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Regioselective Addition of Dithiophosphinic Acids to Vinyl Sulfides and Selenides: An Efficient Route Toward Functional Dithiophosphinates

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ABSTRACT: *Earlier unknown S-[1-(organosulfanyl)ethyl]- and S-[1-(organoselenyl)ethyl] dithiophosphinates were synthesized in 85–97% yields by regioselective addition of dithiophosphinic acids to diverse vinyl sulfides and selenides under mild conditions (ambient temperature, Et_2O, 3 h).* © 2014 Wiley Periodicals, Inc. Heteroatom Chem. 00:1–6, 2014; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21215

INTRODUCTION

Over the past decades, the addition of S–H species to C=C double bonds attracts a great interest of researchers as one of most efficient and atom-economic route toward C–S bond formation [1]. This reaction, referred now to as thiol-ene addition, has numerous advantages over alternative methods for the synthesis of organosulfur compounds due to its "click" characteristics. Among the latter are mild reaction conditions (usually room temperature and atmospheric pressure), high regioselectivity, as well as rapid and almost quantitative formation of target products with a minimum of by-products (if any) [1]. Owing to these benefits, the thiol-ene reaction currently has a wide application in such diverse areas as small molecule organic synthesis [1], biochemistry [2], and polymer and material science [3].

However, while this reaction has been broadly investigated with diverse thiols (involving natural ones) [1], the addition of compounds containing, for example, P–S–H functionalities, in particular, thiophosphinic and -phosphoric acids, across C=C double bonds, has received significantly less attention. In previous studies, the addition of *O*,*O*'-dialkyldithiophosphoric acids to electron-deficient alkenes proceeding in an anti-Markovnikov fashion has been mainly investigated [4]. Unactivated substrates (aliphatic alkenes, terpenes) react with these acids to give the Markovnikov-type adducts [5], often along with products of carbocationic rearrangements [5, 6]. As for electron-rich alkenes, to our knowledge, only Markovnikov addition of $Ph_2P(S)SH$ and $(EtO)_2P(S)SH$ to aryl vinyl ethers [7] and vinyl acetate [8] has been described without providing reliable proofs for a structure of the prepared adducts.

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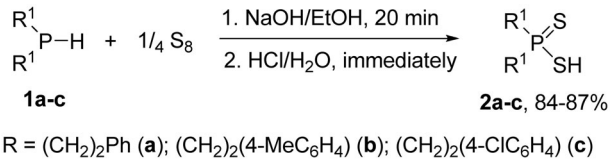


SCHEME 1. Synthesis of the starting acids **2a–c**.

To further extend the potential of addition of phosphorus thioacids to alkenes as an efficient approach to functional *S*-esters, in this work we have studied the reaction of dithiophosphinic acids with vinyl sulfides and selenides. The latter are chosen as ene-components due to (i) their availability [9] and (ii) potential usefulness of the designed products, i.e., earlier unknown dithiophosphinic *S*-esters, which are expected to be prospective iniferters [10], S/Se sources for fabrication of semiconducting nanocrystals [11], as well as new generation pesticides [12].

RESULTS AND DISCUSSION

The starting dithiophosphinic acids were synthesized by the one-pot procedure from secondary phosphines **1a–c**, which now are readily accessible from red phosphorus and styrenes [13]. The oxidation of **1a–c** with elemental sulfur in the presence of alkali (1:0.25:1.1 molar ratio, EtOH, room temperature, 20 min), followed by acidification of the formed sodium dithiophosphinate with aqueous HCl produced the pure acids **2a–c** in high yields (Scheme 1).

The examination of the prepared acids **2a–c** in a reaction with diverse vinyl sulfides **3a–c** and selenides **3d,e** (equimolar reactant ratio) has showed that the addition to latter is carried out in diethyl ether at ambient temperature for 3 h to afford Markovnikov-type adducts **4a–g** in 85–97% yield (Table 1). The reaction is strictly regioselective, because no by-products have been found in reaction mixtures (^{1}H and ^{31}P NMR). This fact is explained by relatively high S–H acidity of the acids **2a–c** (e.g., pK_a of aqueous ethanolic solution of Et_2PS_2H is 2.8 [14]) and by the electron-rich nature of the C=C bond within vinyl chalcogenides **3a–e** [15] that favors their easy hydrofunctionalization.

