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Hypervalent Organoselenium(II) Compounds with Organophosphorus Ligands. Crystal and Molecular Structure of $[2-(i\text{Pr}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{Se}[\text{S}_2\text{PR'}_2]$ (R' = Ph, O*i*Pr)

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Abstract. Redistribution reactions between diorganodiselenides of type $[2-(R_2NCH_2)C_6H_4]_2Se_2$ [R = Et, *i*Pr] and bis(diorganophosphinothioyl disulfanes of type $[R'_2P(S)S]_2$ (R = Ph, O*i*Pr) resulted in the hypervalent $[2-(R_2NCH_2)C_6H_4]SeSP(S)R'_2$ [R = Et, R' = Ph (**1**), O*i*Pr (**2**); R = *i*Pr, R' = Ph (**3**), O*i*Pr (**4**)] species. All new compounds were characterized by solution multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{31}P, ^{77}Se) and the solid compounds **1**, **3**, and **4** also by FT-IR spectroscopy. The crystal and molecular structures of **3** and **4** were determined by single-crystal X-ray diffraction. In both compounds the N(1) atom is intramolecularly coordinated to the selenium atom, resulting in T-shaped coordination arrangements of type (*C*,*N*)SeS. The dithio organophosphorus ligands act monodentate in both complexes, which can be described as essentially monomeric species. Weak intermolecular S···H contacts could be considered in the crystal of **3**, thus resulting in polymeric zig-zag chains of *R* and *S* isomers, respectively.

Introduction

An increased interest towards organoselenium compounds containing an intramolecular *E*→Se (*E* = N, O) interaction was observed during the last years,[1–3] mainly due to their potential applications in organic synthesis, either as catalysts or as transfer reagents,[4–12] in biology and medicine as enzyme mimics or chemotherapeutic products,[13–16] in material science as single source precursors for CVD processes,[17] etc.

The intramolecular *E*→Se (*E* = N, O) interaction provides an increased thermal and hydrolytic stability and favors the formation of monomeric species. The ability of 2-(*N*,*N*-dimethylaminomethyl)phenyl and related organic ligands to establish such internal interactions was used to prepare different hypervalent organoselenium compounds of type Ar_2Se_2, ArSe*X* (*X* = halogen), ArSeL (L = dithio ligand) or metal arylselenolates.[7–15,17,18]

Recently, we reported on the synthesis, solution behavior and molecular structures of various hypervalent organoselenium compounds containing the $2-(Me_2NCH_2)C_6H_4$[19,20] and $2-\{Z(CH_2CH_2)_2NCH_2\}C_6H_4$ (*Z* = O, NMe)[21,22] groups as well as metal organoselenolates containing the fragment $[2-(R_2NCH_2)C_6H_4]SeM$ (R = Me, Et; *M* = Au, Zn, Cd).[17,18]

The organoselenium compounds $[2-(Me_2NCH_2)C_6H_4]Se[S_2PR'_2]$ (R' = Ph, O*i*Pr) were found to exhibit monomeric structures,[20] while in species of type $[2-\{Z(CH_2CH_2)_2NCH_2\}C_6H_4]Se[S_2PR'_2]$ supramolecular architectures realized by weak S···H (*Z* = MeN, R' = Ph) and N···H (*Z* = MeN, R' = O*i*Pr) intermolecular contacts or polymeric chains realized by weak O···H interactions (*Z* = O, R' = O*i*Pr) were described.[21]

In order to increase the basicity of the coordinating amino group and to complete our investigations on organoselenium complexes with dithiophosphorus ligands, we decided to use the 2-(*N*,*N*-diethylaminomethyl)phenyl group $(2-(Et_2NCH_2)C_6H_4)$ and the 2-(*N*,*N*-diisopropylaminomethyl)phenyl group $(2-(iPr_2NCH_2)C_6H_4)$ as organic ligands with pendant arms that can exhibit a (*C*,*N*) coordination towards the selenium atom. Herein we report on the syntheses and spectroscopic characterization of new hypervalent compounds of type $[2-(R_2NCH_2)C_6H_4]Se[S_2PR'_2]$ [R = Et, R' = Ph (**1**), O*i*Pr (**2**); R = *i*Pr, R' = Ph (**3**), O*i*Pr (**4**)].

