

Dedicated to Professor Dumitru Oancea
on the occasion on his 75th anniversary

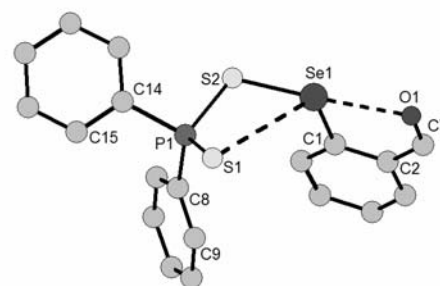
NEW HYPERVALENT ORGANOSELENIUM COMPOUNDS WITH O→Se INTRAMOLECULAR INTERACTIONS

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New organoselenium(II) compounds containing the 2-(O=CH)C₆H₄Se fragment are described. The reaction between [2-(O=CH)C₆H₄]₂Se₂ and [R₂P(S)S]₂ in a 1:1 molar ratio resulted in the formation of the organoselenium(II) derivatives [2-(O=CH)C₆H₄]SeSP(S)R₂ [R = Ph (1), OPrⁱ (2)]. Compound 1 was obtained also by reacting [2-(O=CH)C₆H₄]SeCl (3) with NH₄[S₂PPh₂] in a 1:1 molar ratio. While compound 1 was isolated as a solid, crystalline product, compound 2 could be evidenced only in equilibrium with the starting materials. The obtained products were investigated by multinuclear NMR (¹H, ¹³C, ³¹P, ⁷⁷Se). Compound 1 was also characterized by IR spectroscopy. The crystal and molecular structures of compounds 1 and 3 were determined by single-crystal X-ray diffraction.



INTRODUCTION

Organoselenium compounds attracted a continuously increased interest during last years due to their potential applications in biology, catalysis and organic synthesis or as precursors for nanomaterials.¹⁻⁷ A special attention was devoted to species containing organic groups with pendant arms capable for N→Se or O→Se intramolecular coordination.⁸⁻¹⁷ Such additional interactions increase the hydrolytic and thermal stability of the respective compounds, favour the isolation of monomeric species and have a significant influence upon the biological or catalytic activity in different processes.

On the other hand, metal or metalloid derivatives of diorganodichalcogenophosphorus acids (Scheme 1) were intensively studied in order to show the influence of the phosphorus ligand coordination

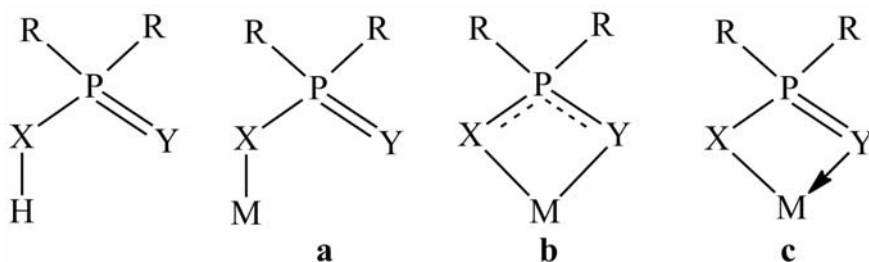
behaviour upon an increased biological or catalytic activity. In their metal complexes, the diorganodichalcogenophosphinato, [R₂PXY]⁻, or phosphato, [(RO)₂PXY]⁻, ligands can mainly behave as monodentate (Scheme 1, structure a) or bidentate (Scheme 1, structures b and c) moieties.¹⁸

We have previously investigated the coordination behaviour of such phosphorus ligands towards several organoselenium(II)¹⁹⁻²¹ and organotellurium(II)²² fragments and for several species the crystal and molecular structure was determined by single crystal X-ray diffraction. In most of the investigated compounds a monodentate behaviour (Scheme 1, structure a) of the phosphorus ligand was observed, e.g. the [2-(R'₂NCH₂)C₆H₄]SeSP(S)R₂ [R' = Me, Et, Prⁱ; R'₂ = MeN(CH₂CH₂)₂, O(CH₂CH₂)₂; R = Ph, OPrⁱ] derivatives are monomeric species with

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intramolecular N→Se coordination.¹⁹⁻²¹ In contrast, for PhSeSP(S)Ph₂ the second sulfur atom in the ligand unit has a weak intramolecular contact with selenium.¹⁹ Moreover, in both PhESP(S)Ph₂ (E = Se,¹⁹ Te²²) the coordination sphere of the heavy chalcogen is completed by S···E (E = Se, Te) intermolecular interactions, thus resulting in polymeric chains and a T-shaped coordination geometry about selenium or tellurium.