On example of available divinyl sulfide [16], it was demonstrated that the divinyl chalcogenides also participate in this reaction. Thus, when twofold amount of acid **2c** was used, the addition to divinyl sulfide takes place on the both vinyl groups, leading to expected diadduct **5** in 90% yield (Scheme 2). According to ^{1}H,^{13}C, and ^{31}P NMR data, this compound was formed as a mixture of the two diastereomers (*RR*/*RS* or *SS*/*SR*) with the ratio of 1:1.

The obtained *S*-esters are white powders (**4a,c,d,g**) or oils (**4b,e,f, 5**), stable to possible symmetrization with formation of dithioacetals and acylals, $(RS)_2$CHMe and $[R_2P(S)S]_2$CHMe. The synthesized compounds were characterized by ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR, IR, and X-ray diffraction (for **4a**) techniques.

The single-crystal X-ray analysis of *S*-ester **4a** revealed that this compound crystallizes in a racemic group *P*-1 with two molecules per unit cell (Fig. 1). The phosphorus atom has a distorted tetrahedral coordination, similar to other reported dithiophosphinate structures [17]. The P–S (2.0996 Å) and P=S (1.9494 Å) bond lengths are consistent with the literature values [17]. The S(3)–P(1)–S(1)–C(15) chain adopts a synclinal conformation with an angle of 33.68°.

CONCLUSION

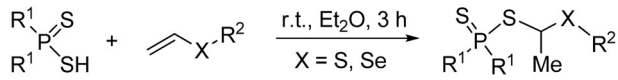
To summarize, the efficient method for the synthesis of hitherto unknown dithiophosphinates bearing dithio- and thioselenoacetal moieties has been developed utilizing electrophilic addition of dithiophosphinic acids to vinyl sulfides and selenides as well as divinyl sulfide. The reaction proceeds under mild condition to provide Markovnikov adducts in high yields. Having in mind that the numerous dithiophosph(in)ates are highly biological active [7, 12], the obtained products represent prospective agrochemicals and drug precursors. The presence of the several chalcogen atoms within compounds **4a–g** and **5** makes them promising ligands for the construction of metal complexes. Also, they can be used as iniferters for living polymerization and capping agents for stabilization of nanoparticles.

EXPERIMENTAL

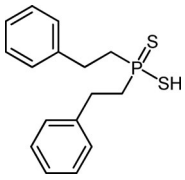
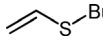
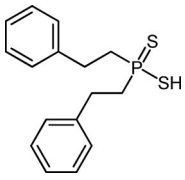
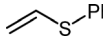
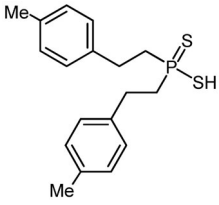
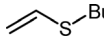
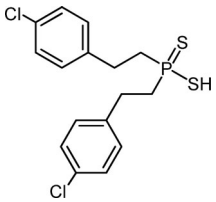
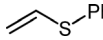
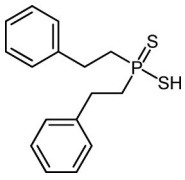
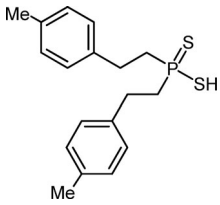
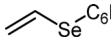
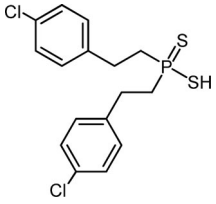
FTIR spectra were recorded on a Bruker Vertex 70 instrument. The^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra were run on a Bruker AV-400 spectrometer (400.13, 100.61 161.98, and 76.31 MHz, respectively). 85% H_3PO_4/H_2O was employed as an external standard for ^{31}P NMR, HMDS was used for ^{1}H and ^{13}C NMR, and Me_2Se was the external standard for ^{77}Se NMR. Melting points (uncorrected) were measured on a Kofler micro hot stage apparatus. The microanalyses were performed on a Flash EA 1112 CHNS analyzer.

