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Chemoselective synthesis of first representatives of bis(diorganothiophosphinyl) selenides, $(R_2P{=}S)_2Se$, from secondary phosphine sulfides and elemental selenium

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ABSTRACT

First bis(diorganothiophosphinyl)selenides, $(R_2P{=}S)_2Se$, have been synthesized in 74–86% yield by the chemoselective interaction of secondary phosphine sulfides with elemental selenium (1:1 molar ratio, 100 °C, 3 h, 1,4-dioxane); the alternative bis(diorganoselenophosphinyl)sulfides, $(R_2P{=}Se)_2S$, are not formed under these conditions.

Currently, the phosphonic acid anhydrides, i.e. bis(diorganophosphinyl) oxides **I**, as well as their sulfur (**II**) and selenium (**III**) heteroanalogues (Fig. 1) attract growing attention as ligands for metal complexes [1], flame retardants [2], selenium sources for the fabrication of selenium-containing nanoparticles [3], potential pharmaceuticals and agrochemicals [4], promising accelerators for the vulcanisation of rubber [5] as well as reagents and building blocks for organic synthesis [6].

For instance, bis(diorganoselenophosphinyl)selenides, $(R_2PSe)_2Se$ (**III**), were successfully applied for the preparation of highly demanded Zn(II), Cd(II), Co(II), Ni(II), Pb(II), Ga(III), In(III) and Bi(III) diselenophosphinates [1c,d,3] which are convenient single-source precursors for the fabrication of metal selenides conductive nanomaterials via chemical vapor deposition (CVD) route (Scheme 1).

In contrast, the mixed bis(diorganoselenophosphinyl)chalcogenides **IV**–**VI** are much less studied [7], whereas their heteroanalogues **VII**–**IX** are still unknown (Fig. 2). Meanwhile, these mixed chalcogenides are prospective precursors to nano-sized semiconducting chalcogenides, potential drugs and agrochemicals, ligands for constructing of multi-purpose metalcomplexes as well as promising reagents for the synthesis of sulfur and selenium containing organophosphorous compounds. Also, bis(diorganochalcogenophosphinyl)chalcogenides represent fundamental interest from the viewpoint of the structural chemistry of heteroatom-containing competitively conjugated systems of $X{=}P{-}X{-}P{=}X$ type ($X{=}O$, S or Se).

Thus, synthesis and study of mixed bis(diorganochalcogenophosphinyl) chalcogenides represent a recognized fundamental challenge in main group inorganic chemistry. In an effort to address this issue, we have synthesized the first representatives of bis(diorganothiophosphinyl) selenides, $(R_2P{=}S)_2Se$, via unknown reaction of secondary phosphine sulfides with elemental Se. It should be pointed out that the course of this reaction is far from being obvious. Indeed, according to previous studies on the interaction of secondary phosphine sulfides with sulfur [8] (Scheme 2), reaction between $R_2P(S)H$ and Se should result in the formation of the thioselenophosphinic acids, i.e. $R_2P(Se)SH$, $R_2P(S)SeH$ or their mixture. On the other hand, it is known [9], that secondary phosphine selenides, $R_2P(Se)H$, react with elemental Se to give selectively bis(diorganoselenophosphinyl)selenides (no traces of the expected acids $R_2P(Se)SeH$ being detectable in the reaction mixtures), Scheme 3.

Our experiments have shown, that the interaction of secondary phosphine sulfides **1a**–**e** with elemental selenium in a 1:1 molar ratio gives rise to the formation of earlier unknown bis(diorganothiophosphinyl) selenides **2a**–**e** in 74–86% isolated yield (Scheme 4) [10]. The reaction

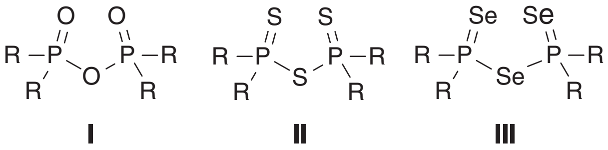

Fig. 1. Bis(diorganochalcogenophosphinyl)chalcogenides.

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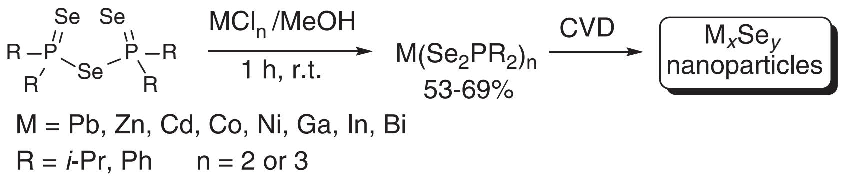


Scheme 1. Application of selenides **III** for production of metal selenides nanomaterials.