As a continuation of our studies, we report here the synthesis and structural characterization of compounds of type [2-(O=CH)C₆H₄]SeSP(S)R₂ (R = Ph, OPrⁱ). Such compounds with a 2-(O=CH)C₆H₄ substituent can be used as starting materials for the synthesis of other related species by condensation with primary amines.



R = alkyl, aryl, alkoxo, aryloxo; X, Y = O, S

Scheme 1

RESULTS

Synthesis

The diorganodiselenide [2-(O=CH)C₆H₄]₂Se₂ gives redistribution reactions in the presence of the disulfanes [R₂P(S)S]₂ (R = Ph, OPrⁱ), as depicted in (*eq. 1*). The salt metathesis reaction between [2-(O=CH)C₆H₄]SeCl (**3**) and NH₄[S₂PPh₂] resulted in [2-(O=CH)C₆H₄]SeSP(S)Ph₂ (**1**) as well (*eq. 2*).

While for **1** a quantitative redistribution reaction (*eq. 1*) was observed after 24 hours both in chloroform and in toluene solutions, at room temperature, and the compound could be isolated as a yellow, microcrystalline solid, in case of **2**, even after refluxing the reaction mixture for about 36 hours in toluene, the reaction was not completed and only a mixture of **2** with the starting materials was obtained, as observed by TLC and NMR spectroscopy. The reaction between [2-

(O=CH)C₆H₄]₂Se₂ and [(PrⁱO)₂P(S)S]₂ was also performed in the absence of any solvent, by melting the reactants and stirring them for 24 hours at 110 °C. Even in this case, a red oil was obtained, which proved to be again a mixture of **2** with the starting materials, in *ca.* 3:1 molar ratio. Thus we could conclude that in case of the redistribution reaction using [(PrⁱO)₂P(S)S]₂ an equilibrium was established.

The products were investigated by multinuclear NMR (¹H, ¹³C, ³¹P and ⁷⁷Se). Compound **1** was investigated also by IR spectroscopy. The molecular structure of compounds **1** and **3** was established by single-crystal X-ray diffraction. The Ortep-like diagrams and the atom numbering schemes for compounds **1** and **3** are presented in Figs. 1 and 2, respectively, while interatomic distances and bond angles are given in Tables 1 and 2.



Table 1

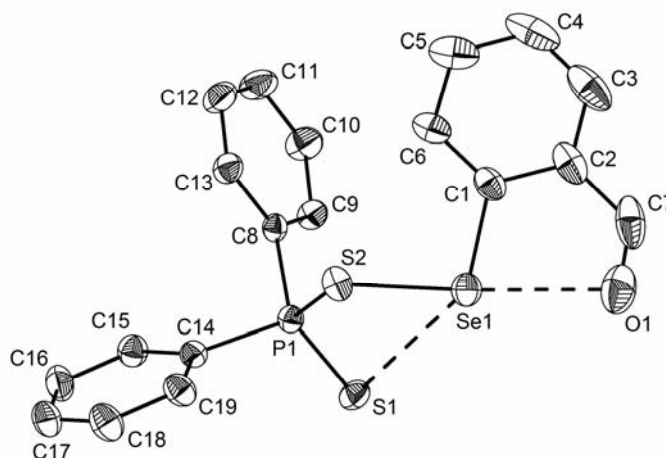
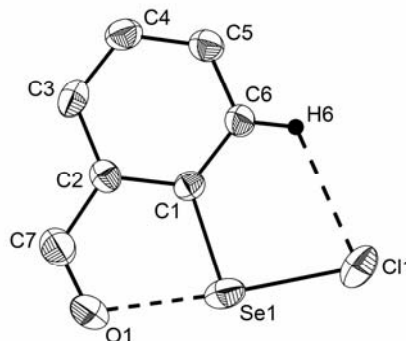
Selected interatomic distances (Å) and angles (deg) in compound **1**

Se1–C1	1.921(4)	C1–Se1–S2	101.37(13)
Se1–S2	2.200(1)	C1–Se1···S1	110.86(12)
Se1···S1	3.650(1)	C1–Se1···O1	76.99(14)
Se1···O1	2.568(4)	S2–Se1···O1	175.10(9)
P1–S1	1.935(1)	S2–Se1···S1	66.44(3)
P1–S2	2.128(1)	S1–P1–S2	114.92(6)

Table 2

Selected interatomic distances (Å) and angles (deg) in compound **3**

Se1–C1	1.907(4)	C1–Se1–C11	97.19(14)
Se1–C11	2.268(2)	C1–Se1···O1	79.11(17)
Se1···O1	2.266(4)	C11–Se1···O1	176.30(11)

Fig. 1 – ORTEP representation at 30% probability and atom numbering scheme for compound **1**.Fig. 2 – ORTEP representation at 30% probability and atom numbering scheme for compound **3**.