All steps of the experiment were carried out in argon atmosphere. Vinyl sulfides [9a] and selenides [9b,c] were prepared by published methods. Secondary phosphines **1a–c** were synthesized

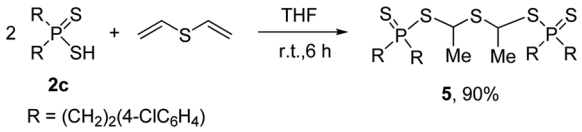
TABLE 1 Atom-Economic Synthesis of *S*-Esters **4a–g**[a]



2a-c **3a-e** **4a-g**, 85-97%

Entry	*Acid*	*Vinyl Chalcogenide*	*Product*	*Yield (%)*[b]
1	 (**2a**)	 (**3a**)	**4a**	94
2	 (**2a**)	 (**3b**)	**4b**	90
3	 (**2b**)	 (**3c**)	**4c**	97
4	 (**2c**)	 (**3b**)	**4d**	91
5	 (**2a**)	(**3d**)	**4e**	85
6	 (**2b**)	 (**3e**)	**4f**	92
7	 (**2c**)	(**3d**)	**4g**	95

[a]Reaction condition: acid **2a–c** (1 mmol), vinyl chalcogenide **3a–e** (1 mmol), diethyl ether, stirring under argon at room temperature for 3 h.
[b]Isolated yield.



SCHEME 2. Addition of acid **2c** to divinyl sulfide.

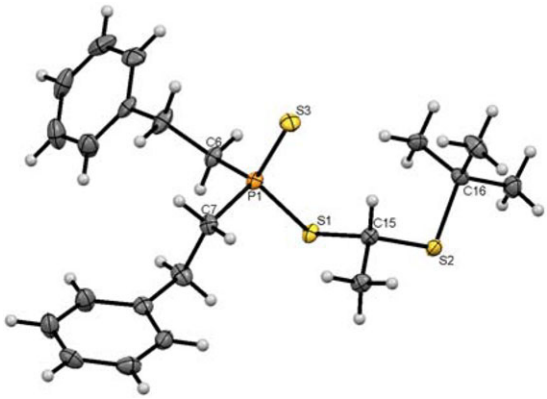


FIGURE 1 X-ray structure of **4a** (50% thermal ellipsoid probability). Selected bond lengths (Å) and angles (deg): S(1)–P(1) 2.0996(6), S(1)–C(15) 1.8468(15), S(2)–C(15) 1.8095(15), S(2)–C(16) 1.8477(16), S(3)–P(1) 1.9494(6), P(1)–C(6) 1.8147(15), P(1)–C(7) 1.8193(16), S(3)–P(1)–S(1) 114.96(3), S(2)–C(15)–S(1) 109.23(7).

from red phosphorus, styrene, 4-chlorostyrene, and 4-methylstyrene, correspondingly, according to protocol [13a]. Divinyl sulfide was prepared as described in [16]. Diethyl ether and THF were distilled over metal sodium prior to use.

*Synthesis of Dithiophosphinic Acids (**2a–c**): General Procedure*

To a mixture of secondary phosphine **1a–c** (4 mmol) and NaOH (176 mg, 4.4 mmol) in EtOH (20 mL), powdered sulfur S_8 (256 mg, 1 mmol) was added and the suspension was stirred until the dissolution of sulfur (ca. 20 min). The resulting solution was diluted with water (30 mL), acidified with HCl (36%, 1 mL), and extracted with chloroform (2 × 20 mL). The extract was dried over Na_2SO_4, the solvent was evaporated, and residue was dried in vacuo (1 Torr) to give pure acid **2a–c**.

