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Organoselenium(II) complexes containing organophosphorus ligands. Crystal and molecular structure of $PhSeSP(S)Ph_2$, $[2\text{-}\{MeN(CH_2CH_2)_2NCH_2\}C_6H_4]SeSP(S)R'_2$ (R′ = Ph, OPr^i) and $[2\text{-}\{O(CH_2CH_2)_2NCH_2\}C_6H_4]SeSP(S)(OPr^i)_2$

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ABSTRACT

Arylselenium(II) derivatives of dithiophosphorus ligands of type $ArSeSP(S)R_2$ [Ar = Ph, R = Ph (**1**), OPr^i (**2**); 2-$[MeN(CH_2CH_2)_2NCH_2]C_6H_4$, R = Ph (**3**), OPr^i (**4**); 2-$[O(CH_2CH_2)_2NCH_2]C_6H_4$, R = OPr^i (**6**)] were prepared by redistribution reactions between Ar_2Se_2 and $[R_2P(S)S]_2$. The derivative $[2\text{-}\{O(CH_2CH_2)_2NCH_2\}C_6H_4]SeSP(S)Ph_2$ (**5**) was obtained by the salt metathesis reaction between $[2\text{-}\{O(CH_2CH_2)_2NCH_2\}C_6H_4]SeCl$ and $NH_4S_2PPh_2$. The compounds were investigated by multinuclear (^1H, ^{13}C, ^{31}P, ^{77}Se) NMR and infrared spectroscopy. The crystal and molecular structures of **1**, **3**, **4** and **6** were determined by single-crystal X-ray diffraction. In compounds **3**, **4** and **6** the N(1) atom is intramolecularly coordinated to the selenium center, resulting in a T-shaped geometry (hypervalent 10-*Se*-3 species). The dithiophosphorus ligands act as anisobidentate in **1** and monodentate in **3**, **4** and **6**. Supramolecular architectures based on intermolecular S···H and N···H contacts between molecular units are formed in the hypervalent derivatives **3** and **4**, while in the compounds **1** and **6** the molecules are associated into polymeric chains through either Se···S or O···H contacts, with no further inter-chain interactions.

1. Introduction

The chemistry of hypervalent organochalcogen derivatives containing ArE moieties (Ar = organic group with pendant arms with potential for N → E intramolecular coordination, E = Se, Te) have attracted continuous interest in last years due both to their increased thermal and hydrolytic stability and their potential applications [1–8]. Selenium compounds with 2-(diorganoaminomethyl)phenyl and related organic groups in which the nitrogen atom is intramolecularly coordinated to the chalcogen center were already used as catalysts in asymmetric synthesis [9–17], as antioxidant reagents or enzyme mimics [1,18–21]. The tellurium analogues were less investigated.

We have previously reported on the synthesis, solution behavior and molecular structure of some chalcogen(I) and chalcogen(II) derivatives containing organic groups with pendant arm containing nitrogen donor atoms, *i.e.* 2-$(Me_2NCH_2)C_6H_4$ [6,22,23], 2-$[O(CH_2CH_2)_2NCH_2]C_6H_4$ and 2-$[MeN(CH_2CH_2)_2NCH_2]C_6H_4$ [24]. The structural investigations on a series of these compounds, *i.e.* diorganodichalcogenides, organochalcogen(II) halides and organochalcogen(II) complexes with dithio ligands (diorganodithiocarbamates, diorganodithiophosphinates and tetraorganodithioimidodiphosphinates) revealed a T-shaped geometry of the chalcogen (Se, Te) atom, due to the intramolecular N → E interaction [6,22–24].

We developed our previous studies on organoselenium dithio complexes by using bulkier organic groups with additional donor atoms in compounds containing dithiophosphorus ligands. It is well known that this type of ligands usually involve both sulfur atoms in coordination to a metal or a metalloid center, acting as chelate or bridging units [25–30]. In the above mentioned complexes the dithio ligands behave monodentate, only one sulfur atom being involved in coordination to the selenium center [6,23]. However, structural changes could arise due to the nature of the *C,N*-organic group attached to selenium or when this is replaced by a phenyl group.

Here we report on the synthesis and spectroscopic characterization of some new hypervalent organoselenium(II) derivatives containing 1,1-dithiophosphinato or 1,1-dithiophosphato ligands, *i.e.* $[2\text{-}\{E(CH_2CH_2)_2NCH_2\}C_6H_4]SeSP(S)R_2$ [E = NMe, R = Ph (**3**), OPr^i (**4**); E = O, R = Ph (**5**), OPr^i (**6**)]. In order to investigate the structural modifications induced by a *C,N*-organic ligand vs. a phenyl group in organoselenium(II) complexes we have also prepared and

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characterized the compounds $PhSeSP(S)R_2$ [R = Ph (**1**), OPr^i (**2**)]. The crystal and molecular structures of compounds **1**, **3**, **4** and **6** were established by single-crystal X-ray diffraction.

2. Results and discussion

2.1. Preparation

The redistribution reactions between stoichiometric amounts of the diorganodiselenides Ar_2Se_2 and the appropriate bis(diorganothiophosphinyl)disulfane were carried out in dichloromethane and afforded the compounds **1**–**4** and **6** in good yields, as yellow crystalline solids, according to the following equation:

$$Ar_2Se_2 + [R_2P(S)S]_2 \rightarrow 2ArSeSP(S)R_2 \quad (1)$$

$Ar = Ph;\ R = Ph(1),\ OPr^i\ (\mathbf{2})$

$Ar = 2\text{-}[MeN(CH_2CH_2)_2NCH_2]C_6H_4;\ R = Ph\ (\mathbf{3}),\ OPr^i\ (\mathbf{4})$

$Ar = 2\text{-}[O(CH_2CH_2)_2NCH_2]C_6H_4;\ R = OPr^i\ (\mathbf{6})$

Compound **6** was obtained using a salt metathesis reaction between the corresponding organoselenium(II) chloride and ammonium diphenyldithiophosphinate [Eq. (2)]:

$$ArSeCl + NH_4S_2PPh_2 \underset{-NH_4Cl}{\rightarrow} ArSeSP(S)Ph_2 \quad (2)$$

$Ar = 2\text{-}[O(CH_2CH_2)_2NCH_2]C_6H_4\ (\mathbf{5})$

All compounds are stable in solid state for indefinite time, but decomposition occurs in solution for the derivatives containing an organic group with pendant arm. We have investigated the reactions between Ar_2Se_2 and $[R_2P(S)S]_2$ directly in an NMR tube for 1 month and we observed an advanced decomposition for compounds **3**, **4** and **6**, while the NMR spectra of the $Ph_2Se_2/[R_2P(S)S]_2$ mixtures remained unchanged after the formation of the desired compounds **1** and **2**.

2.2. NMR spectra

The solution behavior of the new compounds **1**–**6** was investigated by multinuclear (^1H, ^{13}C, ^{31}P, ^{77}Se) NMR spectroscopy, at room temperature. ^1H and ^{13}C resonances were assigned using 2D NMR experiments, according to the numbering diagram depicted in Scheme 1.

In all compounds the proton and carbon resonances corresponding to the organic groups attached to the phosphorus atom are split into two components of equal intensity, due to the phosphorus–proton and phosphorus–carbon couplings, respectively. The alkyl region of the ^1H NMR spectra of compounds **2**, **4** and **6** exhibits a pattern which is indicative for the diastereotopic nature of the CH_3 of the isopropoxy groups attached to phosphorus, *i.e.* two doublet resonances for the H_A and H_B methyl protons, respectively.

