

Fluorinated Phosphorus-selenium Heteroatom Compounds: Phenylphosphonofluorodiselenoic Salts, Adducts and Esters

Guoxiong Hua, Junyi Du, Alexandra M. Z. Slawin and J. Derek Woollins*

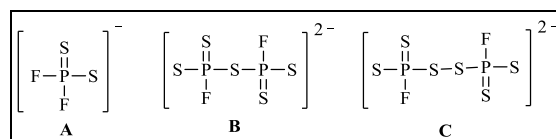
EaStCHEM School of Chemistry, University of St Andrews, Fife, KY16 9ST, UK

Supporting Information

ABSTRACT: 2,4-Bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide [PhP(Se)(μ -Se)]₂, Woollins' reagent (**WR**), reacts with dry KF or tetrabutylammonium fluoride (TBAF) at room temperature generating the corresponding potassium and tetrabutylammonium phenyldiselenofluorophosphinates **1** and **2** in almost quantitative yields. Treating **1** with equimolar amounts of tetraphenylphosphonium chloride or 1,3-dimesityl-*lH*-imidazol-3-ium chloride in THF at room temperature afforded the corresponding organic adducts **3** and **4** in 90% and 87% yields. Reaction of **1** with mono- and di-halogenated alkanes gave a series of esters of phenylphosphonofluorodiselenoates **5** - **8** and **9** in 79% - 93% yields. Two representative crystal structures are reported.

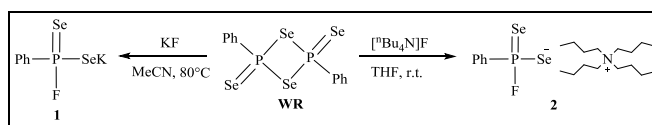
Organophosphorus-fluorine compounds (OPFCs) bearing P-F bonds have been of considerable interest since the 1970's due to their diverse chemical and biological activities. They are an important class of organophosphorus compounds and are recognized as selective phosphorylating agents in synthesis, and efficient inhibitors of several classes of enzymes.¹⁻¹² The thiophosphate anions **A** - **C** (Scheme 1) were first prepared from the reaction of alkali metal fluorides and P₄S₁₀ by Roesky and coworkers.^{13,14} Since then, the synthesis of thiophosphoryl halides S=PF₃ and S=PFCl₂, and their derivatives S=PF₂NH₂, S=PFCINH₂, S=PF₂N=PF₂X (X = Br, NH₂ or OH), S=PF₂N=PCl₃ and S=PF₂N=PF₂N=C=NSiMe₃ was reported.¹⁵⁻²⁰ However, there are few examples of the synthesis of simple phosphonofluorodithioates ROP(S)(S')F containing a fluorine atom attached directly to the phosphorus atom.^{15,21,22} The nucleoside phosphonofluorodithioate monoesters were prepared *via* oxidation of nucleoside phosphonodithioate with I₂ in pyridine in the presence of TMSCl, followed by addition of triethylamine trihydrofluoride (TAF).^{23,24} Similar analogues were obtained from a one-pot sequential reaction of 1,3,2-dithiaphospholane P(III) derivatives, which were converted readily into the corresponding P(V) compounds by addition of elemental sulfur and finally into phosphonofluorodithioates by further treatment with TBAF.²⁵ The importance of phosphoro-fluorine compounds in pure and applied chemistry invigorated our interest in synthesizing new phosphorodiselenoates bearing the P-F motif.

2,4-Bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide [PhP(Se)(μ -Se)]₂, Woollins' reagent (**WR**), has become known as a versatile selenation reagent in synthetic chemistry in recent years²⁶⁻⁴⁰ because of its ease of preparation and handling.⁴¹ As part of our investigation into the reactivity of **WR** towards inorganic or organic substrates herein, we report the synthesis of potassium and tetrabutylammonium salts of phenylphosphonofluorodiselenoates, and the related organic adducts and esters. To the best of our knowledge this is the first reported synthesis and characterization of phenylphosphonofluorodiselenoate [PhP(Se)(Se)F]⁻ and its structural analogues, providing a valuable addition to the library of phosphorodiselenoate compounds.