*Diphenethyldithiophosphinic Acid (**2a**).* White powder, yield 1070 mg (87%); mp 64°C (hexane). IR (KBr), cm^{-1}: 2513 (S–H), 745 (P–C), 625 (P=S), 584, 510 (P–S). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.37 (m, 4H, CH_2P), 2.78 (br s, 1H, SH), 2.98–3.05 (m, 4H, CH_2Ph), 7.14–7.22 (m, 10H, Ph). ^{13}C NMR (100.62 MHz, acetone-d_6): δ = 29.6 (*C*H_2Ph), 42.9 (d, $^1J_{PC}$ = 49.6 Hz, CH_2P), 125.9 (*p*-C in Ph), 128.4 (*o*-C in Ph), 128.5 (*m*-C in Ph), 142.5 (d, $^3J_{PC}$ = 16.8 Hz, *ipso*-C in Ph). ^{31}P NMR (161.98 MHz, acetone-d_6): δ = 69.10. Anal. Calcd for $C_{16}H_{19}PS_2$: C, 62.71; H, 6.25; S, 20.93. Found: C, 62.93; H, 6.37; S, 21.08.

*Bis(4-methylphenethyl) Dithiophosphinic Acid (**2b**).* White powder, yield 1130 mg (84%); mp 70°C (hexane). IR (KBr), cm^{-1}: 2537 (S–H), 732 (P–C), 610 (P=S), 534, 480, 465 (P–S). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.35 (br s, 7H, Me, SH), 2.39–2.45 (m, 4H, CH_2P), 3.02–3.09 (m, 4H, CH_2Ar), 7.12–7.14 (m, 8H, Ar). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 21.0 (Me), 28.7 (*C*H_2Ar), 40.7 (d, $^1J_{PC}$ = 48.3 Hz, CH_2P), 128.3 (C-2,6 in Ar), 129.5 (C-3,5 in Ar), 136.3 (C-4 in Ar), 136.9 (d, $^3J_{PC}$ = 16.4 Hz, C-1 in Ar). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 68.38. Anal. Calcd for $C_{18}H_{23}PS_2$: C, 64.64; H, 6.96; S, 19.17. Found: C, 64.80; H, 7.17; S, 19.35.

*Bis(4-chlorophenethyl)dithiophosphinic Acid (**2c**).* White powder, yield 1290 mg (86%); mp 106°C (hexane). IR (KBr), cm^{-1}: 2569 (S–H), 734 (P–C), 612, 656 (P=S), 490, 481 (P–S). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.21 (br s, 1H, SH), 2.36–2.43 (m, 4H, CH_2P), 3.04–3.09 (m, 4H, CH_2Ar), 7.16 (d, ^3J = 8.4 Hz, 4H, H-2,6 in Ar), 7.29 (d, ^3J = 8.4 Hz, 4H, H-3,5 in Ar). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 28.4 (*C*H_2Ar), 40.4 (d, $^1J_{PC}$ = 49.1 Hz, CH_2P), 128.8 (C-2,6 in Ar), 129.6 (C-3,5 in Ar), 132.5 (C-4 in Ar), 138.3 (d, $^3J_{PC}$ = 15.9 Hz, C-1 in Ar). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 67.32. Anal. Calcd for $C_{16}H_{17}Cl_2PS_2$: C, 51.20; H, 4.57; S, 17.09. Found: C, 51.37; H, 4.73; S, 17.31.

*Synthesis of S-Esters (**4a–g**): General Procedure*

To a solution of vinyl chalcogenide **3a–e** (1 mmol) in diethyl ether (7 mL), acid **2a–c** (1 mmol) was added and the suspension was stirred at ambient temperature for 3 h. The solvent was removed from the resulting mixture, and the residue was purified by flash chromatography (neutral alumina, $CHCl_3$) to give *S*-esters **4a–g**.