DISCUSSION

Spectroscopy

The NMR spectra in CDCl_3 solutions are in accordance with a pure compound **1** and a mixture of **2** and the starting materials, respectively. We have to mention that in the following discussion we refer to compound **1** and the NMR resonances

of compound **2** as they could be identified in the reaction mixture. The ^1H and ^{13}C NMR spectra exhibit the expected resonances for the organic groups attached to phosphorus and to selenium, respectively, both in the aliphatic and in the aromatic regions, as appropriate. The ^1H and ^{13}C NMR resonances for the respective atoms in the organic groups attached to phosphorus are split in two components of equal intensity due to the phosphorus – proton and phosphorus – carbon

couplings, respectively. The ^1H NMR spectrum of compound **2** deserves a special attention. It contains in the aliphatic region two doublets corresponding to the diastereotopic methyl groups in the $\text{POCH}(\text{CH}_3)_2$ moiety and a multiplet resonance characteristic for the $\text{POCH}(\text{CH}_3)_2$ protons. The ^{13}C NMR spectrum of this compound displays in the aliphatic region three doublet resonances which were assigned to the carbon atoms of the diastereotopic CH_3 and the CH groups, respectively, thus suggesting the equivalence of the two $\text{OCH}(\text{CH}_3)_2$ groups attached to phosphorus in solution.

The ^{31}P and ^{77}Se NMR spectra display singlet resonances, shifted in comparison with the δ values observed for the starting materials,²³⁻²⁵ but in the range observed for other related compounds.^{19-21,26}

The infrared spectra of compound **1** shows strong bands at 652, 534 and 1654 cm^{-1} , characteristic for the $\nu_{\text{as}}(\text{PS}_2)$ and $\nu_{\text{s}}(\text{PS}_2)$ stretching vibrations in the $[\text{Ph}_2\text{PS}_2]^-$ ligand and the $\text{CH}=\text{O}$ group, respectively.

Crystal and molecular structure of [2-(O=CH) C_6H_4] $\text{SeSP}(\text{S})\text{Ph}_2$ (**1**) and [2-(O=CH) C_6H_4] SeCl (**3**)

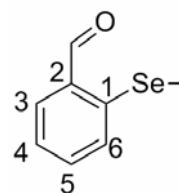
Both compounds have monomeric structures, stabilized by the intramolecular coordination of the oxygen atom in the aldehyde group to selenium. The $\text{O}\cdots\text{Se}$ interatomic distances of 2.568(4) Å in **1** and 2.266(4) Å in **3** are much shorter than the sum of the van der Waals radii of the two elements [$\Sigma r_{\text{vdW}}(\text{Se},\text{O})$ 3.40 Å²⁷] and even shorter than those observed in other organoselenium compounds with such interactions, *e.g.* [2-(O=CH) C_6H_4] $_2\text{Se}_2$ (range 2.720 – 2.751 Å)^{28,29} and [2-(O=CMe) C_6H_4] $_2\text{Se}_2$ [range 2.613(3) – 2.649(4) Å].³⁰ Due to the presence of the aldehyde functionality, the [2-(O=CH) C_6H_4] Se fragment is planar. In case of the chloride **3** a strong intramolecular $\text{Cl}\cdots\text{H}$ interaction is established [$\text{Cl1}\cdots\text{H6}$ 2.591(2) Å; *cf.* $\Sigma r_{\text{vdW}}(\text{Cl},\text{H})$ 3.01 Å²⁷], thus constraining the whole molecule to a planar structure. The $\text{O}\cdots\text{Se}$ intramolecular interaction determines a distorted T-shaped coordination geometry about selenium in **3** [$\text{Cl1}-\text{Se1}\cdots\text{O1}$ 176.30(11)°]. If the two lone pairs are considered as well, the coordination geometry might be described as a *pseudo*-trigonal bipyramid with O1 and Cl1 in apices and the whole molecule as a 10-*Se*-3 hypercoordinated species.³¹