Results and Discussion

The diorganodithiophosphinato (**1** and **3**) and the diorganodithiophosphato (**2** and **4**) derivatives were obtained by redistribution reactions between the diorganodiselenides $[2-(R_2NCH_2)C_6H_4]_2Se_2$ (R = *i*Pr or Et), with the corresponding bis(diorganophosphinothioyl)disulfane $[R'_2P(S)S]_2$ (R' = Ph, O*i*Pr), according to the reaction depicted in Equation (1). Except compound **2**, which is an orange oil, all the other compounds are stable, yellow crystalline solids. Elemental analysis and NMR spectroscopic data are in agreement with the anticipated formulas. The solution behavior of the new compounds **1**–**4** was investigated by multinuclear (^{1}H, ^{13}C, ^{31}P, ^{77}Se) NMR spectroscopy at room temperature.

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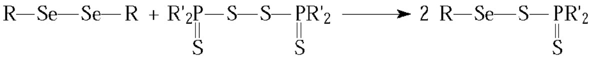
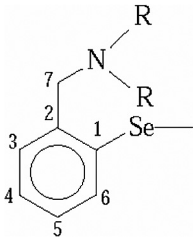


$$R{-}Se{-}Se{-}R + R'_2P(=S){-}S{-}S{-}P(=S)R'_2 \longrightarrow 2\ R{-}Se{-}S{-}P(=S)R'_2 \qquad (1)$$

R = 2-(Et$_2$NCH$_2$)C$_6$H$_4$; R' = Ph (1)
R = 2-(Et$_2$NCH$_2$)C$_6$H$_4$; R' = O*i*Pr (2)
R = 2-(*i*Pr$_2$NCH$_2$)C$_6$H$_4$; R' = Ph (3)
R = 2-(*i*Pr$_2$NCH$_2$)C$_6$H$_4$; R' = O*i*Pr (4)

The ^{1}H and ^{13}C NMR resonances were assigned using 2D NMR experiments, according to the diagram depicted in Scheme 1.



Scheme 1. Numbering scheme for NMR resonance assignments.

The room temperature ^{1}H and ^{13}C NMR spectra show the expected resonances for the organic groups attached to selenium and to phosphorus atoms, respectively. In all spectra the resonances are split in two components of equal intensity, due to phosphorus–proton and phosphorus–carbon couplings, respectively. In all investigated phosphorus-containing species, as well as in the corresponding diselenides,[17,23] no evidence for an intramolecular N→Se coordination was observed in the ^{1}H NMR spectra. In the aliphatic region the two organic groups attached to the nitrogen atoms, as well as the CH_2 benzylic protons, respectively, appear to be equivalent in solution at the NMR time scale. This should be consistent either to the absence of any N→Se interaction or to a very fast process involving dissociation and regeneration of the internal N→Se interaction, with pyramidal inversion at the central nitrogen atom.[24] The isopropoxy groups attached to phosphorus atoms in compounds **2** and **4** exhibit a pattern, which is indicative for their diastereotopic nature, i.e. two doublet resonances for the H_A and H_B methyl protons, respectively.

The ^{77}Se NMR chemical shifts for compounds **1**–**4** are in the range 587–628 ppm (Table 1), low field shifted in comparison with the starting diorganodiselenides, [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ and [2-(*i*Pr$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$, thus indicating the formation of the selenium–sulfur bonds. A similar behavior was observed in case of the derivatives 2-[*Z*(CH$_2$CH$_2$)$_2$NCH$_2$]C$_6$H$_4$SeSP(S)R'$_2$[21] and 2-[Me$_2$NCH$_2$]C$_6$H$_4$SeSP(S)R'$_2$ (Table 1). The ^{31}P NMR resonances are high field, in case of the dithiophosphato, and low field, in case of the dithiophospinato derivatives, respectively, shifted in comparison with the starting disulfanes, [(Ph$_2$P(S)S]$_2$ and [(*i*PrO)$_2$P(S)S]$_2$, respectively, as it was also observed for the related species [2-(Me$_2$NCH$_2$)C$_6$H$_4$]SeSP(S)R'$_2$ (R' = Ph, O*i*Pr[20]) and 2-[*Z*(CH$_2$CH$_2$)$_2$NCH$_2$]C$_6$H$_4$SeSP(S)R'$_2$ (*Z* = NMe or O, R' = Ph, O*i*Pr[21]) (see Table 1).