*S-1-(Tert-butylsulfanyl)ethyl Diphenethyldithiophosphinate (**4a**)*

Colorless solid, yield 397 mg (94%); mp 62°C (hexane). IR (KBr), cm^{-1}: 752 (P–C), 633 (P=S), 558, 473 (P–S). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.47 (s, 9H, *t*-Bu), 1.81 (d, $^3J_{HH}$ = 7.0 Hz, 3H, *Me*CH), 2.24 -2.34 (m, 4H, CH_2P), 2.91–3.13 (m, 4H, CH_2Ph), 4.75 (dq, $^3J_{PH}$ = 10.6 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, SCHS), 7.20–7.31 (m, 10H, Ph). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 28.4 (*C*H_2Ph), 28.7 (d, $^3J_{PC}$ = 3.0 Hz, *Me*CH), 30.9

(Me in *t*-Bu), 37.6 and 39.7 (2d, $^1J_{PC}$ = 48.7 and 47.0 Hz, respectively, CH_2P), 45.4 (C in *t*-Bu), 46.4 (d, $^2J_{PC}$ = 3.0 Hz, SCHS), 126.96, 126.02 (*p*-C in Ph), 127.71, 127.74 (*o*-C in Ph), 128.15, 128.18 (*m*-C in Ph), 139.7 and 139.9 (2d, $^3J_{PC}$ = 16.5 Hz, *ipso*-C in Ph). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 71.88. Anal. Calcd for $C_{22}H_{31}PS_3$: C, 62.52; H, 7.39; S, 22.76. Found: C, 63.00; H, 7.57; S, 22.92.

*S-1-(Phenylsulfanyl)ethyl Diphenethyldithiophosphinate (***4b***).* Yellowish oil, yield 398 mg (90%). IR (film), cm^{-1}: 749 (P–C), 697 (P=S), 558, 475 (P–S). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.64 (d, $^3J_{HH}$ = 7.0 Hz, 3H, *Me*CH), 2.12–2.21 (m, 4H, CH_2P), 2.58–2.92 (m, 4H, C*H*$_2$Ph), 4.78 (dq, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, SCHS), 7.10 (d, $^3J_{HH}$ = 7.4 Hz, 2H, *o*-H in PhS), 7.03–7.27 (m, 11H, Ph, *p*-H in PhS), 7.44 (d, $^3J_{HH}$ = 7.2 Hz, 2H, *m*-H in PhS). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 25.1 (*Me*CH), 28.5, 28.7 (*C*H_2Ph), 38.0 and 39.2 (2d, $^1J_{PC}$ = 48.7 and 47.8 Hz, respectively, CH_2P), 51.3 (SCHS), 126.1, 126.2 (*p*-C in Ph), 128.0 (*o*-C in Ph, *p*-C in PhS), 128.3, 128.4 (*m*-C in Ph), 128.7 (*o*-C in PhS), 133.1 (*ipso*-C in PhS), 133.2 (*m*-C in PhS), 139.9 and 140.0 (2d, $^3J_{PC}$ = 16.4 and 16.8, 5 Hz, respectively, *ipso*-C in Ph). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 74.01. Anal. Calcd for $C_{24}H_{27}PS_3$: C, 65.12; H, 6.15; S, 21.73. Found: C, 64.88; H, 5.95; S, 21.48.

*S-1-(Isobutylsulfanyl)ethyl bis(4-methyl phenethyl) Dithiophosphinate (***4c***).* White solid, yield 436 mg (97%); mp 87°C (hexane). IR (KBr), cm^{-1}: 757 (P–C), 654 (P=S), 562, 485 (P–S). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.01, 1.02 (2d, $^3J_{HH}$ = 6.8 Hz, 6H, *Me*$_2$CH), 1.78 (d, $^3J_{HH}$ = 6.9 Hz, 3H, *Me*CH), 1.89 (dq, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 6.9 Hz, 1H, Me$_2$C*H*), 2.33 (s, 6H, *Me*Ar), 2.27–2.42 (m, 4H, CH_2P), 2.53 and 2.74 (2dd, each 1H, $^2J_{HH}$ = 12.6 Hz, $^3J_{HH}$ = 7.5 Hz, CH_2S), 2.94–3.08 (m, 4H, C*H*$_2$Ar), 4.60 (dq, $^3J_{PH}$ = 11.0 Hz, $^3J_{HH}$ = 6.9 Hz, 1H, SCHS), 7.06–7.13 (m, 8H, Ar). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 21.0 (Me), 21.9, 22.3 (*Me*Ar), 26.1 (*Me*CH), 28.4 (Me$_2$*C*H), 28.7 (*C*H_2Ar), 39.0 and 39.6 (2d, $^1J_{PC}$ = 48.0, CH_2P), 41.0 (CH_2S), 49.6 (SCHS), 128.2 (C-2,6 in Ar), 129.4 (C-3,5 in Ar), 136.1, 136.2 (C-4 in Ar), 137.2 and 137.3 (2d, $^3J_{PC}$ = 16.8 and 17.0 Hz, respectively, C-1 in Ar). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 73.34. Anal. Calcd for $C_{24}H_{35}PS_3$: C, 63.96; H, 7.83; S, 21.34. Found: C, 63.70; H, 8.10; S, 21.17.