The ^{31}P NMR spectra of compounds **1**–**6** show singlet resonances, shifted in comparison with the starting disulfanes ($[Ph_2P(S)S]_2$, δ_P 69.6 ppm; $[(Pr^iO)_2P(S)S]_2$, δ_P 81.6 ppm), as also observed for the related $[2\text{-}(Me_2NCH_2)C_6H_4]SeSP(S)R_2$ (R = Ph, δ_P 65.1 ppm; R = OPr^i, δ_P 90.0 ppm) [23].

The alkyl region in the room temperature NMR spectra of compounds **3**–**6** exhibit, with respect to the pendant arm of the organic group bound to selenium, $2\text{-}[E(CH_2CH_2)_2NCH_2]C_6H_4$ (E = NMe, O), a singlet resonance for the H_7 protons and two broad resonances for the $H_{8,11}$ and $H_{9,10}$ protons. A similar pattern was observed for the R_2Se_2 starting materials [24] and suggests a considerable weakness of the intramolecular N → Se interaction which allows a fast conformational change of the six-membered morpholinyl or piperazinyl ring. This contrasts with halides RSeX containing similar organic groups for which the $H_{8,11}$ and $H_{9,10}$ protons became non-equivalent as result of the stronger intramolecular N → Se interaction, *i.e.* pro-*cis* and pro-*trans* with respect to the position of the selenium atom in relation to the $E(CH_2CH_2)_2N$ ring.

The ^{77}Se resonances for compounds **3**–**6** (δ_{Se} range 552.1–585.1 ppm) are downfield shifted with respect to those observed for the phenylselenium derivatives **1** (δ_{Se} 486.3 ppm) and **2** (δ_{Se} 462.6 ppm) or the starting diselenides, $[2\text{-}\{E(CH_2CH_2)_2NCH_2\}\text{-}C_6H_4]_2Se_2$ (E = NMe, δ_{Se} 425.4 ppm; E = O, δ_{Se} 425.4 ppm) [24]. They are upfield shifted in comparison with the related $[2\text{-}\{E(CH_2CH_2)_2NCH_2\}C_6H_4]SeI$ (E = NMe, δ_{Se} 700.0 ppm, at +60 °C, in $CDCl_3$; E = O, δ_{Se} 702.0 ppm, at +26 °C, in $CDCl_3$) [24], a behavior consistent with the decreased deshielding of the selenium resonances as the electronegativity of the attached substituent decreases [31].

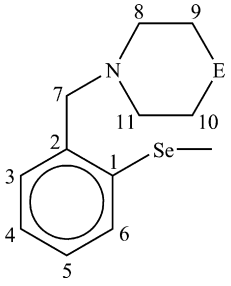
2.3. Infrared spectra

The IR spectra for compounds **1**–**6** exhibit strong absorption bands in the regions 660–640 and 550–500 cm^{-1} which were assigned to asymmetric and symmetric $\nu(PS_2)$ stretching vibrations in the dithiophosphorus ligands attached to the organoselenium(II) moieties.

2.4. Crystal and molecular structure of $PhSeS(S)PPh_2$ (**1**) and $[2\text{-}\{E(CH_2CH_2)_2NCH_2\}C_6H_4]SeS(S)PR'_2$ [E = NMe, R′ = Ph (**3**), OPr^i (**4**); E = O, R′ = OPr^i (**6**)]

In order to reveal the changes produce by replacement of the phenyl group attached to selenium by a potential *C,N*-chelating ligand and the competition for internal coordination between the nitrogen from the pendant arm in the $2\text{-}\{E(CH_2CH_2)_2NCH_2\}C_6H_4$ group and the sulfur atoms of a dithiophosphorus ligand moiety, the molecular structures of compounds **1**, **3**, **4** and **6** were determined. Single-crystals suitable for X-ray diffraction studies were obtained from a CH_2Cl_2/*n*-hexane (1:5, v/v) mixture for **1**, **3** and **6**, and from a $CDCl_3$/*n*-hexane (1:4, v/v) mixture for **4**, respectively.

Selected interatomic distances and angles for **1** are listed in Table 1 and an ORTEP diagram is shown in Fig. 1a. The dith-



Scheme 1.

Table 1
Selected interatomic distances (Å) and angles (°) in **1**.

Se(1)–C(1)	1.908(6)	Se(1)···S(2)	3.795(2)
Se(1)–S(1)	2.205(2)	Se(1)···S(1a)[a]	3.590(2)
P(1)–S(1)	2.119(2)	P(1)–C(7)	1.814(6)
P(1)–S(2)	1.935(3)	P(1)–C(13)	1.806(7)
C(1)–Se(1)-S(1)	101.8(2)	S(1)–P(1)–S(2)	114.71(12)
C(1)–Se(1)···S(2)	122.2(2)	C(7)–P(1)–C(13)	106.3(3)
C(1)–Se(1)···S(1a)[a]	83.8(2)	S(1)–P(1)–C(7)	107.1(2)
S(1)–Se(1)···S(2)	63.00(6)	S(1)–P(1)–C(13)	98.6(2)
S(1)–Se(1)···S(1a)[a]	174.44(6)	S(2)–P(1)–C(7)	114.0(2)
S(2)–Se(1)···S(1a)[a]	113.85(5)	S(2)–P(1)–C(13)	114.7(2)
P(1)–S(1)–Se(1)	102.62(9)	P(1)–S(2)···Se(1)	62.62(8)
		Se(1)···S(1a)–Se(1a)[a]	103.03(6)

[a] Symmetry equivalent atoms (x, $0.5 - y$, $-0.5 + z$) are given by "a".

