the volatile products were removed was identified as selenium (0.017 g, 0.22 mmol). The volatile products could not be cleanly separated by fractional distillation and were identified by NMR spectroscopy as $[(\text{CF}_3)_2\text{P}]_2\text{Se}$ (14 mol%, 0.12 mmol), $(\text{CF}_3)_2\text{PI}$ (25 mol%, 0.21 mmol), $[(\text{CF}_3)_2\text{P}]_2\text{S}$ (27 mol%, 0.23 mmol) and $(\text{CF}_3)_2\text{P(S)I}$ (34 mol%, 0.28 mmol).

(e) With sulphur

When the selenide (0.521 g, 1.25 mmol) was heated at 100° (2 days) with excess of flowers of sulphur, selenium was eliminated and the main product was identified by IR spectroscopy as $[(\text{CF}_3)_2\text{P}]_2\text{S}$. When the tube was reheated at 150° (6 days), the major volatile product was $(\text{CF}_3)_2\text{P(S)SP}(\text{CF}_3)_2$ (0.477 g, 1.18 mmol; 94% yield based on $(\text{CF}_3)_2\text{P}$ units used).

(f) With water

The reaction of $[(\text{CF}_3)_2\text{P}]_2\text{Se}$ with water was studied many times. Details of four typical experiments are given in Table 2. The reaction mixture was normally

shaken overnight at room temperature and then heated for a few hours at 40° before removing the volatile products of the reaction, which were separated by vacuum fractionation and identified by molecular weight measurements and IR, NMR and mass spectroscopy. The aqueous hydrolysate was examined by NMR spectroscopy; integration established the relative amounts of the anions.

TABLE 2

QUANTITATIVE DETAILS OF THE HYDROLYSIS OF $[(CF_3)_2P]_2Se$

$H_2O : [(CF_3)_2P]_2Se$	CF_3H^a	$(CF_3)_2PH^a$	$(CF_3)_2POSe^{2- a}$	$(CF_3)_2PSe_2^{2- a}$	$CF_3PHO_2^{- a}$
124	54	83	42	23	54
115	59	75	40	25	64
84	61	67	50	25	58
<50	45	60	68	20	41

^a Yield of each product expressed as mol% of $[(CF_3)_2P]_2Se$ taken.

(g) *With alkali*

In a typical experiment, the selenide (0.247 g, 0.592 mmol) was shaken with 20% sodium hydroxide solution (2 ml) for 8 h to give CF_3H (0.109 g, 1.56 mmol) (Found: mol. wt. 70.2) as the only volatile product. The hydrolysate was examined by ¹⁹F NMR spectroscopy which showed the existence of doublets at $\phi = 75.4$ ppm ($^2J(FP) = 88$ Hz; intensity 3) and $\phi = 77.0$ ppm ($^2J(FP) = 80$ Hz; intensity 1) assigned to $CF_3PO_2Se^{2-}$ and $CF_3POSe_2^{2-}$ respectively. The ¹H NMR spectrum showed the presence of HPO_3^{2-} (τ 2.8, $^1J(HP) = 680$ Hz).

Reaction of the diphosphoxane, $[(CF_3)_2P]_2O$, with water

The phosphorus compound (0.107 g, 0.30 mmol) and water (0.5 ml) reacted below room temperature to liberate CF_3H (0.042 g, 0.60 mmol). NMR spectroscopy showed that the only fluorine-containing ion in solution was $CF_3PHO_2^-$.

Reaction of di[bis(trifluoromethyl)phosphino]sulphide with water

When $[(CF_3)_2P]_2S$ (0.084 g, 0.23 mmol) and water (0.5 ml) were heated at 40° (16 h), the volatile products were CF_3H (0.031 g, 0.44 mmol) and H_2S (0.007 g, 0.22 mmol). Again, $CF_3PHO_2^-$ was found by NMR spectroscopy to be the only fluorine-containing ion in solution.

ACKNOWLEDGEMENTS

M.J.H. thanks the S.R.C. for financial support.

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