*S-1-(Phenylsulfanyl)ethyl bis(4-chlorophenethyl) phosphinodithioate (***4d***).* White solid, yield 465 mg (91%); mp 105°C (hexane). IR (KBr), cm^{-1}: 755, 743 (P–C), 663, 657 (P=S), 504, 487 (P–S). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.78 (t, $^3J_{HH}$ = 6.8 Hz, 3H, Me), 2.20–2.29 (m, 4H, CH_2P), 2.64–3.05 (m, 4H, C*H*$_2$Ar), 4.88 (dq, $^3J_{PH}$ = 12.2 Hz, $^3J_{HH}$ = 6.8 Hz, 1H, SCHS), 7.04 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H-2,6 in Ar), 7.12 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H-3,5 in Ar), 7.25–7.36 (m, 7H, H-2,3,5,6 in Ar, *o*-*p*-H in PhS), 7.58 (d, $^3J_{HH}$ = 7.2 Hz, 2H, *m*-H in PhS). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 25.4 (*Me*CH), 28.2, 28.4 (*C*H_2Ar), 38.0 and 39.2 (2d, $^1J_{PC}$ = 49.3 and 47.9 Hz, respectively, CH_2P), 51.9 (SCHS), 128.5 (*p*-C in PhS), 128.8, 128.9 (C-2,6 in Ar), 129.1 (*o*-C in PhS), 129.7 (C-3,5 in Ar), 132.3, 132.4 (C-4 in Ar), 133.2 (*ipso*-C in PhS), 133.7 (*m*-C in PhS), 138.6 and 138.7 (2d, $^3J_{PC}$ = 16.4 and 16.8 Hz, respectively, C-1 in Ar). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 73.32. Anal. Calcd for $C_{24}H_{25}Cl_2PS_3$: C, 56.35; H, 4.93; S, 18.81. Found: C, 56.92; H, 4.60; S, 19.08.

*S-1-(Pentylselanyl)ethyl Diphenethyldithiophosphinate (***4e***).* Yellowish oil, yield 411 mg (85%). IR (film), cm^{-1}: 749 (P–C), 698 (P=S), 559, 495, 470 (P–S). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 0.91 (t, $^3J_{HH}$ = 7.0 Hz, 3H, Me), 1.38 (m, 4H, CH_2), 1.78 (m, 2H, CH_2), 1.90 (d, $^3J_{HH}$ = 7.0 Hz, 3H, *Me*CH), 2.33–2.46 (m, 4H, CH_2P), 2.77 and 2.84 (m, each 1H, CH_2Se), 2.91–3.12 (m, 4H, C*H*$_2$Ph), 4.68 (dq, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, SCHSe), 7.20–7.27 (m, 10H, Ph). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 14.0 (*Me*CH_2), 22.3 (Me*C*H_2), 26.1 (CH_2Se), 27.1 (*Me*CH), 29.1 (*C*H_2Ph), 30.0 (*C*H_2Pr), 32.2 (*C*H_2Et), 37.3 (d, $^2J_{PC}$ = 3.4 Hz, SCHSe), 38.6 and 39.4 (2d, $^1J_{PC}$ = 48.0 and 47.4 Hz, respectively, CH_2P), 126.5, 126.6 (*p*-C in Ph), 128.3 (*m*-C in Ph), 128.7 (*o*-C in Ph), 140.1 and 140.2 (2d, $^3J_{PC}$ = 16.4 Hz, *ipso*-C in Ph). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 74.37. ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = 349.4. Anal. Calcd for $C_{23}H_{33}PS_2Se$: C, 57.13; H, 6.88; S, 13.26. Found: C, 57.42; H, 6.60; S, 13.72.