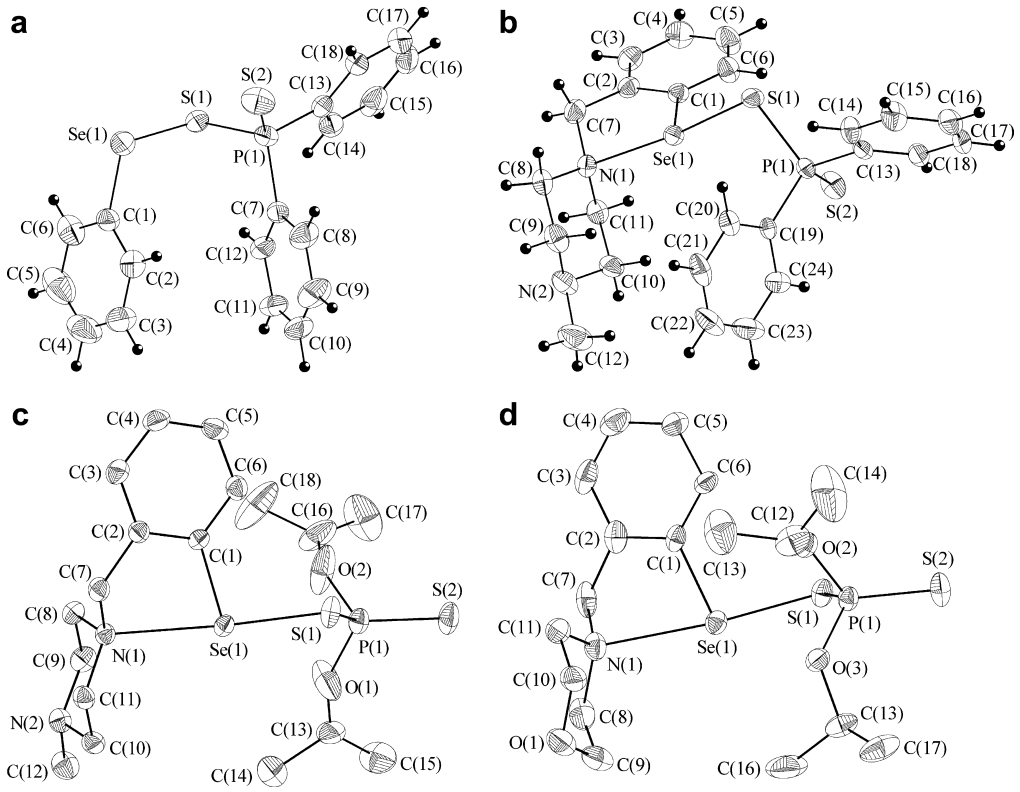


Fig. 1. ORTEP representation and atom numbering scheme for (a) **1**; (b) the (*R*)-**3** isomer; (c) the (*R*)-**4** isomer; and (d) the (*S*)-**6** isomer (30% and 20% probability for **1**/**3**, and **4**/**6**, respectively; for compounds **4** and **6** hydrogen atoms are omitted for clarity).

iophosphinato ligand is primary connected to the selenium through S(1) atom [Se(1)–S(1) 2.205(2) Å], resulting in a V-shaped geometry of the covalent bonds around the selenium center, with a C(1)–Se(1)–S(1) angle of 101.8(2)°, as also observed in the related $PhTeS(S)PPh_2$ [C–Te–S 99.2(1)°] [28]. The Se(1)–S(1) bond distance of 2.205(2) Å is within the expected range for covalent selenium–sulfur single bonds, but significant shorter than in [2-$(Me_2NCH_2)C_6H_4$]SeS(S)PR_2 [2.340(1) and 2.337(1) Å for R = Ph and OPr^i, respectively], where a strong intramolecular N···Se interaction is established in *trans* to the Se–S bond [23].

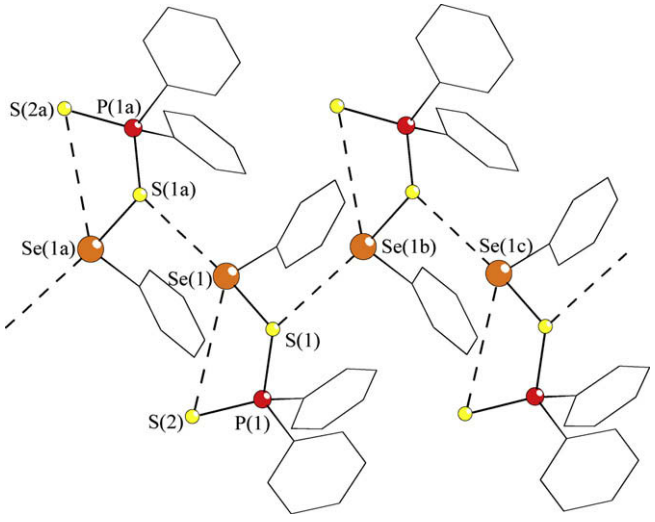


Fig. 2. View of the chain polymer in the crystal of **1** based on intermolecular Se···S contacts [symmetry equivalent atoms (x, 0.5 − y, −0.5 + z), (x, 0.5 − y, 0.5 + z) and (x, y, 1 + z) are given by "a", "b" and "c", respectively].

A weak intramolecular Se···S interaction, shorter than the sum of the van der Waals radii of the corresponding atoms, is also established by the S(2) atom doubly bonded to phosphorus Se(1)···S(2) 3.795(2) Å; cf. the sums of the covalent and van der Waals radii are Σr_{cov}(Se,S) 2.21 Å and Σr_{vdW}(Se,S) 3.85 Å [32]. The four-membered SeS_2P ring is not planar, but folded along the

Table 2
Selected interatomic distances (Å) and angles (°) for compounds **3**, **4** and **6.**

	3	**4**	**6**
Se(1)–C(1)	1.943(4)	1.938(4)	1.943(7)
Se(1)–N(1)	2.463(4)	2.529(3)	2.557(7)
Se(1)–S(1)	2.2973(12)	2.2769(12)	2.276(2)
Se(1)···S(2)[a]	4.037(1)	5.132(2)	5.126(3)
P(1)–S(1)	2.0799(16)	2.0413(16)	2.056(3)
P(1)–S(2)	1.9379(15)	1.9079(16)	1.923(3)
N(1)–C(7)	1.465(5)	1.452(5)	1.462(12)
N(1)–C(8)	1.456(5)	1.453(5)	1.474(11)
N(1)–C(11)	1.466(5)	1.461(5)	1.467(10)
C(1)–Se(1)–S(1)	98.69(12)	98.29(12)	99.7(2)
C(1)–Se(1)–N(1)	77.8(1)	77.4(1)	75.2(3)
N(1)–Se(1)–S(1)	174.6(1)	173.5(7)	172.9(2)
P(1)–S(1)–Se(1)	97.99(5)	103.19(6)	102.01(10)
C(7)–N(1)–C(8)	112.6(4)	112.5(3)	114.1(9)
C(7)–N(1)–C(11)	112.5(4)	112.6(3)	113.8(8)
C(8)–N(1)–C(11)	110.8(3)	110.5(3)	109.1(7)
Se(1)–N(1)–C(7)	96.4(2)	94.5(2)	92.3(5)
Se(1)–N(1)–C(8)	111.4(2)	113.5(2)	112.4(5)
Se(1)–N(1)–C(11)	112.5(2)	112.5(2)	114.6(5)
S(1)–P(1)–S(2)	117.09(8)	109.73(8)	109.74(14)
X(1)–P(1)–X(2)[b]	107.15(18)	98.2(3)	99.8(3)

[a] Non-bonding distance.
[b] X(1) and X(2) are C(13) and C(24) for **3**, O(1A) and O(2A) for **4**, and O(2) and O(3) for **6**.

S(1)···S(2) axis [dihedral angle of 48.2° between the P(1)/S(1)/S(2) and Se(1)/S(1)/S(2) planes].

In the crystal additional, even stronger, intermolecular Se···S interactions [Se(1)···S(1a) 3.590(2) Å] are established between S(1) atom covalent bonded to selenium and the selenium center of a neighboring molecule, thus resulting in a zig-zag chain polymer (Fig. 2). However, the phosphorus–sulfur distances within the ligand moiety are consistent with single P–S and double P=S bonds P(1)–S(1) 2.119(2), P(1)–S(2) 1.935(3) Å in **1**; cf. P–S 2.077(1) and P=S 1.954(1) Å in $Ph_2P(S)SH$ [33]. Thus, the overall coordination pattern of the dithiophosphinato ligand in **1** is bimetallic triconnective which contrast with that found in the related tellurium analogue, $PhTeS(S)PPh_2$, *i.e.* monodentate biconnective pattern (only the sulfur atom single bonded to phosphorus is bridging two tellurium atoms, while the sulfur atom doubly bonded to phosphorus is not involved in interaction with the heavier chalcogen atoms) [28].