Scheme 1. The fluorinated thiophosphate anions **A** - **C**.

WR reacted with two equivalents of fresh dry potassium fluoride at 80 °C in acetonitrile under N₂ atmosphere for 1 h giving potassium phenylphosphonofluorodiselenoate **1** in 84% yield; or with two equivalents of tetrabutylammonium fluoride (TBAF) at room temperature in tetrahydrofuran for 1 h to give tetrabutylammonium phenylphosphonofluorodiselenoate **2** in 99% yield (Scheme 2). Both reactions were fast and very straightforward and must be performed in a moisture and oxygen-free atmosphere.

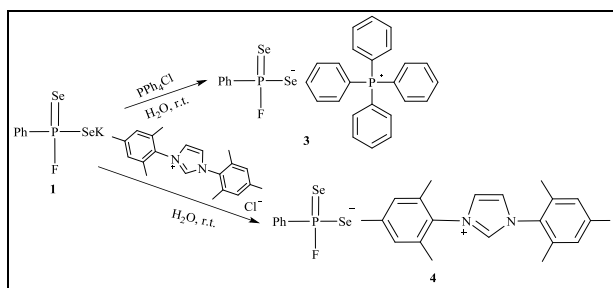


Scheme 2. Synthesis of potassium and tetrabutylammonium salts of phenylphosphonofluorodiselenoate **1** and **2**.

Compound **1** was obtained as a pale yellow solid and is insoluble in organic solvents but soluble in oxygen-free water. Compound **2** was obtained as brown sticky oil and is soluble in organic solvents, and shows good air stability at room temperature. **1** and **2** were fully characterized by ¹H, ¹³C, ³¹P, ⁷⁷Se and ¹⁹F NMR, IR spectroscopy and mass spectrometry. Both compounds showed the anticipated molecular ion peaks [M-K]⁺ or [M-N^tBu₄]⁺ and satisfactory accurate mass measurement. The ³¹P NMR spectra exhibit doublets at $\delta_p = 105.1$ ppm in compound **1** and 102.6 ppm in compound **2**, respectively, attributed to the P-F single bond. Each signal is flanked by one set of small satellites with ¹J(P,Se) coupling constants being 728 (for compound **1**) and 770 Hz (for compound **2**); these values are considerably bigger than those in similar PSe₂ ions^{27,42} indicating the significant electronic effect of the fluorine atom. In the ¹⁹F NMR spectra, doublets are observed (¹J(P,F) coupling constants of 1073 Hz for **1** and 1068 Hz for **2**) in accord with the known literature values,^{14,43} along with small ²J(Se,F) satellites with coupling constants of 31.0 Hz for compound **1** and 31.5 Hz for compound **2**. Furthermore, the ⁷⁷Se NMR spectra showed double doublets at $\delta_{Se} = 136.3$ ppm with a ¹J(P,Se) coupling constant of 728 Hz and a ²J(Se,F) coupling constant of 31.0 Hz for compound **1**, and at $\delta_{Se} = 139.5$ ppm with a ¹J(P,Se) coupling constant of 770 Hz and a ²J(Se,F) coupling constant of 31.5 Hz for compound **2**. In the ¹H NMR spectra, compound **1** showed only phenyl protons, while in compound **2** signals for the phenyl and n-butyl groups were observed.

Treating **1** with an equimolar amount of tetraphenylphosphonium chloride in degassed water in room temperature led to the formation of tetraphenylphosphonium phenylphosphonofluorodiselenoate **3** in 90% yield as a white solid. Similarly,

reacting compound **1** with 1,3-dimesityl-*1H*-imidazol-3-ium chloride under identical conditions provided 1,3-dimesityl-*1H*-imidazol-3-ium phenylphosphonofluoridodiselenoate **4** in 87% yield as a pale pink solid (Scheme 3). Both compounds **3** and **4** are air stable and soluble in normal organic solvents. The ^{31}P , ^{77}Se and ^{19}F NMR spectra of compounds **3** and **4** showed similar patterns to **1** with identical $^1J(\text{P},\text{F})$, $^1J(\text{P},\text{Se})$ and $^2J(\text{Se},\text{F})$ coupling constants.