*S-1-(Hexylselanyl)ethyl Bis(4-methylphenethyl) Dithiophosphinate (***4f***).* Yellowish oil, yield 483 mg (92%). IR (film), cm^{-1}: 738, 714 (P–C), 654 (P=S), 528, 483 (P–S). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 0.85 (t, $^3J_{HH}$ = 6.7 Hz, 3H, Me), 1.26–1.38 (m, 6H, CH_2), 1.68–1.75 (m, 2H, CH_2), 1.84 (d, $^3J_{HH}$ = 6.8 Hz, 3H, *Me*CH), 2.24–2.36 (m, 4H, CH_2P), 2.29 (s, 6H, *Me*Ar), 2.67–3.00 (m, 6H, CH_2Se, C*H*$_2$Ar), 4.64 (dq, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 6.7 Hz, 1H, SCHSe), 7.02–7.08, (m, 8H, Ar).^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 14.1 (*Me*CH_2), 21.1 (*Me*Ar), 22.6 (Me*C*H_2), 26.2 (*Me*CH), 27.1 (CH_2Se), 28.8 (*C*H_2Ar), 29.8 (*C*H_2Pr), 30.4 (*C*H_2Bu), 31.4 (*C*H_2Et), 37.3 (d, $^2J_{PC}$ = 3.4 Hz, SCHSe), 37.82 and 39.70 (2d,

$^1J_{PC}$ = 48.3 and 47.0 Hz, respectively, CH_2P), 128.2 (C-2,6 in Ar), 129.52 (C-3,5 in Ar), 136.1,136.2 (C-4 in Ar), 137.2 and 137.4 (2d, $^3J_{PC}$ = 16.4 and 17.0 Hz, respectively, C-1 in Ar). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 74.56. ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = 349.1. Anal. Calcd for $C_{26}H_{39}PS_2Se$: C, 59.41; H, 7.48; S, 12.20. Found: C, 59.62; H, 7.60; S, 12.61.

*S-1-(Pentylselanyl)ethyl Bis(4-chlorophenethyl) phosphinodithioate (***4g***).* White solid, yield 524 mg (95%); mp 57°C (hexane). IR (KBr), cm^{-1}: 779, 740 (P–C), 658 (P=S), 514, 484 (P–S). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 0.87 (t, $^3J_{HH}$ = 6.8 Hz, 3H, Me), 1.29–1.37 (m, 4H, CH_2), 1.70–1.77 (m, 2H, CH_2), 1.85 (d, $^3J_{HH}$ = 6.9 Hz, 3H, *Me*CH), 2.23–2.37 (m, 4H, CH_2P), 2.68–3.05 (m, 6H, CH_2Se, C*H*$_2$Ar), 4.62 (dq, $^3J_{PH}$ = 12.5 Hz, $^3J_{HH}$ = 6.8 Hz, 1H, SCHSe), 7.09 (d, $^3J_{HH}$ = 7.8 Hz, 4H, H-2,6 in Ar), 7.26 (d, $^3J_{HH}$ = 7.3 Hz, 4H, H-3,5 in Ar). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 14.1 (*Me*CH_2), 22.3 (Me*C*H_2), 26.2 (*Me*CH), 27.1 (CH_2Se), 28.6 (*C*H_2Ar), 30.1 (*C*H_2Pr), 32.3 (*C*H_2Et), 37.4 (d, $^2J_{PC}$ = 3.0 Hz, SCHSe), 38.6 and 39.3 (2d, $^1J_{PC}$ = 48.7 and 47.9 Hz, respectively, CH_2P), 128.9 (C-2,6 in Ar), 129.7 (C-3,5 in Ar), 132.4, 132.5 (C-4 in Ar), 137.7 and 137.8 (2d, $^3J_{PC}$ = 16.4 and 16.0 Hz, respectively, C-1 in Ar). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 73.88. ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = 351.3. Anal. Calcd for $C_{23}H_{31}Cl_2PS_2Se$: C, 50.00; H, 5.66; S, 11.61. Found: C, 50.46; H, 5.60; S, 12.02.