It was previously noted [6,24,34–39] that the intramolecular coordination of the nitrogen atom to the metal center in compounds containing 2-$(R_2NCH_2)C_6H_4$ groups induces planar chirality due to the non-planar MC_3N ring thus formed [the aromatic ring

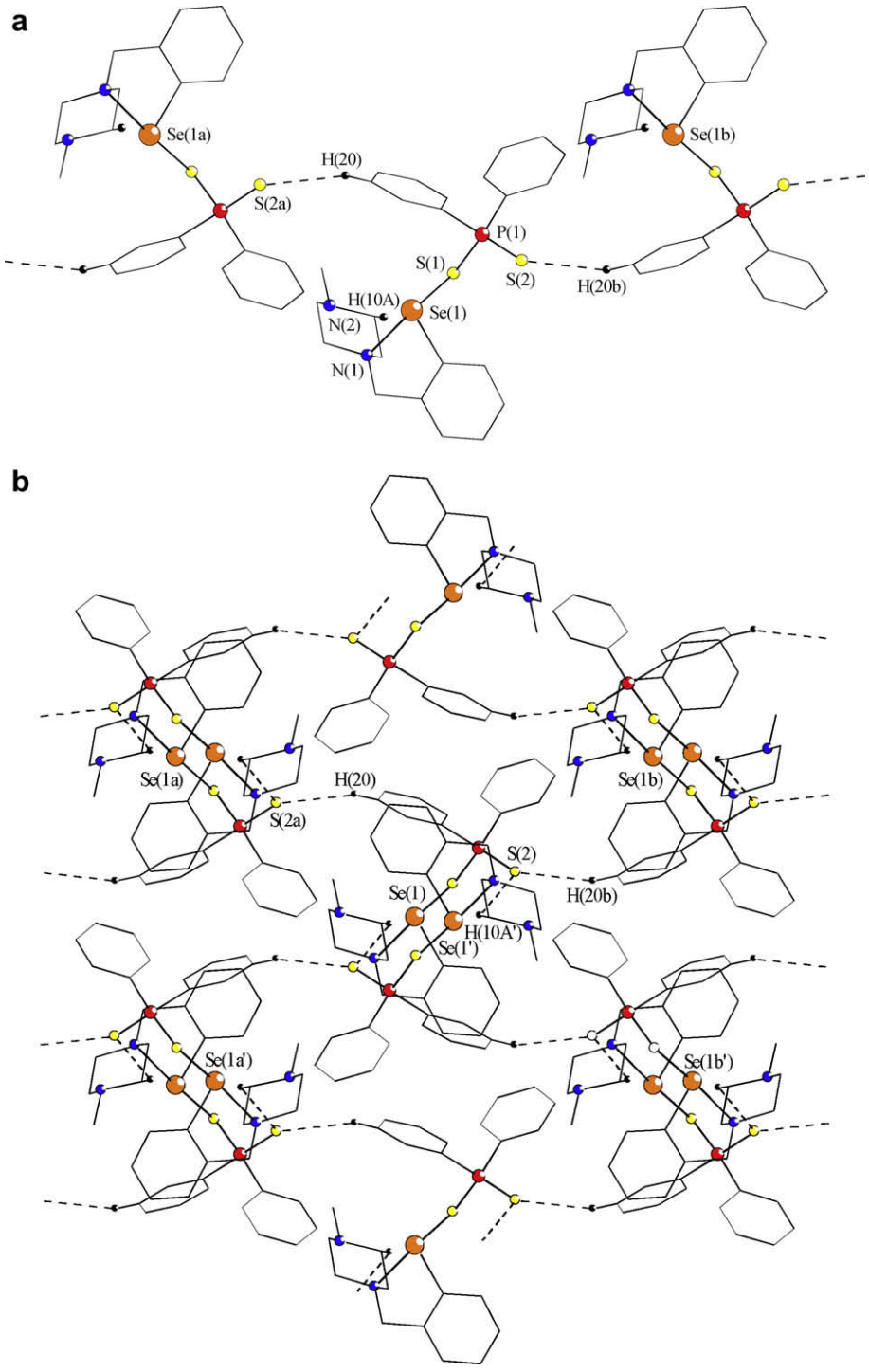


Fig. 3. (a) View along the *a* axis of the chain polymer based on sulfur–hydrogen contacts between alternating *S* and *R* isomers; (b) View along the *a* axis of the double-layer based on sulfur–hydrogen contacts in the crystal of **3** [only hydrogens involved in intermolecular contacts are shown; symmetry equivalent atoms (x, $1.5 - y$, $0.5 + z$), (x, $1.5 - y$, $-0.5 + z$) and ($1 - x$, $1 - y$, $-z$) are given by "a", "b" and "prime", respectively].

and the nitrogen atom being the chiral plane and the pilot atom] and therefore the compounds usually crystallize as racemates [40]. Indeed, due to strong intramolecular Se···N interactions [Se(1)–N(1) 2.463(4), 2.529(3) and 2.557(7) in **3**, **4** and **6**, respectively; cf. Σr_{cov}(Se,N) 1.87 Å, Σr_{vdW}(Se,N) 3.54 Å [32], compounds **3** and **4** crystallize as 1:1 mixtures of *R* and *S* isomers, while for **6** the crystal contains only the isomer *S*. Selected interatomic distances and angles are listed in Table 2 and the ORTEP diagrams for (*R*)-**3**, (*R*)-**4** and (*S*)-**6** isomers are depicted in Fig. 1b–d.

The internal Se···N interactions are much stronger in **3**, **4** and **6** than in the diselenides used as starting materials, *i.e.* [2-{$MeN(CH_2CH_2)_2NCH_2$}C_6H_4]$_2Se_2$ [Se···N 3.135(3)/2.739(3) Å] and [2-{$O(CH_2CH_2)_2NCH_2$}C_6H_4]$_2Se_2$ [Se···N 2.813(2)/2.825(3) Å] [24]. This behavior is consistent with the higher electronegativity of the S(1) atom placed in *trans* to the N(1) atom in the N–Se–S fragment [N(1)–Se(1)–S(1) 174.6(1), 173.5(7) and 172.9(2)° in **3**, **4** and **6**, respectively] and/or with the better leaving group character of the dithiophosphorus anion compared to an $ArSe^-$ anion due to