Scheme 3. Derivatives **3** and **4** of potassium phenylphosphonofluoridodiselenoate **1**.

Crystals of **3** and **4** suitable for X-ray analysis were obtained by diffusion of hexane into dichloromethane solutions at room temperature. X-ray structural analysis of **3** and **4** (Figures 1 and 2) reveals they crystallize as ion-separated species. The phenylphosphonofluoridodiselenoate anion contains a distorted tetrahedral phosphorus atom with P-Se bond distances [2.1136(16), 2.1163(14) Å in compound **3**, and 2.119(3), 2.108(3) Å in compound **4**] shorter than those found in amine salts of bisdiselenophosphonic acid [2.1280(11)-2.1350(12) Å],⁴⁴ however, being still intermediate between single bond [*ca.* 2.38 Å] and double bond [P=Se double bond length *ca.* 2.08 Å],⁴⁵ indicating the delocalisation of the negative charge over the FPSe_2 fragment.

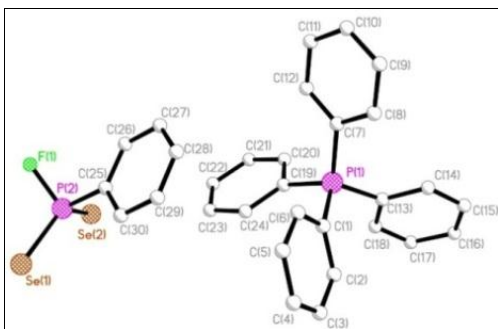


Figure 1. X-ray crystal structure of **3** (Hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$) (esds in parentheses): Se(1)-P(2) 2.1136(16), Se(2)-P(2) 2.1163(14), F(1)-P(2) 1.604(3); Se(1)-P(2)-Se(2) 108.83(14), Se(1)-P(2)-F(1) 107.47(10), Se(2)-P(2)-F(1) 106.44(10).

Reacting **1** with an equimolar amount of halogenated alkanes in dry THF in room temperature generates a series of esters of phenylphosphonofluoridodiselenoates **5 - 8** in 84% - 92% yields (Scheme 4). Furthermore, 1,4-phenylenebis(methylene) bis(phenylphosphonofluoridodiselenoate) **9** was prepared by the reaction of compound **1** with 0.5 equivalents of 1,4-bis(bromomethyl)benzene under identical conditions in 79% yield as shown in Scheme 5. The esters **5 - 9** are air-stable oils or pastes and are soluble in common organic solvents such as dichloromethane, trichloromethane, acetone and THF. Compounds **5 - 9** were fully characterized by multinuclear NMR and IR spectroscopy and accurate mass measurement. All new compounds showed the anticipated molecular ion peaks $[\text{M}]^+$, and were con-

firmed by satisfactory accurate mass measurements. The ^{31}P NMR spectra of esters **5-9** showed two doublets ($\delta_{\text{P}} = 102.6 - 103.5$ ppm) with ^{31}P - ^{19}F coupling constants ($J(\text{P},\text{F}) = 1141 - 1146$ Hz), flanked by selenium satellites with ^{31}P - ^{77}Se coupling constants ($J(\text{P},\text{Se}) = 481 - 496$ Hz and $904 - 909$ Hz), indicating the presence of both P-Se single bond and P=Se double bond in these heteroatom compounds. In the ^{19}F NMR spectra of compounds **5 - 9**, doublets ($\delta_{\text{F}} = -58.5 - -55.8$ ppm) were observed with the corresponding ^{31}P - ^{19}F coupling constants, each was accompanied by selenium satellites with ^{19}F - ^{77}Se coupling constants ($J(\text{F},\text{Se}) = 17.1 - 19.0$ Hz and $33.3 - 35.4$ Hz). This was further supported by the ^{77}Se NMR spectra which showed double doublets with the respective matching ^{31}P - ^{77}Se and ^{19}F - ^{77}Se coupling constants. For compounds **5** and **9**, two diastereoisomers were observed in multi-NMR spectra in 2 : 1 and 1 : 4 intensity ratio, respectively.