The ^{77}Se chemical shifts of compounds **1**–**4**, as well as for the other related species containing dithiophosphorus ligands and listed in Table 1, are in agreement with a deshielding with respect to the corresponding diselenides. The δ_{77Se} values are intermediate between the values observed for the diaryl diselenides used as starting materials and the corresponding arylselenium halides (i.e. δ_{77Se} for [2-(R$_2$NCH$_2$)C$_6$H$_4$]SeCl, R = Et, 1016.7 ppm; R = Me 1030 ppm[19,28]), in accordance with the lower electronegativity of the dithiophosphorus ligands in comparison with the X^- groups (*X* = Cl, Br, and I).

The IR spectra for compounds **1**, **3**, and **4** exhibit strong absorption bands in the regions 660–640 and 550–500 cm^{-1}, which were assigned to asymmetric and symmetric ν(PS$_2$) stretching vibrations in the dithiophosphorus ligands attached to the organoselenium(II) moieties.

Single crystals of **3** and **4** suitable for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into a CH$_2$Cl$_2$ solution. The molecular structures are depicted in Figure 1 and Figure 2, respectively, and selected interatomic distances and angles are listed in Table 2.

Compounds **3** and **4** can be described as hypervalent 10-Se-3 species.[29] Both organoselenium compounds are monomeric and each of them exhibits a strong intramolecular N→Se coordination [N(1)–Se(1) 2.675(4) Å in **3** and 2.662(7) Å in **4**; cf. the sum of the corresponding van der Waals radii, Σr_{vdW}(Se,N) 3.54 Å[30]], *trans* to the selenium–sulfur bond [N(1)–Se(1)–S(1) 174.45(8)° in **3** and 176.92(8)° in **4**, respectively], thus resulting in a distorted T-shaped [(*C*,*N*)SeS core] coordination arrangement around the selenium atom. The N→Se interactions are slightly larger than those observed for other related compounds: [2-(Me$_2$NCH$_2$)C$_6$H$_4$]SeSP(S)R$_2$ [R = Ph 2.359(2) Å, R = O*i*Pr 2.397(2) Å[20]], [2-{*Z*(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]SeSP(S)R$_2$ [*Z* = O, R = O*i*Pr 2.557(7) Å; *Z* = MeN, R = Ph 2.463(4) Å, R = O*i*Pr 2.529(3) Å[21]]. The distortion of the coordination arrangement is mainly determined by constrains arising from the five-membered C$_3$NSe chelate rings, particularly the C(1)–Se(1)–N(1) angle 77.52(1)° in **3** and 76.89(1)° in **4**, respectively]. The overall coordination arrangement around the selenium atom can be considered as distorted pseudo-trigonal bipyramidal, with C(1) and the two lone pairs in equatorial positions.

The five-membered C$_3$SeN chelate rings in both compounds are not planar, the nitrogen atom being displaced out of the best plane defined through the residual C$_3$Se system [dihedral angle C$_3$Se/SeNC 42.9(2)° in **3** and 44.54(2)° in **4**, respectively]. The N→Se intramolecular coordination induces planar chirality (with the aromatic ring and the nitrogen atom as chiral plane and pilot atom, respectively). As a consequence, the compounds crystallize as 1:1 mixtures of R_N and S_N isomers. The internal N→Se interactions are stronger in **3** and **4** than in the diselenide used as starting material, i.e. 2.675(4) Å in **3** and 2.662(7) Å in **4** versus 2.782 and 2.988 Å in [2-(*i*Pr$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$.[23] This behavior is in agreement with the slightly higher electronegativity of the S(1) atom placed in *trans* to the N(1) atom in the N–Se–S fragment and with the better leaving group character of the dithiophosphorus ligand compared to an ArSe$^-$ group.

Table 1. ^{31}P and ^{77}Se NMR spectroscopic data for compounds of type RSeSP(S)R'$_2$ and the corresponding starting materials.