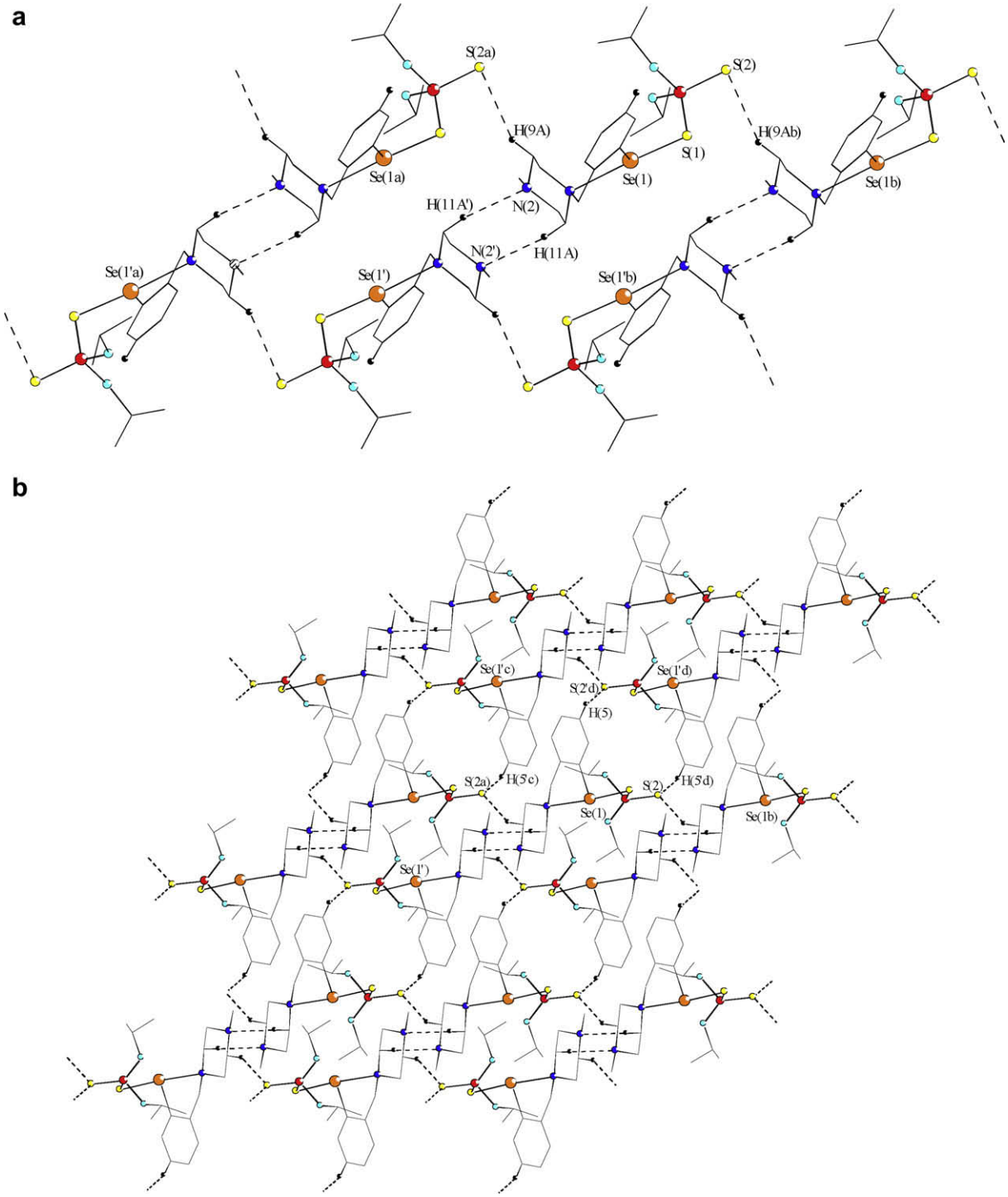


Fig. 4. (a) View of the chain polymer of dimers based on nitrogen–hydrogen and sulfur–hydrogen contacts between *R* and *S* isomers; (b) View of the layer based on sulfur–hydrogen contacts in the crystal of **4** [only hydrogens involved in intermolecular contacts are shown; symmetry equivalent atoms $(2-x, 1-y, 1-z)$, $(x, -1+y, z)$, $(x, 1+y, z)$, $(2-x, -y, 1-z)$, $(2-x, 2-y, -1-z)$, $(2-x, 1-y, 2-z)$ and $(2-x, 2-y, 2-z)$ are given by "prime", "a", "b", "prime a", "prime b", "prime c" and "prime d", respectively].

better charge delocalization in the former. However the internal Se···N interactions in the title compounds are weaker than in the related [2-(Me_2NCH_2)C_6H_4]SeS(S)PR_2 derivatives [Se–N 2.359(2) and 2.397(2) Å for R = Ph and OPr^i, respectively] [23].

As in the parent diselenides [2-{E(CH_2CH_2)$_2$$NCH_2$}$C_6H_4$]$_2$$Se_2$ [24], the piperazinyl and morpholinyl rings exhibit a *chair* conformation which prevents further intramolecular coordination of the N(2) or O(1) atoms to the selenium centers in compounds **3**, **4** and **6**, and thus a (*C*,*N*,*E*)-monometallic triconnective pattern of the organic ligand.

The resulting T-shaped geometry of the (*C*,*N*)SeS core is similar to those observed in the [2-(Me_2NCH_2)C_6H_4]SeS(S)PR_2 derivatives. The distortion of the coordination geometry is mainly due to constrains arising from the five-membered C_3NSe chelate rings, particularly the C(1)–Se(1)–N(1) angle [77.8(1), 77.4(1) and 75.2(3)° in **3**, **4** and **6**, respectively]. The overall coordination geometry around the selenium atom can be considered as distorted *pseudo*-trigonal bipyramidal, with C(1) and the two lone pairs in equatorial positions (hypervalent 10-Se-3 species [41]).

In contrast to the phenylselenium derivative **1**, the internal Se···N interaction prevents any intra- or intermolecular secondary interactions between selenium and the sulfur atoms of the organophosphorus ligand. In compounds **4** [Se(1)···S(2) 5.132(2) Å] and **6** [Se(1)···S(2) 5.126(3) Å] the non-bonded sulfur atom is twisted as far as possible from the selenium atom, while in **3** the S(2) atom is brought closer to the selenium center at a distance [4.037(1) Å] however longer than the sum of the van der Waals radii of the corresponding atoms [cf. Σr_{vdW}(Se,S) 3.85 Å] [32].

As result, the dithio ligands act monometallic monoconnective in compounds **3**, **4** and **6** and the phosphorus–sulfur distances within the ligand moiety are consistent with single P–S and double P═S bonds as was also observed in the related [2-(Me_2NCH_2)C_6H_4]-SeS(S)PR_2 derivatives [23]. The Se(1)–S(1) bond distances [2.2973(12), 2.2769(12) and 2.276(2) Å in **3**, **4** and **6**, respectively] are within the expected range for covalent selenium–sulfur single bonds and of similar magnitude to those found in [2-(Me_2NCH_2)C_6H_4]SeS(S)PR_2 [Se(1)–S(1) 2.340(1) and 2.337(1) Å for R = Ph and OPr^i, respectively] [23] They are longer than in **1** [2.205(2) Å] due to the *trans* effect of the internal Se···N interaction.

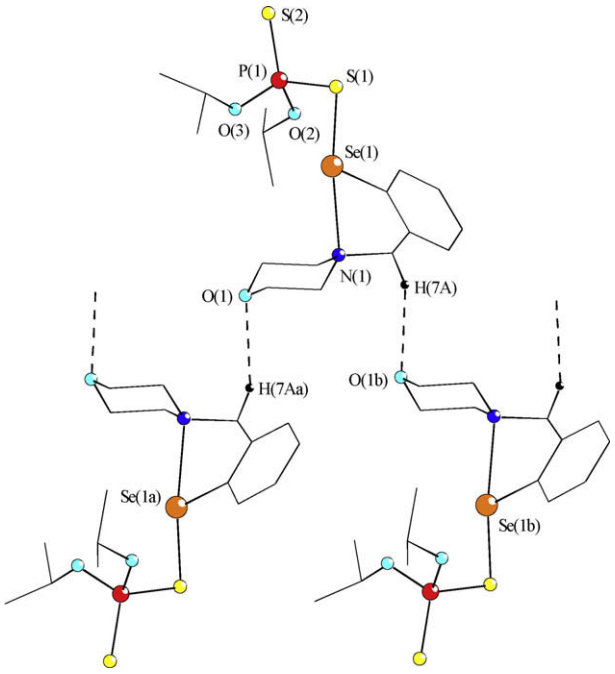


Fig. 5. View of the chain polymer based on sulfur–hydrogen contacts between *S* isomers in the crystal of **6** [only hydrogens involved in intermolecular contacts are shown; symmetry equivalent atoms (−0.5 + *x*, 0.5 − *y*, 2 − *z*) and (0.5 + *x*, 0.5 − *y*, 2 − *z*) are given by "a" and "b", respectively].