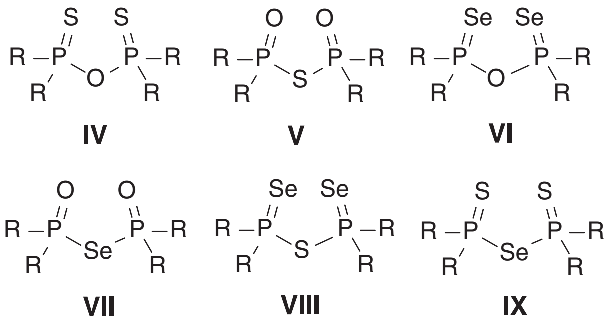
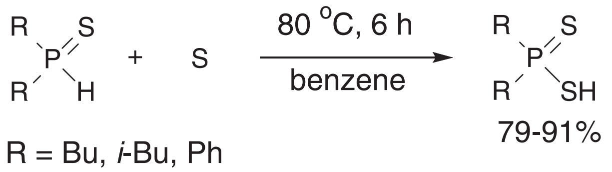
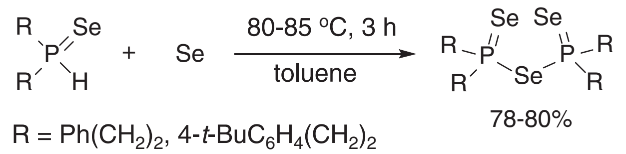


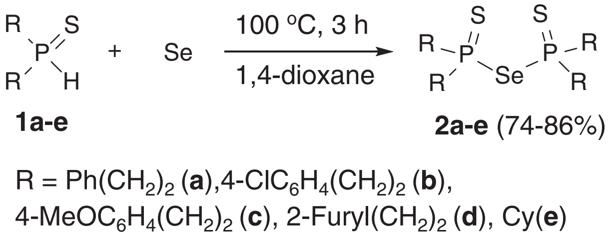
Fig. 2. Mixed bis(diorganochalcogenophosphinyl)chalcogenides.



Scheme 2. Reaction of secondary phosphine sulfides with elemental sulfur.



Scheme 3. Reaction of secondary phosphine selenides with elemental selenium.



Scheme 4. Chemoselective synthesis of bis(diorganothiophosphinyl)-selenides **2a**–**e**.

proceeds in 1,4-dioxane at 100 °C for 3 h with high degree of chemoselectivity: no the expected bis(diorganoselenophosphinyl)sulfides, $(R_2P{=}Se)_2S$, are formed (^{31}P NMR).

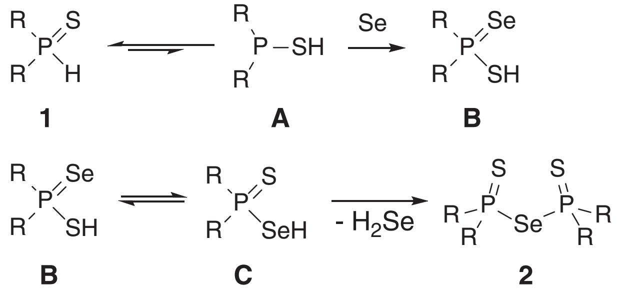
Also, the release of H_2Se as reaction by-product was detected by color test with the $Cd(OAc)_2$ solution. The energy dispersive X-ray analysis of the resulting red precipitate showed the formation of CdSe without admixture of CdS.

Bis(diorganothiophosphinyl)selenides **2a**–**e** are air-stable solids, well soluble in common solvents such as benzene, 1,4-dioxane, chloroform and acetone. Interestingly, on contact with DMSO, these compounds undergo oxidation to precipitate red selenium powder.

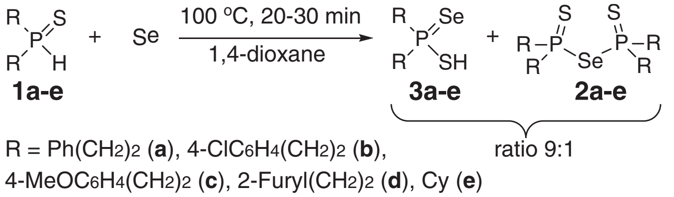
Selenides **2a**–**e** have been characterized by ^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR as well as IR spectroscopy. In solution ^{31}P NMR spectra of bis(diorganothiophosphinyl)selenides, the resonance of two magneto-equivalent phosphorus atoms is observed as sharp singlet at 71.53–72.71 ppm (except for **2e**, 98.49 ppm) flanked by single set of ^{77}Se satellites with $^1J_{PSe}=361$–378 Hz, indicating only P–Se bond present in the each compound. Meanwhile, the solution ^{77}Se NMR spectra are comprised of a triplet at 212–294 ppm ($^1J_{PSe}=361$–378 Hz) due to the splitting on two magneto-equivalent phosphorus atoms. As expected, the solution ^{1}H and ^{13}C NMR spectra of selenides **2a**–**e** were confirming the presence of corresponding organo-groups connecting with the phosphorus atoms. The presence of the P=S groups in compounds **2a**–**e** is supported by a strong bands at 602–608 cm^{-1} in solid-state IR spectra.