Compound	^{77}Se NMR	^{31}P NMR	Ref.
[2-(Me$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$	430.0		[25]
[2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$	427.4		[17]
[2-(*i*Pr$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$	406.0		[23]
[2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}]$_2$Se$_2$	424.0		[22]
[2-{MeN(CH$_2$CH$_2$)$_2$NCH$_2$}]$_2$Se$_2$	425.4		[22]
[Ph$_2$P(S)S]$_2$		69.6	[26]
[(*i*PrO)$_2$P(S)S]$_2$		81.6	[27]
[2-(Me$_2$NCH$_2$)C$_6$H$_4$]SeS(S)PPh$_2$	617.7^{a}	65.1	[20]
[2-(Me$_2$NCH$_2$)C$_6$H$_4$]SeS(S)P(O*i*Pr)$_2$	635.0^{a}	90.0	[20]
[2-(Et$_2$NCH$_2$)C$_6$H$_4$]SeS(S)PPh$_2$	608	64.0	–$^{a)}$
[2-(*i*Pr$_2$NCH$_2$)C$_6$H$_4$]SeS(S)PPh$_2$	569	64.0	–$^{a)}$
[2-(Et$_2$NCH$_2$)C$_6$H$_4$]SeS(S)P(O*i*Pr)$_2$	628	88.8	–$^{a)}$
[2-(*i*Pr$_2$NCH$_2$)C$_6$H$_4$]SeS(S)P(O*i*Pr)$_2$	587	86.2	–$^{a)}$
[2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]SeSP(S)Ph$_2$	552.1	65.3	[21]
[2-{MeN(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]SeSP(S)Ph$_2$	562.8	65.3	[21]
[2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]SeS(S)P(O*i*Pr)$_2$	573.9	87.7	[21]
[2-{MeN(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]SeS(S)P(O*i*Pr)$_2$	585.1	88.2	[21]

a) This work.

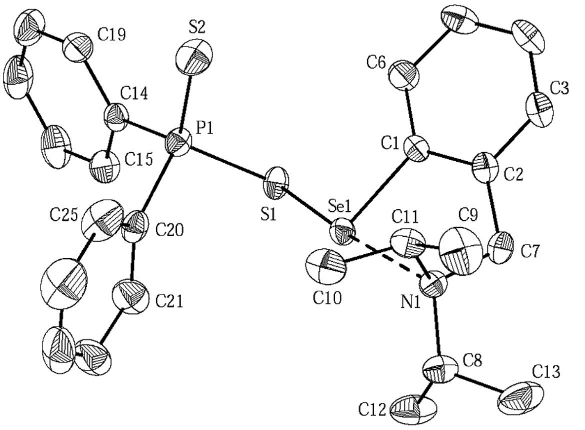


Figure 1. ORTEP representation at 30 % probability and atom numbering scheme for the *R*-**3** isomer; hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths /Å and angles /° for compounds **3** and **4**, as determined by single-crystal X-ray diffraction.

	3	**4**
Se(1)–C(1)	1.944(4)	1.928(4)
Se(1)–N(1)	2.675(4)	2.662(7)
Se(1)–S(1)	2.265(2)	2.249(1)
P(1)–S(1)	2.089(2)	2.056(2)
P(1)=S(2)	1.945(2)	1.913(2)
C(1)–Se(1)–N(1)	77.52(1)	76.89(1)
C(1)–Se(1)–S(1)	98.30(14)	100.23(12)
N(1)–Se(1)–S(1)	174.45(8)	176.92(8)
P(1)–S(1)–Se(1)	99.64(6)	100.46(6)
S(1)–P(1)–S(2)	116.81(8)	110.84(8)
C(11)–N(1)–C(7)	113.7(4)	112.9(3)
C(11)–N(1)–C(8)	114.8(4)	114.9(3)
C(7)–N(1)–C(8)	111.8(4)	113.3(3)
C(11)–N(1)–Se(1)	105.72(24)	106.24(25)
C(7)–N(1)–Se(1)	91.13(24)	90.71(21)
C(8)–N(1)–Se(1)	117.14(25)	116.2(2)

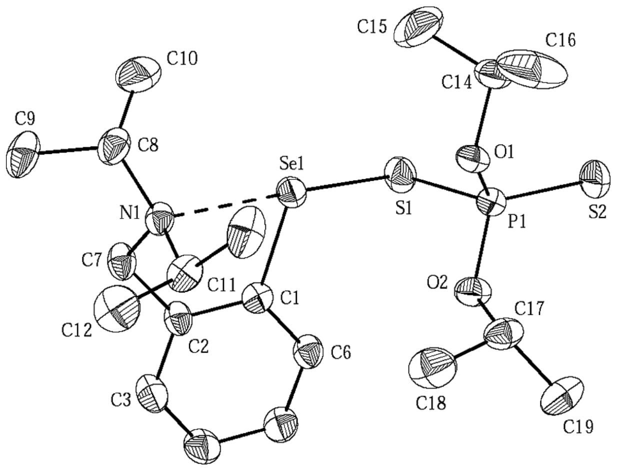


Figure 2. ORTEP representation at 30 % probability and atom numbering scheme for the *R*-**4** isomer; hydrogen atoms are omitted for clarity.