In compound **1** the organophosphorus ligand, $[\text{Ph}_2\text{PS}_2]^-$, behaves as an anisobidentate moiety towards selenium, being primary coordinated

through S2 [$\text{Se1}-\text{S2}$ 2.200(1) Å and $\text{Se1}\cdots\text{S1}$ 3.650(1) Å; *cf.* $\Sigma r_{\text{cov}}(\text{Se},\text{S})$ 2.21 Å and $\Sigma r_{\text{vdW}}(\text{Se},\text{S})$ 3.85 Å²⁷]. A bidentate behaviour was also observed in $\text{PhSeSP}(\text{S})\text{Ph}_2$,¹⁹ by contrast with the monodentate, monometallic monoconnective behaviour observed in compounds containing an organic group with pendant arm capable for $\text{N}\rightarrow\text{Se}$ intramolecular coordination, *e.g.* [2-($\text{R}'_2\text{NCH}_2$) C_6H_4] $\text{SeSP}(\text{S})\text{R}_2$ [$\text{R}' = \text{Me}, \text{Et}, \text{Pr}^i$; $\text{R}'_2 = \text{MeN}(\text{CH}_2\text{CH}_2)_2, \text{O}(\text{CH}_2\text{CH}_2)_2$; $\text{R} = \text{Ph}, \text{OPr}^i$].¹⁹⁻²¹ In this way a see-saw coordination geometry is realized about selenium [$\text{S2}-\text{Se1}\cdots\text{O1}$ 175.10(9)°]. Due to the secondary interactions the coordination number to selenium increases, and, if we take into account also the lone pairs of selenium, the compound might be described as a 12-*Se*-4 hypercoordinated species, with a *pseudo*-octahedral environment about the $\text{Se}(\text{II})$ atom.³¹ The phosphorus-sulfur interatomic distances have typical values for single P-S and double P=S bonds, *cf.* P-S 2.077(1) and P=S 1.954(1) Å in $\text{Ph}_2\text{P}(\text{S})\text{SH}$,²⁶ similarly with the related compounds reported previously.¹⁹⁻²²

EXPERIMENTAL

The starting materials were obtained following literature procedures: [2-(O=CH) C_6H_4] $_2\text{Se}_2$,²⁵ [2-(O=CH) C_6H_4] SeCl (**3**),³² $[\text{Ph}_2\text{P}(\text{S})\text{S}]_2$,²³ $[(\text{PriO})_2\text{P}(\text{S})\text{S}]_2$,²⁴ and $\text{NH}_4[\text{S}_2\text{PPh}_2]$.³³ Elemental analyses were performed on a Flash EA 1112 analyzer. Melting points were measured on an Electrothermal 9200 apparatus and are not corrected. The IR spectrum of compound **1** was recorded on a Jasco FT IR spectrometer, as KBr pellets. ^1H , ^{13}C , ^{31}P and ^{77}Se NMR spectra were recorded in CDCl_3 solution on a BRUKER Avance instrument operating at 600.13, 150.90, 242.94 and 114.45 MHz, respectively. The ^1H chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (CHCl_3 , 7.26 ppm). The ^{13}C chemical shifts are reported in δ units (ppm) relative to the peak of the deuterated solvent (CDCl_3 , 77.16 ppm).³⁴ The ^1H and ^{13}C NMR resonances were assigned according to the numbering scheme in Scheme 2



Scheme 2

by using 2D NMR experiments (COSY, HSQC and HMBC). The ^{31}P chemical shifts are reported in δ units (ppm) relative to H_3PO_4 85% as external standard. The ^{77}Se NMR spectra were obtained using Ph_2Se_2 as external standard and the chemical shifts are reported relative to Me_2Se ($\delta = 0$ ppm) by assuming that the resonance of the standard is at $\delta = 461$ ppm.³⁵ The NMR spectra were processed using the *MestReC* and *MestReNova* software.³⁶

Synthesis of [2-(O=CH)C₆H₄]SeSP(S)Ph₂ (1)

(a) A reaction mixture of [2-(O=CH)C₆H₄]₂Se₂ (0.53 g, 1.44 mmol) and [Ph₂P(S)S]₂ (0.72 g, 1.44 mmol) in 5 mL CHCl₃ was stirred at room temperature for 12 hours. The solvent was removed at reduced pressure and the remained product was washed with n-hexane to give **1** as a yellow solid. Yield: 1.22 g (98%).