Apparently, reaction pathway involves oxidation of corresponding trivalent tautomeric form **A** of secondary phosphine sulfide **1** with elemental selenium. The resulting SH-acid **B** in its tautomeric SeH-form **C** undergoes the intermolecular condensation eliminating H_2Se to give selenide **2** (Scheme 5). The possible intermolecular condensation of SH-acid **B** with elimination of H_2S does not take place, likely due to the unfavorable cleavage of P–S bond in comparison with weaker P–Se bond in acid **C**. This rationalization explains satisfactorily, why only bis(diorganothiophosphinyl)selenides **2a**–**e** were exclusively formed and no possible bis(diorganoselenophosphinyl)sulfides, $(R_2P{=}Se)_2S$, were detectable in the reaction mixtures.

The mechanism proposed is in compliance with our finding that the reaction can be stopped at the acid **B** formation stage when the reaction lasts 20–30 min only (Scheme 6). Eventually, thioselenophosphinic *S*-acids **3a**–**e** have been prepared in solution (1,4-dioxane) with minor admixture of selenides **2a**–**e** (up to 10%).



Scheme 5. Plausible mechanistic pathway of the reaction between secondary phosphine sulfides **1** and elemental selenium.



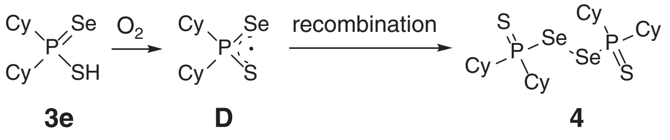
Scheme 6. Synthesis of thioselenophosphinic *S*-acids **3a**–**e**.

The SH-form of the acids **3a**–**e** unambiguously follows from their ^{31}P and ^{77}Se NMR spectra that well agrees with the Murai's data on preparation of similar acids, $R_2P(Se)SH$, by acidification of their salts [11]. Acids **3a**–**e** were prepared only in solution state because their isolation lead to the decomposition.

We have accidentally found that the storage of the above 1,4-dioxane solution of acid **3e** and selenide **2e** (their ratio was *ca.* 9:1) in the presence of air (4–6 °C, 2 days) gives the formation of co-crystals of selenide **2e** with corresponding diselenide, $(Cy_2P{=}S)_2Se_2$ (**4**). We believe that the diselenide **4** is produced via air oxidation of $Cy_2P(Se)SH$. Apparently, such oxidative coupling is triggered by the hydrogen (H•) transfer from acid **3e** by the action of oxygen (on air) to generate free radicals **D**, which undertakes then selective recombination to form diselenide **4** (Scheme 7).

The molecular structures of selenide **2e** and diselenide **4** in co-crystal have been determined by single-crystal X-ray diffraction analysis [12]. The S(1)–P(1)–Se(1)–P(2)–S(2) unit of selenide **2e** has a *syn-anti* conformation (Fig. 3). Meanwhile, both S(3)–P(3)–Se(3)–Se(2) and S(4)–P(4)–Se(2)–Se(3) units in diselenide **4** adopt *syn* conformation with P(3)–Se(3)–Se(2)–P(4) dihedral angle of 94.82° (Fig. 4). The close congeners of diselenide **4**, bis(5,5-dimethyl-2-thioxo-dioxaphosphorinan-2-yl)diselenide [13], bis[6-*O*,6′-*O*-(1,2:3,4-diisopropylidene-R-D-galactopyranosyl)dithuophosphoryl]diselenide [14], $[\text{Ph}t\text{-BuP(S)}]_2Se_2$ [15] and $[(t\text{-BuCH}_2O)_2P(S)]_2Se_2$ [16], have the same conformation of S═P–Se–Se–P═S chain. The Se–Se distance in diselenide **4** [2.3012(9) Å] fall close to the values found in the related diselenides [13–16]. The coordination geometry around the phosphorus atoms in **2e** and **4** is distorted from ideal tetrahedral geometry, apparently, due to steric effects of the cyclohexyl groups. The single P–Se bond distances [2.3014(13), 2.2604(13) Å for **2e**, and 2.3199(13), 2.3054(14) Å for **4**] are similar to those in other compounds containing the $P^{(V)}$-Se unit [17]. Likewise, all the P═S bond distances in the range of 1.9712(15)–2.0017(15) Å are comparable with the literature values reported for compounds bearing P═S bonds [18]. It should be noted, that the shortest Se…Se intermolecular contacts exist between diselenide molecules in co-crystal as evident from the Se(3)…Se(3) distance of 3.479 Å, which is significantly less than the sum of the van der Waals radii of Se (3.80 Å).