The dithiophosphorus ligands act as monodentate, monometallic monoconnective moieties in both complexes. They are connected to selenium through S(1) [Se(1)–S(1) 2.265(2) Å in **3** and 2.249(1) Å in **4**], whereas the second sulfur atom is pushed far away from the coordination sphere of the selenium atom [Se(1)–S(2) 4.007(3) Å in **3** and 5.081(2) Å in **4**, versus Σr_{vdW}(S,Se) 3.85 Å[30]]. The internal N→Se interaction prevents any intra- or intermolecular secondary interaction between selenium and the sulfur atoms of the organophosphorus ligand, by contrast with the situation found in the polymeric PhSeSP(S)Ph$_2$, where the dithiophosphinato ligand acts anisobidentate, as a bimetallic triconnective moiety, with the same sulfur atom bridging two selenium atoms from neighboring molecules.[21]

The Se(1)–S(1) bond lengths are within the expected range for covalent selenium–sulfur single bonds, similarly with the values found in other related compounds, i.e. [2-(Me$_2$NCH$_2$)C$_6$H$_4$]SeSP(S)R$_2$ [R = Ph 2.340(7) Å, R = O*i*Pr

2.337(1) Å[20]] [2-{Z(CH_2CH_2)$_2$NCH_2}C_6H_4]SeSP(S)R_2 [*Z* = O, R = O*i*Pr 2.256(7) Å; *Z* = MeN, R = Ph 2.297(1) Å, R = O*i*Pr 2.277(1) Å[21]], but longer than in PhSeSP(S)Ph_2 [2.205(2) Å[21]] due to the *trans* effect of the internal N→Se interaction.

The phosphorus–sulfur distances within the ligand moieties are consistent with single P–S and double P=S bonds: P(1)–S(1) 2.089(2) Å in **3** and 2.056(2) Å in **4**, P(1)=S(2) 1.945(2) Å in **3** and 1.913(2) Å in **4**, cf. P–S 2.077(1) and P=S 1.954(1) Å in $Ph_2P(S)SH$,[31] similarly to the situations observed in the other related compounds.[20,21]

In the crystal of compound **3** the second sulfur atom is also involved in weak S(2)···H_{phenyl} contacts (S(2)···H(17') 2.952(4) Å, cf. Σr_{vdW}(S,H) 3.05 Å,[30] thus resulting in polymeric chains of *R* and *S* isomers, respectively (Figure 3). No further interactions between these chains were observed in the crystal of compound **3**. Weak S···H interactions were previously found in the related [2-{MeN(CH_2CH_2)$_2$NCH_2}C_6H_4]SeSP(S)R_2 (R = Ph, O*i*Pr), For these species polymeric associations containing both *R* and *S* isomers in the same chain are built.[21]

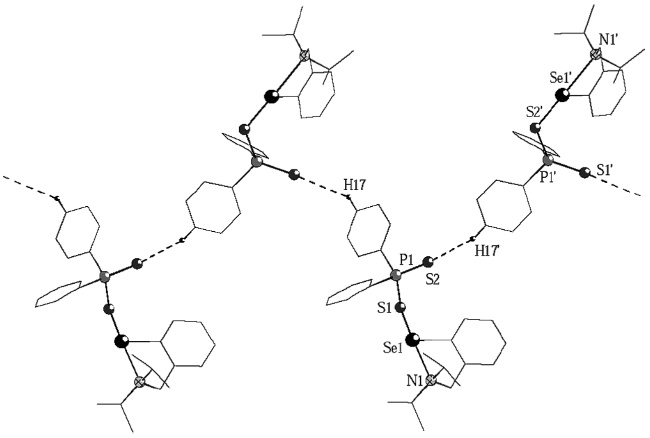


Figure 3. View of the chain polymer based on S···H contacts between *R* isomers in the crystal of **3** (only hydrogens involved in intermolecular contacts are shown) [symmetry equivalent atoms (2.5 – *x*, –0.5 + *y*, 0.5 – *z*) are given by "prime"].

Conclusions

Replacement of methyl by ethyl or isopropyl groups at the nitrogen atom of the pendant arm in hypervalent organoselenium(II) complexes of the type [2-(R_2NCH_2)C_6H_4]SeS(P)SR'$_2$ (R = Me, Et, *i*Pr, R' = Ph, O*i*Pr) does not affect dramatically the structure. A strong internal N→Se interaction is established in solid state, thus resulting in a distorted T-shaped (*C,N*)SeS core. The strength of the N→Se interaction in solid state seems not to be sensitive to the change of methyl by isopropyl groups in the pendant arm.