(b) A reaction mixture of [2-(O=CH)C₆H₄]SeCl (**3**) (0.26 g, 1.18 mmol) and NH₄[S₂PPh₂] (0.32 g, 1.18 mmol) in 50 mL dichloromethane was stirred at room temperature for 8 hours. NH₄Cl was removed by filtration. The solvent was evaporated at reduced pressure and the solid product was washed with n-hexane and dried under reduced pressure. Yield: 0.47 g (92%). M.p. = 118 °C. Anal. Calcd. for C₁₉H₁₅OPS₂Se (MW 433.39): C, 52.66; H, 3.49%; Found: C, 52.81; H, 3.68%. ¹H NMR: δ 7.33 (1H, t, H-5, ³J_{HH} = 7.5 Hz), 7.38–7.42 (5H, m, H-4 + PC₆H₅-meta), 7.45–7.47 (2H, m, PC₆H₅-para), 7.78 (1H, d, H-6, ³J_{HH} = 7.1 Hz), 7.98 (4H, dd, PC₆H₅-ortho, ³J_{HH} = 7.4, ³J_{PH} = 14.4 Hz), 8.03 (1H, d, H-3, ³J_{HH} = 7.5 Hz), 10.02 (1H, s, CH=O). ¹³C NMR: δ 126.22 (s, C-5), 128.47 (d, PC₆H₅-meta, ³J_{PC} = 13.8 Hz), 129.05 (s, C-3), 131.77 (d, PC₆H₅-ortho, ²J_{PC} = 11.0 Hz), 132.04 (d, PC₆H₅-para, ⁴J_{PC} = 2.9 Hz), 133.87 (d, PC₆H₅-ipso, ¹J_{PC} = 81.4 Hz), 134.15 (s, C-4), 134.24 (s, C-2), 135.04 (s, C-6), 138.19 (s, C-1), 192.88 (s, CH=O). ³¹P NMR: δ 64.8 (s, ¹J_{PC} = 81.2 Hz). ⁷⁷Se NMR: δ 610.6 (s).

Synthesis of [2-(O=CH)C₆H₄]SeSP(S)(OPrⁱ)₂ (2)

A reaction mixture of [2-(O=CH)C₆H₄]₂Se₂ (0.53 g, 1.44 mmol) and [(PrⁱO)₂P(S)S]₂ (0.61 g, 1.44 mmol) in 50 mL

toluene was stirred under reflux for 36 hours. The solvent was removed at reduced pressure and the remained red oil proved to be a mixture of the desired product **2** and residual starting materials. The starting diorganodiselenide was removed by washing with n-hexane (2 x 15 mL), but the attempts to separate the title compound and the unreacted [(PrⁱO)₂P(S)S]₂ by column chromatography resulted in subsequent decomposition. ¹H NMR (compound **2**): δ 1.29 [6H, d, POCH(CH₃)₂, ³J_{HH} = 6.2 Hz], 1.30 [6H, d, POCH(CH₃)₂, ³J_{HH} = 6.2 Hz], 4.83–4.93 [2H, m, POCH(CH₃)₂], 7.46 (1H, d, H-5, ³J_{HH} = 7.3 Hz), 7.64 (1H, dd, H-4, ³J_{HH} = 7.3, ⁴J_{HH} = 1.7 Hz), 7.91 (1H, dd, H-6, ³J_{HH} = 7.4, ⁴J_{HH} = 1.9 Hz), 8.29 (1H, d, H-3, ³J_{HH} = 7.3 Hz), 10.15 (1H, s, CH=O). ¹³C NMR (compound **2**): δ 23.48 [d, POCH(CH₃)₂, ³J_{PC} = 5.83 Hz], 23.65 [d, POCH(CH₃)₂, ³J_{PC} = 4.27 Hz], 74.29 [d, POCH(CH₃)₂, ²J_{PH} = 7.36 Hz], 126.25 (s, C-5), 129.26 (s, C-3), 134.21 (s, C-4 + C-2), 135.19 (s, C-6), 138.51 (s, C-1), 193.01 (s, CH=O). ³¹P NMR (compound **2**): δ 83.2 (s, ²J_{PC} = 93.5 Hz). ⁷⁷Se NMR (compound **2**): δ 635.9 (s). ¹H NMR (residual [(PrⁱO)₂P(S)S]₂): δ 1.41 [6H, d, POCH(CH₃)₂, ³J_{HH} = 5.6 Hz], 1.43 [6H, d, POCH(CH₃)₂, ³J_{HH} = 5.9 Hz], 4.83–4.93 (2H, m, POCH(CH₃)₂). ³¹P NMR (residual [(PrⁱO)₂P(S)S]₂): δ 81.7 (s).