*S-1-[(1-[Bis(4-chlorophenethyl)phosphorothioyl]sulfanylethyl)sulfanyl]ethyl Bis(4-chloro-Phenethyl) dithiophosphinate (***5***)*

To a solution of divinyl sulfide (86 mg, 1 mmol) in THF (5 mL), acid **2c** (751 mg, 2 mmol) was added and the solution was stirred at ambient temperature for 6 h. The solvent was removed from the resulting mixture, and the residue was purified by flash chromatography (neutral alumina, $CHCl_3$) to give diadduct **5** as mixture of the two diastereomers (1:1 ratio). Colorless oil, yield 752 mg (90%). IR (film), cm^{-1}: 734, 706 (P–C), 656, 606 (P=S), 515, 484 (P–S). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.80 and 1.82 (2d, $^3J_{HH}$ = 6.8 Hz, 6H, Me), 2.24–2.31 and 2.37–2.49 (2m, each 4H, CH_2P), 2.89–3.02 (m, 8H, C*H*$_2$Ar), 4.71–4.87 (m, 2H, SCHS), 7.08–7.16 (m, 8H, H-2,6 in Ar), 7.24–7.28 (m, 8H, H-3,5 in Ar). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 25.4 and 25.5 (*Me*CH), 27.9 and 28.2 (*C*H_2Ar), 38.3, 38.7, 38.9, and 39.2 (4d, $^1J_{PC}$ = 48.3, 48.7, 47.8 and 47.4 Hz, respectively, PCH_2), 47.5 and 48.8 (SCHS), 128.4 and 128.5 (C-2,6 in Ar), 129.2 and 129.4 (C-3,5 in Ar), 131.9, 132.0, and 132.1 (C-4 in Ar), 138.2 and 138.3 (2d, $^3J_{PC}$ = 16.4 and 15.9 Hz, respectively, C-1 in Ar). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 71.46 and 73.53 with the ratio of 1:1. Anal. Calcd for $C_{36}H_{40}Cl_4P_2S_5$: C, 51.67; H, 4.82; S, 19.16. Found: C, 51.98; H, 5.11; S, 19.42.

Crystallography of **4a**

The single crystals of **4a** were obtained by slow evaporation of its hexane solution at 6–8°C for overnight. The suitable sample was analyzed on a Bruker D8 Venture diffractometer with Mo K_α (λ = 0.71073 Å) using the ϕ and ω scans. The structure was solved and refined by direct methods, and non-hydrogen atoms were refined anisotropically using SHELX [18]. The coordinates of the hydrogen atoms were calculated from geometrical positions. CCDC 1000860 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data **4a**: $C_{22}H_{31}PS_3$ (M = 422.62), triclinic, space group *P*-1, a = 5.8614(13) Å, b = 13.008(3) Å, c = 15.547(3) Å, α = 100.999(6), β = 94.431(6), γ = 94.877(6), V = 1154.1(4) Å^3, Z = 2, T = 100.0 K, μ(Mo K_α) = 0.395 mm^{-1}, D_{calc} = 1.216 g/cm^3, 5580 reflections measured ($4.58 \le 2\theta \le 60.32$), 4763 unique ($R_{int}$ = 0.0765, R_{sigma} = 0.0381), which were used in all calculations. The final R_1 was 0.0340 [$I > 2\sigma(I)$], and wR_2 was 0.0848 (all data).

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