Experimental Section

General: Solvents were dried by standard procedures and were freshly distilled prior to use. The diorganodiselenides [2-(R_2NCH_2)C_6H_4]$_2Se_2$ (R = Et[17], *i*Pr[23]) and the bis(diorganophosphinothioyl)disulfanes, [R'$_2$P(S)S]$_2$ (R' = Ph[26], O*i*Pr[27]) were prepared according to published methods. All other reagents were obtained from Aldrich or Merck and were used as received.

Multinuclear NMR spectra were recorded at room temperature, in dry $CDCl_3$, with a BRUKER DRX 400 instrument operating at 400.1, 100.61, 161.97, and 76.31 MHz for ^{1}H, ^{13}C, ^{31}P and ^{77}Se, respectively. The ^{1}H and ^{13}C chemical shifts are reported in ppm relative to the residual peak of the solvent (ref. $CHCl_3$: ^{1}H 7.26, ^{13}C 77.0 ppm), whereas ^{31}P chemical shifts are reported relative to H_3PO_4 85 %. The ^{77}Se spectra were obtained using diphenyl diselenide as external standard. Chemical shifts are reported relative to dimethyl selenide ($\delta = 0$) by assuming that the resonance of the standard is at $\delta = 461$.[32] ^{1}H and ^{13}C resonances were assigned using 2D NMR experiments (COSY, HMQC and HMBC). The NMR spectra were processed with the MestReC and MestReNova software.[33] Infrared spectra in the range 400–4000 cm^{-1} for compounds **1**, **3** and **4** were recorded with a Jasco FTIR machine, using KBr pellets. Elemental analyses were performed with a VarioEL analyzer. Melting points were measured with an Electrothermal 9200 apparatus and are not corrected.

Crystal Structure Determination: The details of the crystal structure determination and refinement for compounds **3** and **4** are given in Table 3. Data were collected with a Bruker SMART APEX diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Single-crystals of **3** and **4** were attached with Paratone 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.[34] The drawings were created with the Diamond program.[35]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained on quoting the depository numbers CCDC-816418 and CCDC-816419 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Synthesis of [2-(Et_2NCH_2)C_6H_4]SeSP(S)Ph_2 (1): Stoichiometric amounts of [2-(Et_2NCH_2)C_6H_4]$_2Se_2$ (0.406g, 0.8 mmol) and [Ph_2P(S)S]$_2$ (0.433g, 0.8 mmol) were stirred in dichloromethane (40 mL) for 12 h, at room temperature. The resulting yellow solution was concentrated under vacuum pump to minimum volume. Hexane was added and the title compound deposited at –25 °C as a microcrystalline yellow solid. Yield: 0.713g (85 %). M.p. 81–82 °C. $C_{23}H_{26}NPS_2Se$ (*M* = 490.52): calcd. C 56.32, H 5.34, N 2.86 %; found: C 56.41, H 5.28, N 2.88 %. **^{1}H NMR:** δ = 0.97 (t, 6 H, NCH_2CH_3, $^{3}J_{HH}$ = 6.7 Hz), 2.59 (q, 4 H, N-CH_2CH_3, $^{3}J_{HH}$ = 6,6 Hz), 3.51 (s, 2 H, CH_2N), 6.95 (d, 1 H, C_6H_4, H_3, $^{3}J_{HH}$ = 5.8 Hz), 7.04 (m, 2 H, C_6H_4, $H_{4,5}$), 7.33 (m, 6 H, C_6H_5-*meta* + *para*), 7.79 (d, 2 H, C_6H_4, H_6, $^{3}J_{HH}$ = 6.8 Hz), 7.93 (dd, 4 H, C_6H_5-*ortho*, $^{3}J_{PH}$ = 12.5, $^{3}J_{HH}$ = 7.0 Hz). **^{13}C NMR:** δ = 9.95 (s, NCH_2CH_3), 44.58 (s, NCH_2CH_3), 58.64 (s, CH_2N), 125.77 (s, C_4), 126.58 (s, C_3), 127.93 (d, C_6H_5-*meta*, $^{3}J_{PC}$ = 12.8 Hz), 130.49 (s, C_6), 131.09 (s, C_6H_5-*para*+C_5), 131.62 (d, C_6H_5-*ortho*, $^{2}J_{PC}$ = 10.9 Hz), 134.77 (s, C_1), 135.65 (d, C_6H_5-*ipso*, $^{1}J_{PC}$ = 81.7 Hz), 138.64 (s, C_2). **^{31}P NMR:** δ = 64.0 s. **^{77}Se NMR:** δ = 608s. **IR** (KBr) = $\nu_{as}(PS_2)$ 657 s, $\nu_s(PS_2)$ 530 s cm^{-1}.