X-ray structure determination

The details of the crystal structure determination and refinement for compounds **1** and **3** are given in Table 3.

Table 3

X-ray crystal data and structure refinement for compounds **1** and **3**

	1	3
Molecular formula	C ₁₉ H ₁₅ OPS ₂ Se	C ₇ H ₅ ClOSe
<i>M</i>	433.36	219.52
Crystal system	Triclinic	Orthorhombic
Space group	<i>P</i> -1	<i>Pna</i> 2(1)
Temperature (K)	294(2)	297(2)
<i>a</i> /Å	8.8962(17)	10.749(6)
<i>b</i> /Å	9.1626(17)	15.211(8)
<i>c</i> /Å	12.839(2)	4.685(3)
<i>α</i> ^o	107.909(3)	90.00
<i>β</i> ^o	106.121(3)	90.00
<i>γ</i> ^o	98.522(3)	90.00
<i>V</i> /Å ³	924.9(3)	766.0(7)
<i>Z</i>	2	4
<i>D</i> _{calc} /gcm ⁻³	1.556	1.904
<i>F</i> (000)	436	424
<i>μ</i> (Mo-Kα)/mm ⁻¹	2.345	5.172
Crystal size (mm ³)	0.31 x 0.26 x 0.22	0.40 x 0.21 x 0.20
<i>θ</i> range for data collection (°)	1.775 to 25.00	2.68 to 24.95
Reflections collected	8740	5268
Independent reflections	3221 [R(int) = 0.0404]	1345 [R(int) = 0.0366]
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3221 / 0 / 217	1345 / 1 / 91
Goodness-of-fit on F ²	1.044	1.090
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0412, <i>wR</i> ₂ = 0.0854	<i>R</i> ₁ = 0.0333, <i>wR</i> ₂ = 0.0708
<i>R</i> indices (all data) ^a	<i>R</i> ₁ = 0.0570, <i>wR</i> ₂ = 0.0948	<i>R</i> ₁ = 0.0370, <i>wR</i> ₂ = 0.0724
Largest difference peak and hole (e Å ⁻³)	0.575 and -0.292	0.446 and -0.263

Data were collected on a Bruker SMART APEX diffractometer by using graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$). The crystals were attached with paraton/N oil on cryoloops and the data were collected at room temperature (297 K). The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used.³⁷ The drawings were created with the Diamond program.³⁸

CONCLUSIONS

The redistribution reaction between the diorganodiselenide $[2-(\text{O}=\text{CH})\text{C}_6\text{H}_4]_2\text{Se}_2$ and $[\text{Ph}_2\text{P}(\text{S})\text{S}]_2$ in a 1:1 molar ratio avoided the isolation of $[2-(\text{O}=\text{CH})\text{C}_6\text{H}_4]\text{SeSP}(\text{S})\text{Ph}_2$ (**1**) as a microcrystalline solid, while the reaction between $[2-(\text{O}=\text{CH})\text{C}_6\text{H}_4]_2\text{Se}_2$ and $[(\text{Pr}^i\text{O})_2\text{P}(\text{S})\text{S}]_2$ proved to be an equilibrium process and the species $[2-(\text{O}=\text{CH})\text{C}_6\text{H}_4]\text{SeSP}(\text{S})(\text{OPr}^i)_2$ (**2**) was only detected in the reaction mixture by NMR in approx. 3:1 molar ratio with the starting materials. Alternatively, compound **1** was obtained by the salt metathesis reaction between $[2-(\text{O}=\text{CH})\text{C}_6\text{H}_4]\text{SeCl}$ (**3**) and $\text{NH}_4[\text{S}_2\text{PPh}_2]$. The single-crystal X-ray diffraction studies revealed a monomeric structure for compounds **1** and **3**, with *C,O*-chelating organic groups attached to selenium. The dithiophosphinato ligand in compound **1** behaves as a bidentate moiety, thus completing a see-saw coordination geometry about selenium.

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Supplementary material

CCDC 1447362 and 1447363 contain the supplementary crystallographic data for compounds **1** and **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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