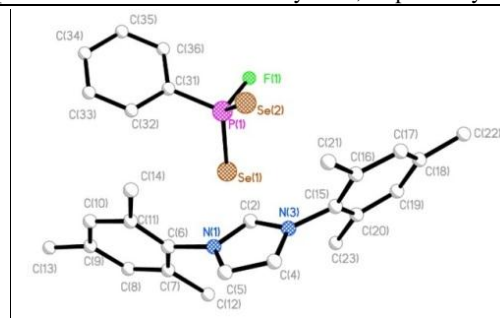
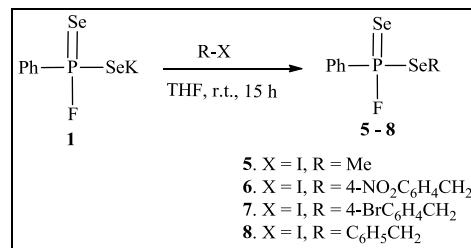
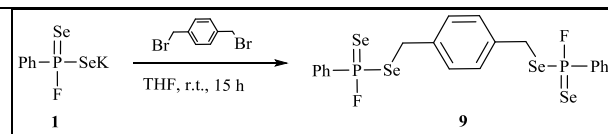


Figure 2. X-ray crystal structure of **4** (Hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$) (esds in parentheses): Se(1)-P(1) 2.119(3), P(1)-F(1) 1.610(5), P(1)-Se(2) 2.108(3); Se(1)-P(1)-Se(2) 120.29(11), Se(1)-P(1)-F(1) 106.2(2), Se(2)-P(1)-F(1) 107.4(3).



Scheme 4. Synthesis of esters of phenylphosphonofluoridodiselenoates **5 - 8**.



Scheme 5. Synthesis of 1,4-phenylenebis(methylene) bis(phenylphosphonofluoridodiselenoate) **9**.

In conclusion, Woollins' reagent reacts with dry KF or tetrabutylammonium fluoride to give the corresponding potassium and tetrabutylammonium salts of phenyldiselenofluorophosphinic acids in almost quantitative yields. Potassium phenyldiselenofluorophosphinic acid was converted readily into the corresponding organic adducts by reacting further with an equimolar amount of tetraphenylphosphonium chloride or 1,3-dimesityl-*1H*-imidazol-3-ium chloride. Furthermore, reaction of potassium phenyldiselenofluorophosphinic acid with mono- and di-halogenated alkanes afforded a series of esters of phenylphosphonofluoridodiselenoates in high yields. The structures of all new compounds have been elucidated using ^1H , ^{13}C , ^{31}P , ^{77}Se , ^{19}F

NMR spectroscopy and accurate mass measurement in conjunction with single crystal X-ray crystallography of two structures.

ASSOCIATED CONTENT

Supporting Information

Experimental, details, crystal data and spectra are available free of charge via the internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

Tel.: (+44)-1334-463384; email: jdw3@st-and.ac.uk

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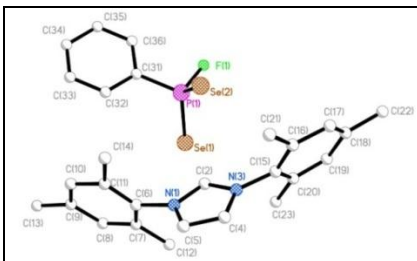
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Entry for the Table of Contents

Phosphorus-selenium Heteroatom Compounds

Fluorinated Phosphorus-selenium Heteroatom Compounds: Phenylphosphonofluorodiselenoic Salts, Adducts and Esters

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Potassium and tetrabutylammonium salts of phenyldiselenofluorophosphinic acids, derived from Woollins' reagent, KF or tetrabutylammonium fluoride (TBAF), were reacted with tetra-phenylphosphonium chloride or 1,3-dimesityl-1*H*-imidazol-3-ium chloride or mono- and di-halogenated alkanes gave a series of the corresponding salts, adducts and esters.