Table 3
X-ray crystal data and structure refinement for compounds **1**, **3**, **4** and **6**

	1	**3**	**4**	**6**
Empirical formula	$C_{18}H_{15}PS_2Se$	$C_{24}H_{27}N_2PS_2Se$	$C_{18}H_{31}N_2O_2PS_2Se$	$C_{17}H_{28}NO_3PS_2Se$
Formula weight	405.35	517.53	481.50	468.45
T (K)	297(2)	297(2)	297(2)	297(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$
Unit cell dimension				
a (Å)	8.9342(9)	12.8194(15)	8.872(2)	8.6070(11)
b (Å)	24.866(2)	11.4702(14)	9.127(2)	14.2873(18)
c (Å)	9.1142(9)	16.784(2)	15.181(3)	18.288(2)
α (°)	90	90	73.120(4)	90
β (°)	117.762(2)	93.397(3)	89.930(4)	90
γ (°)	90	90	84.225(4)	90
V (Å^3)	1791.7(3)	2463.7(5)	1169.8(4)	2248.9(5)
Z	4	4	2	4
D_{calc} (g cm^{-3})	1.503	1.395	1.367	1.384
Absorption coefficient (mm^{-1})	2.411	1.772	1.866	1.941
F(000)	816	1064	500	968
Crystal size (mm)	0.29 × 0.19 × 0.18	0.44 × 0.23 × 0.14	0.30 × 0.26 × 0.21	0.38 × 0.24 × 0.21
θ Range for data collection (°)	2.58–25.00	2.15–25.00	2.30–25.49	1.81–25.00
Reflections collected	12890	12622	11347	16415
Independent reflections [R_{int}]	3162 [0.0492]	4329 [0.0462]	4106 [0.0458]	3962 [0.0873]
Data/restraints/parameters	3162/0/200	4329/0/272	4106/63/309	3962/0/231
Goodness-of-fit on F^2	1.230	1.136	1.093	1.094
Final R indices[a]				
R_1	0.0840	0.0565	0.0494	0.0740
wR_2	0.1643	0.1134	0.1014	0.1342
R indices (all data)				
R_1	0.1040	0.0739	0.0623	0.1000
wR_2	0.1733	0.1199	0.1093	0.1438
Largest difference peak and hole (e Å^{-3})	0.815 and −0.380	0.568 and −0.435	0.255 and −0.441	0.469 and −0.473

[a] $I > 2\sigma(I)$.

Even if no intermolecular interactions between heavy atoms are observed for compounds **3**, **4** and **6**, different types of supramolecular architectures are built in their crystals through S(2)···H, N(2)···H and/or $O_{morpholinyl}$···H contacts between the molecular units [cf. Σr_{vdW}(S,H) ca. 3.05 Å; Σr_{vdW}(N,H) ca. 2.74 Å; Σr_{vdW}(O,H) ca. 2.60 Å] [32]. Thus, in the crystal of **3** chains of alternating *R* and *S* isomers are formed through S···$H_{aryl(P)}$ contacts [S(2)···H(20b) 2.74 Å] (Fig. 3a). Weaker inter-chain S···$H_{MeN\text{-}methylene\text{-}ring}$ contacts [S(2)···H(10A′) 2.93 Å] result in a double-layer architecture in which each *R* isomer is connected to four *S* isomers and *vice-versa* (Fig. 3b). In the crystal of **4** not only S(2) atoms but also the N(2) atoms are involved in contacts with hydrogens. Dimer units of *R*- and *S* isomers are formed through N_{Me}···$H_{N\text{-}methylene\text{-}ring}$ contacts [N(2)···H(11A′) 2.67 Å], which are further associated into a chain polymer of dimers through inter-dimer S···$H_{MeN\text{-}methylene\text{-}ring}$ contacts [S(2)···H(9Ab) 2.95 Å] (Fig. 4a). Even weaker S···H_{aryl} contacts [S(2)···H(5′d) 3.01 Å] result in a layer of dimers (Fig. 4b), with no further contacts between parallel layers.

By contrast, in the crystal of **6** the S(2) atoms are not involved in any intermolecular contacts but chain polymers are formed between *S* isomers through weak $O_{morpholinyl}$···$H_{methylene}$ contacts [O(1)···H(7Aa) 2.58 Å] (Fig. 5), with no further inter-chain contacts.

3. Conclusions

New $ArSeSP(S)R_2$ [Ar = Ph, R = Ph (**1**), OPr^i (**2**); 2-[$MeN(CH_2CH_2)_2NCH_2$]C_6H_4, R = Ph (**3**), OPr^i (**4**); 2-[$O(CH_2CH_2)_2NCH_2$]C_6H_4, R = Ph (**5**), OPr^i (**6**)] were prepared and their structure was investigated both in solution and in solid state. The NMR data suggest a considerable weakness of the intramolecular N → Se interaction which allows a fast conformational change of the six-membered piperazinyl or morpholinyl ring. In solid state the presence of a *C,N*-organic group attached to selenium prevents any intra- or intermolecular Se···S interactions, as observed for $PhSeSP(S)Ph_2$ derivative. Compound **6** has crystallized in optically pure form. Compounds **3**, **4** and **6** exhibit a T-shaped coordination geometry, *i.e.* (*C,N*)SeS core (hypervalent 10-*Se*-3 species). Supramolecular architectures are built in solid state through intermolecular contacts between hydrogen atoms and heavier electronegative (sulfur, nitrogen and oxygen) atoms, *i.e.* layer networks for derivatives **3** and **4**, and polymeric chains for compounds **1** and **6**, with no further inter-chain interactions.

4. Experimental

4.1. Materials and procedures

All reactions were carried out under argon using standard Schlenk techniques. Solvents were dried by standard procedures and were freshly distilled prior to use. Ph_2Se_2 (Aldrich) was commercially available. The other starting materials were prepared according to the literature methods: $[R_2P(S)S]_2$ (R = Ph [42], OPr^i [43]), $Ph_2PS_2NH_4$ [44], R_2Se_2 (R = 2-[$MeN(CH_2CH_2)_2NCH_2$]C_6H_4, 2-[$O(CH_2CH_2)_2NCH_2$]C_6H_4) [24]. Room temperature ^1H, ^{13}C and ^{31}P NMR spectra (in dried $CDCl_3$), including 2D experiments, were recorded on a Bruker Avance DRX 300 instrument operating at 300.1, 75.5 and 121.4 MHz, respectively. The chemical shifts are reported in ppm relative to the residual peak of solvent (ref. $CHCl_3$: ^1H 7.26, ^{13}C 77.0 ppm) and H_3PO_4 85%, respectively. The ^{77}Se NMR spectra were obtained on a Bruker Avance DRX 400 instrument operating at 76.3 MHz. The ^{77}Se NMR chemical shifts are referred to external dimethylselenide (0.0 ppm) using as external standard dimethyldiselenide (275.0 ppm) [45]. IR spectra were recorded in the range 4000–400 cm^{-1} as KBr pellets on a Jasco FT/IR-615 instrument. Elemental analyses were performed on a VarioEL analyzer.