In summary, first representatives of bis(diorganothiophosphinyl) selenides have been synthesized in high yield via unknown reaction of secondary phosphine sulfides and selenium. The reaction proceeds chemoselectively and opens rewording opportunities for systematic studies of bis(diorganothiophosphinyl)selenides, which are promising building blocks for organic synthesis, versatile ligands for metal clusters as well as precursors for drugs and agrochemicals. The result represent significant contributions to both phosphorus and chalcogen inorganic chemistry.



Scheme 7. Formation of diselenide **4** via two-electron oxidation of *S*-acid **3e**.

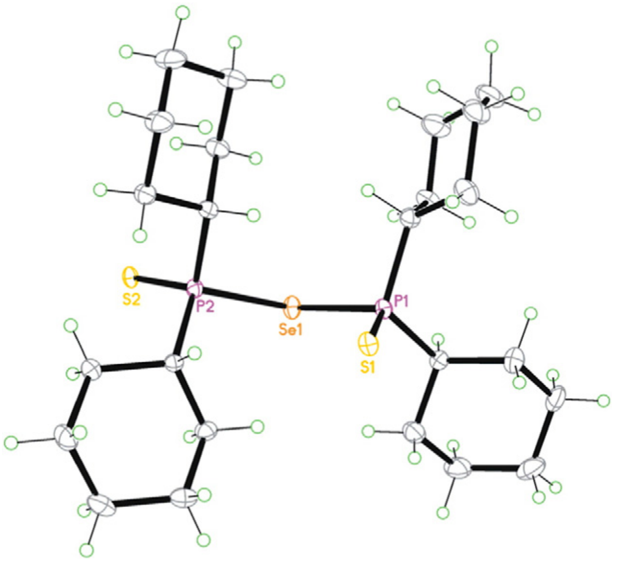


Fig. 3. X-ray structure of monoselenide **2e** in the co-crystal (50% thermal ellipsoid). Selected bond lengths [Å] and angles [°]: Se(1)–P(1) 2.3014(13); Se(1)–P(2) 2.2604(13); S(1)–P(1) 2.0017(15); S(2)–P(2) 1.9862(15); P(1)–Se(1)–P(2) 107.88(4); Se(1)–P(1)–S(1) 117.09(6); and Se(1)–P(2)–S(2) 103.33(5).

Acknowledgments

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Appendix A. Supplementary material

Supplementary data (general experimental methods, synthetic procedures, crystallographic details, and analytical data for the synthesized compounds) to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.01.019.

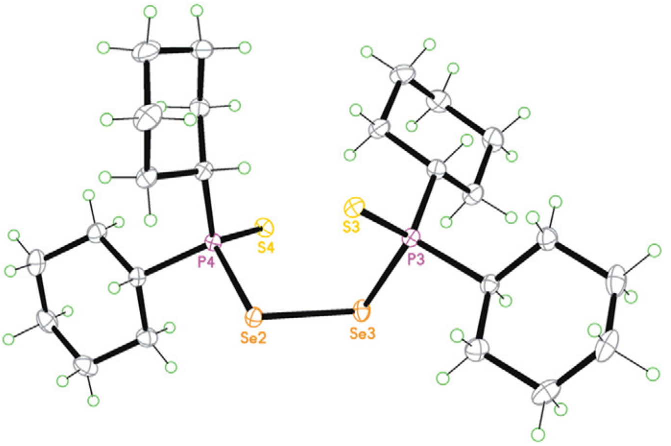

Fig. 4. X-ray structure of diselenide **4** in the co-crystal (50% thermal ellipsoid). Selected bond lengths [Å] and angles [°]: Se(2)–Se(3) 2.3012(9); Se(2)–P(4) 2.3199(13); Se(3)–P(3) 2.3054(14); S(3)–P(3) 1.9830(15); S(4)–P(4) 1.9712(15); Se(3)–Se(2)–P(4) 100.40(3); Se(2)–Se(3)–P(3) 104.75(3); Se(3)–P(3)–S(3) 115.25(6); and Se(2)–P(4)–S(4) 115.48(6).

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[10] General procedure for the preparation of bis(diorganothiophosphinyl)selenides **2a**-**e** from secondary phosphine sulfides **1a**-**e** and elemental selenium: A flask equipped with reflux condenser, stirrer and Ar inlet/outlet was charged with a solution of secondary phosphine sulfide **1a**-**e** (1 mmol) in 1,4-dioxane (8 ml) and amorphous grey selenium (0.079 g, 1.0 mmol). The suspension was stirred under reflux with simultaneous blowing off H_2Se formed during the reaction (3 h). After removal of the solvent, the residue (crude product) obtained was purified by reprecipitation from diethyl ether into hexane at 6–8 °C and dried in *vacuo* (1 Torr) to give the compounds **2a**-**e** in 74-86% yield.

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