Compounds **2**–**4** were prepared similarly.

[2-(Et_2NCH_2)C_6H_4]SeSP(S)(O*i*Pr)$_2$ (2): From [2-(Et_2NCH_2)C_6H_4]$_2Se_2$ (0.390 g, 0.8 mmol) and [(iPrO)$_2$P(S)S]$_2$ (0.345 g, 0.8 mmol), as an or-

Table 3. X-ray crystallographic data for **3** and **4**.

	3	**4**
Molecular formula	$C_{25}H_{30}NPS_2Se$	$C_{19}H_{34}NO_2PS_2Se$
M	518.55	482.52
Temperature /K	297(2)	297(2)
Crystal size /mm	0.34 × 0.32 × 0.30	0.31 × 0.28 × 0.26
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	P2(1)
Radiation /Å	Mo-K_α, 0.71073	Mo-K_α, 0.71073
Unit cell dimension		
a /Å	10.118(9)	8.326(5)
b /Å	15.250(13)	16.722(9)
c /Å	16.711(14)	9.391(5)
α /°	90.00	90.00
β /°	93.956(14)	112.343(9)
γ /°	90.00	90.00
V /Å^3	2572(4)	1209.3(11)
Z	4	2
D_{calc} /g·cm^{-3}	1.339	1.325
F(000)	1072	504
μ(Mo-K_α) /mm^{-1}	1.697	1.804
θ Range for data collections /°	1.81 to 25.00	2.34 to 25.00
Reflections collected	11721	11708
Independent reflections	4455 [R(int) = 0.0447]	4258 [R(int) = 0.0382]
Max. and min. transmissions	0.6301 and 0.5962	0.6513 and 0.6047
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4455 / 0 / 275	4258 / 1 / 243
Goodness-of-fit on F^2	1.060	1.039
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0574, wR_2 = 0.1191$	$R_1 = 0.0377$, $wR_2 = 0.0798$
R indices (all data)	$R_1 = 0.0729$, $wR_2 = 0.1254$	$R_1 = 0.0420$, $wR_2 = 0.0814$
Largest difference peak and hole /e·Å^{-3}	0.706 and –0.391	0.289 and –0.322

ange oil. Yield: 0.573 g (78 %). $C_{17}H_{30}NO_2PS_2Se$ (M = 454.48): calcd. C 44.93, H 6.65, N 3.08 %; found: C 45.12, H 6.48, N 3.15 %. **^{1}H NMR:** δ = 1.03 (t, 6 H, NCH_2CH_3, $^3J_{HH}$ = 7.1 Hz), 1.16 [d, 6 H, $POCH(CH_3)_2$, $^3J_{HH}$ = 5.9 Hz], 1.25 [d, 6 H, $POCH(CH_3)_2$, $^3J_{HH}$ = 5.9 Hz], 2.66 (q, 4 H, NCH_2CH_3, $^3J_{HH}$ = 7.1 Hz), 3.69 (s, 2 H, CH_2N), 4.75 [sept, 2 H, $POCH(CH_3)_2$, $^3J_{HH}$ = 6.0 Hz], 7.1 (m, 2 H, C_6H_4, $H_{3,4}$), 7.16 (t, 1H C_6H_4, H_5), 7.96 (d, 1 H, C_6H_4, H_6, $^3J_{HH}$ = 7.9 Hz). **^{13}C NMR:** δ = 10.04 [s, $NCH(CH_3)_2$], 23.4 [d, $POCH(CH_3)_2$, $^3J_{PC}$ = 5.6 Hz], 23.72 [d, $POCH(CH_3)_2$, $^3J_{PC}$ = 4.1 Hz], 44.52 (s, NCH_2CH_3), 58.85 (s, CH_2N), 72.8 [d, $POCH(CH_3)_2$, $^2J_{PC}$ = 6.8 Hz], 125.86 (s, C_4), 126.87 (s, C_3), 127.95 (s, C_6), 130.26 (s, C_5), 134.96 (s, C_1), 138.61 (s, C_2). **^{31}P NMR:** δ = 88.8 s. **^{77}Se NMR:** δ = 628 s.