4.2. Preparation of phenylselenium(II) diphenyldithiophosphinate, $PhSeSP(S)Ph_2$ (**1**)

Stoichiometric amounts of Ph_2Se_2 (1.0 g, 3.2 mmol) and $[(Ph_2P(S)S]_2$ (0.80 g, 3.2 mmol) in $CHCl_3$ (30 ml) were stirred for 48 h. The solvent was removed in vacuum and the residual oil was worked up with *n*-hexane (5 ml) when the title compound deposited as a yellow powder. Yield: 1.87 g (72%). M.p. 58–60 °C. Anal. Calc. for $C_{18}H_{15}PS_2Se$: C, 53.33; H, 3.73. Found: C, 53.27; H, 3.65%. ^1H NMR: δ 7.12dd (2H, Se–C_6H_5-*meta*, $^3J_{HH}$ 7.6 Hz), 7.21t (1H, Se–C_6H_5-*para*, $^3J_{HH}$ 7.4 Hz), 7.40 m (8H, Se–C_6H_5-*ortho* + P–C_6H_5-*meta* + P–C_6H_5-*para*), 7.87ddd (4H, P–C_6H_5-*ortho*, $^3J_{PH}$ 14.1, $^3J_{HH}$ 7.0, $^4J_{HH}$ 1.6 Hz). ^{13}C NMR: δ 128.37d (P–C_6H_5-*meta*, $^3J_{PC}$ 13.2 Hz), 128.53 (Se–C_6H_5-*para*), 128.90 (Se–C_6H_5-*meta*), 130.19 (Se–C_6H_5-*ipso*), 131.84d (P–C_6H_5-*ortho*, $^2J_{PC}$ 10.9 Hz), 131.96d (P–C_6H_5-*para*, $^4J_{PC}$ 3.4 Hz), 132.93 (Se–C_6H_5-*ortho*, $^2J_{SeC}$ 12.1 Hz), 133.18d (P–C_6H_5-*ipso*, $^1J_{PC}$ 82.3 Hz). ^{31}P NMR: δ 66.2 ($^1J_{PC}$ 82.7 Hz). ^{77}Se NMR: δ 486.3. IR (cm^{-1}): $\nu_{as}(PS_2)$ 652vs, $\nu_s(PS_2)$ 517vs.

4.3. Preparation of phenylselenium(II) diisopropyldithiophosphate, $PhSeSP(S)(OPr^i)_2$ (**2**)

Prepared and worked up as for compound **1**, from Ph_2Se_2 (0.5 g, 1.6 mmol) and $[(Pr^iO)_2P(S)S]_2$ (0.68 g, 1.6 mmol) in $CHCl_3$. Yield: 0.83 g (70%). M.p. 80–81 °C. Anal. Calc. for $C_{12}H_{19}O_2PS_2Se$: C, 39.02; H, 5.19. Found: C, 39.21; H, 5.02%. ^1H NMR: δ 1.16d [$6H_A$, P–O–CH(CH_3)$_2$, $^3J_{HH}$ 6.2 Hz], 1.32d [$6H_B$, P–O–CH(CH_3)$_2$, $^3J_{HH}$ 6.1 Hz], 4.80dh (2H, P–O–C*H*(CH_3)$_2$, $^3J_{PH}$ 12.4, $^3J_{HH}$ 6.2 Hz), 7.28 m (3H, Se–C_6H_5-*meta* + *para*), 7.70 m (2H, Se–C_6H_5-*ortho*). ^{31}P NMR: δ 81.1. ^{77}Se NMR: δ 462.6. IR (cm^{-1}): $\nu_{as}(PS_2)$ 638vs, $\nu_s(PS_2)$ 497s.

4.4. Preparation of [C,N-2-(N-methylpiperazinylmethyl)phenyl]-selenium(II) diphenyldithiophosphinate, [2-{$MeN(CH_2CH_2)_2NCH_2$}-C_6H_4]$SeSP(S)Ph_2$ (**3**)

A mixture of [2-{$MeN(CH_2CH_2)_2NCH_2$}C_6H_4]$_2Se_2$ (0.193 g, 0.36 mmol) and $[(Ph_2P(S)S]_2$ (0.179 g, 0.36 mmol) in $CHCl_3$ (25 ml) was stirred for 48 h, at room temperature. The clear yellow solution was then concentrated in vacuum and layered with *n*-hexane. At low temperature (5 °C) the title compound deposited as a yellow crystalline solid. Yield: 0.25 g (67%). M.p. 133 °C. Anal. Calc. for $C_{24}H_{27}N_2PS_2Se$: C, 55.70; H, 5.26; N, 5.41. Found: C, 55.43; H, 5.34; N, 5.27%. ^1H NMR: δ 2.24s (3H, N–CH_3), 2.44br (8H, $H_{8,9,10,11}$), 3.42s (2H, H_7), 6.96d (1H, H_3, $^3J_{HH}$ 6.1 Hz), 7.06 m (2H, $H_{4,5}$), 7.35s,br (6H, P–C_6H_5-*meta* + *para*), 7.84d (1H, H_6, $^3J_{HH}$ 7.2 Hz), 7.95dd (4H, P–C_6H_5-*ortho*, $^3J_{PH}$ 12.7, $^3J_{HH}$ 6.6 Hz). ^{13}C NMR: δ 45.58 (N–CH_3), 51.66 ($C_{8,11}$), 54.15 ($C_{9,10}$), 62.39 (C_7), 125.95 (C_4), 127.00 (C_3), 127.99d (P–C_6H_5-*meta*, $^3J_{PC}$ 12.7 Hz), 128.08 (C_5), 130.57 (C_6), 131.25 (P–C_6H_5-*para*), 131.57d (P–C_6H_5-*ortho*, $^2J_{PC}$ 10.8 Hz), 134.24 (C_2), 135.15d (P–C_6H_5-*ipso*, $^1J_{PC}$ 83.2 Hz), 137.68 (C_1). ^{31}P NMR: δ 65.3. ^{77}Se NMR: δ 562.8. IR (cm^{-1}): $\nu_{as}(PS_2)$ 656s, $\nu_s(PS_2)$ 534vs.

4.5. Preparation of [C,N-2-(N-methylpiperazinylmethyl)phenyl]-selenium(II) diisopropyldithiophosphate, [2-{$MeN(CH_2CH_2)_2NCH_2$}-C_6H_4]$SeSP(S)(OPr^i)_2$ (**4**)

Prepared and worked up as for compound **3**, from [2-{$MeN(CH_2CH_2)_2NCH_2$}C_6H_4]$_2Se_2$ (0.167 g, 0.31 mmol) and $[(Pr^iO)_2P(S)S]_2$ (0.132 g, 0.31 mmol) in $CHCl_3$. Yield: 0.23 g (77%). M.p. 78–80 °C. Anal. Calc. for $C_{18}H_{31}N_2O_2PS_2Se$: C, 44.90; H, 6.49; N, 5.82. Found: C, 45.01; H, 6.64; N, 5.82%. ^1H NMR: δ 1.19d [$6H_A$, P–O–CH(CH_3)$_2$, $^3J_{HH}$ 6.2 Hz], 1.28d [$6H_B$, P–O–CH(CH_3)$_2$, $^3J_{HH}$

6.2 Hz], 2.31s (3H, N–CH_3), 2.53, 2.61br [8H, $H_{8,9,10,11}$], 3.61s (2H, H_7), 4.78dh [2H, P–O–CH(CH_3)$_2$, $^3J_{PH}$ 12.2, $^3J_{HH}$ 6.1 Hz], 7.10 m (2H, $H_{3,4}$), 7.21 m (1H, H_5), 7.98d (1H, H_6, $^3J_{HH}$ 7.9 Hz). ^{13}C NMR: δ 23.36d [C_A, P–O–CH(*C*H$_3$)$_2$, $^3J_{PC}$ 5.7 Hz], 23.67d [C_B, P–O–CH(*C*H$_3$)$_2$, $^3J_{PC}$ 4.2 Hz], 45.83 (N–*C*H$_3$), 51.88 ($C_{8,11}$), 54.40 ($C_{9,10}$), 62.69 (C_7), 73.02d [P–O–*C*H(CH$_3$)$_2$, $^2J_{PC}$ 6.9 Hz], 125.96 (C_4), 127.26 (C_3), 128.14 (C_5), 130.51 (C_6), 134.63 (C_2), 137.73 (C_1). ^{31}P NMR: δ 88.2. ^{77}Se NMR: δ 585.1. IR (cm^{-1}): ν_{as}(PS$_2$) 642vs, ν_s(PS$_2$) 552s.

4.6. Preparation of [C,N-2-(N-morpholinylmethyl)phenyl]-selenium(II)diphenyldithiophosphinate, [2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}-C$_6$H$_4$]SeSP(S)Ph$_2$ (**5**)

Stoichiometric amounts of [2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]SeCl (0.113 g, 0.39 mmol) and Ph$_2$P(S)SNH$_4$ (0.104 g, 0.39 mmol) were stirred in CH$_2$Cl$_2$ (50 ml) for 12 h, at room temperature. The solution was concentrated in vacuum to minimum volume and then kept at low temperature (−20°) for 24 h, when the title compound deposited as a pale yellow solid. The compound was filtered off and recrystallized from CH$_2$Cl$_2$/*n*-hexane (1:5, v/v). Yield: 0.17 g (85%). M.p. 179 °C. Anal. Calc. for C$_{23}$H$_{24}$NOPS$_2$Se: C, 54.76; H, 4.79; N, 2.78. Found: C, 54.48; H, 4.54; N, 2.62%. ^{1}H NMR: δ 2.42br (4H, $H_{8,11}$), 3.38s (2H, H_7), 3.55t (4H, $H_{9,10}$, $^3J_{HH}$ 4.2 Hz), 6.95d (1H, H_3, $^3J_{HH}$ 7.0 Hz), 7.04 m (2H, $H_{4,5}$), 7.33 m (6H, P–C$_6$*H*$_5$-*meta* + *para*), 7.82d (1H, H_6, $^3J_{HH}$ 7.5 Hz), 7.92dd (4H, P–C$_6$H$_5$-*ortho*, $^3J_{PH}$ 13.9, $^3J_{HH}$ 7.0 Hz). ^{13}C NMR: δ 51.93 ($C_{8,11}$), 62.66 (C_7), 66.07 ($C_{9,10}$), 125.86 (C_4), 127.07 (C_3), 127.82d (P–*C*$_6$H$_5$-*meta*, $^3J_{PC}$ 13.2 Hz), 127.92 (C_5), 130.36 (C_6), 131.15 (P–*C*$_6$H$_5$-*para*, $^4J_{PC}$ 2.8 Hz), 131.33d (P–*C*$_6$H$_5$-*ortho*, $^2J_{PC}$ 10.8 Hz), 133.91 (C_1), 134.71d (P–*C*$_6$H$_5$-*ipso*, $^1J_{PC}$ 82.9 Hz), 137.19 (C_2). ^{31}P NMR: δ 65.3 ($^1J_{PC}$ 82.6 Hz). ^{77}Se NMR: δ 552.1.

4.7. Preparation of [C,N-2-(N-morpholinylmethyl)phenyl]-selenium(II)diisopropyldithiophosphate, [2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}-C$_6$H$_4$]SeSP(S)(OPr^i)$_2$ (**6**)

Stoichiometric amounts of [2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]$_2$Se$_2$ (0.27 g, 0.53 mmol) and [(Pr^{i}O)$_2$P(S)S]$_2$ (0.23 g, 0.53 mmol) were stirred in CH$_2$Cl$_2$ (30 ml) for 12 h, at room temperature. The yellow solution was concentrated in vacuum to minimum volume and then kept at low temperature (−20 °C) for 24 h, when the title compound deposited as a yellow solid. The compound was filtered off and recrystallization from CH$_2$Cl$_2$/*n*-hexane (1:5, v/v) affords isolation of the title compound as yellow crystals. Yield: 0.32 g (63%). M.p. 137–138 °C. Anal. Calc. for C$_{17}$H$_{28}$NO$_3$PS$_2$Se: C, 43.59; H, 6.02; N, 2.99. Found: C, 43.24; H, 5.83; N, 2.62%. ^{1}H NMR: δ 1.19d [6H$_A$, P–O–CH(C*H*$_3$)$_2$, $^3J_{HH}$ 6.0 Hz], 1.28d [6H$_B$, P–O–CH(C*H*$_3$)$_2$, $^3J_{HH}$ 6.0 Hz], 2.56br (4H, $H_{8,11}$), 3.61s (2H, H_7), 3.75t (4H, $H_{9,10}$, $^3J_{HH}$ 4.2 Hz), 4.78dh [2H, P–O–CH(CH$_3$)$_2$, $^3J_{PH}$ 12.0, $^3J_{HH}$ 6.0 Hz], 7.12m (2H, $H_{3,4}$), 7.23 m (1H, H_5), 7.99d (1H, H_6, $^3J_{HH}$ 7.9 Hz). ^{13}C NMR: δ 23.29d [C_A, P–O–CH(*C*H$_3$)$_2$, $^3J_{PC}$ 5.6 Hz], 23.63d [C_B, P–O–CH(*C*H$_3$)$_2$, $^3J_{PC}$ 4.0 Hz], 52.28 ($C_{8,11}$), 63.11 (C_7), 66.48 ($C_{9,10}$), 73.16d [P–O–*C*H(CH$_3$)$_2$, $^2J_{PC}$ 6.8 Hz], 126.07, 127.52 ($C_{3,4}$), 128.26 (C_5), 130.60 (C_6), 134.56 (C_1), 137.40 (C_2). ^{31}P NMR: δ 87.7. ^{77}Se NMR: δ 573.9. IR (cm^{-1}): ν_{as}(PS$_2$) 644vs, ν_s(PS$_2$) 553s.

4.8. X-ray structure determination

The details of crystal structure determination and refinement for compounds PhSeSP(S)Ph$_2$ (**1**), [2-{MeN(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]-SeSP(S)Ph$_2$ (**3**), [2-{MeN(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]SeSP(S)(OPr^i)$_2$ (**4**) and [2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]SeSP(S)(OPr^i)$_2$ (**6**) are given in Table 3. Data were collected with a Bruker SMART APEX diffractometer by using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). For this purpose, block crystals were attached with epoxy glue 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. The isopropoxy groups of compound **4** are disordered over two positions and the atoms have been refined with a site occupancy of 57:43 (A/B). The Flack parameter for compound **6** is 0.038(18). In both cases, the C–C bonds were restrained to 1.54 Å. The software package SHELX-97 was used for structure solving and refinement [46]. The drawings were created with the program DIAMOND [47].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.12.011.

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