[2-(*i*Pr$_2$NCH$_2$)C$_6$H$_4$]SeSP(S)Ph$_2$ (3): From [2-(*i*Pr$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ (0.301 g, 0.7 mmol) and $[Ph_2P(S)S]_2$ (0.345 g, 0.8 mmol), as a yellow solid. Yield: 0.575 g (89 %). M.p. 106 °C. $C_{25}H_{30}NPS_2Se$ (M = 518.57): calcd. C 57.90, H 5.83, N 2.70 %; found: C 57.78, H 5.88, N 2.73 %. **^{1}H NMR:** δ = 1.02 (d, 12 H, $NCH(CH_3)_2$, $^3J_{HH}$ = 6.6 Hz), 3.04 (sept, 2 H, $NCH(CH_3)_2$, $^3J_{HH}$ = 6,6 Hz), 3.62 (s, 2 H, CH_2N), 6.97 (m, 1 H, C_6H_4, H_3), 7.02 (m, 2 H, C_6H_4, $H_{4,5}$), 7.34 (m, 6 H, C_6H_5-*meta+para*), 7.69 (m, 1 H, C_6H_4, H_6), 7.93 (dd, 4 H, C_6H_5-*ortho*, $^3J_{PH}$ = 13.8, $^3J_{HH}$ = 7.5 Hz). **^{13}C NMR:** δ = 20.49 [s, $NCH(CH_3)_2$], 49.32 (s, CH_2N), 52.02 [s, $NCH(CH_3)_2$], 126.01 (s, C_4), 127.0 (s, C_3), 127.57 (s, C_6), 128.03 (d, C_6H_5-*meta*, $^3J_{PC}$ = 13.05 Hz), 130.12 (s, C_5), 131.24 (s, br., C_6H_5-*ortho* + $\mathbf{C_5}$, $^3J_{PC}$ = 10.8 Hz), 131.64 (d, C_6H_5-*ipso*, $^1J_{PC}$ = 90.1 Hz), 134.24 (s, C_1), 139.97 (s, C_2). **^{31}P NMR:** δ = 64s. **^{77}Se NMR:** δ = 569s. **IR** (KBr) = ($\nu_{as}(PS_2)$ 643 s, $\nu_s(PS_2)$ 550 m cm^{-1}.

[2-(*i*Pr$_2$NCH$_2$)C$_6$H$_4$]SeSP(S)(O*i*Pr)$_2$ (4): From [2-(*i*Pr$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ (0.304 g, 0.7 mmol) and [(*i*PrO)$_2$P(S)S]$_2$ (0.290 g, 0.7 mmol), as a yellow solid. Yield: 0.481 g (81 %). M.p. 58 °C. $C_{19}H_{34}NO_2PS_2Se$ (M = 482.54): C 47.29, H 7.10, N 2.90 %; found: C 47.38, H 7.29, N 3.02 %. **^{1}H NMR:** δ = 1.11 [d, 12 H, $NCH(CH_3)_2$, $^3J_{HH}$ = 6.6 Hz], 1.16 [d, 6 H, $POCH(CH_3)_2$, $^3J_{HH}$ = 6.1 Hz], 1.27 [d, 6 H, $POCH(CH_3)_2$, $^3J_{HH}$ = 6.1 Hz], 3.16 [sept, 2 H, $POCH(CH_3)_2$, $^3J_{HH}$ = 6.6 Hz], 3.64 (s, 2 H, CH_2N), 4.77 [sept, 2 H, $NCH(CH_3)_2$, $^3J_{HH}$ = 6,1 Hz], 7.1 (m, 2 H, C_6H_4, $H_{3,4}$), 7.18 (m, 1 H, C_6H_4, H_5), 7.91 (d, 1 H, C_6H_4, H_6). **^{13}C NMR:** δ = 20.57 [s, $NCH(CH_3)_2$], 23.34 [d, $POCH(CH_3)_2$, $^3J_{PC}$ = 5.6 Hz], 23.69 [d, $POCH(CH_3)_2$, $^3J_{PC}$ = 4.2 Hz], 49.33 (s, CH_2N), 52.39 [s, $NCH(CH_3)_2$], 73.12 [d, $POCH(CH_3)_2$, $^2J_{PC}$ = 6.7 Hz], 126.08 (s, C_4), 127.28 (s, C_3), 127.71 (s, C_6), 130.03 (s, C_5), 134.67 (s, C_1), 140.04 (s, C_2). **^{31}P NMR:** δ = 86.2s. **^{77}Se NMR:** δ = 587s. **IR** (KBr) = $\nu_{as}(PS_2)$ 655 s, $\nu_s(PS_2)$ 531 s cm^{-1}.

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