Iodophosphane Selenides: Building Blocks for Supramolecular Soft–Soft Chain, Helix, and Base-Pair Arrays

Jörg Jeske, Wolf-W. du Mont,* and Peter G. Jones[a]

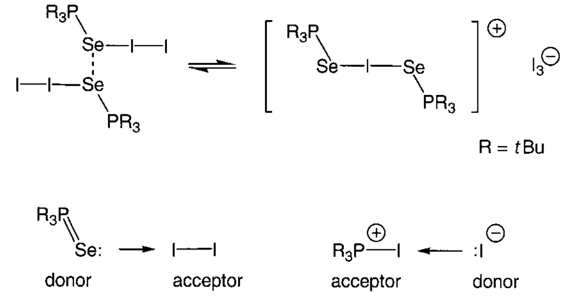
Abstract: Structure determinations on di-*tert*-butyliodophosphane selenide **1** and *c*-hexyldiiodophosphane selenide **2** reveal that intermolecular donor–acceptor interactions between nucleophilic selenium atoms and electrophilic iodine atoms lead to chains or helices that are interconnected by Se···Se contacts, building up layer structures. In the adduct of **1** with molecular iodine (**3**), **1** acts as donor through Se(=P) and as weak acceptor through I(−P). These interactions lead to base-pair-like dimers $[t\mathrm{Bu_2P(Se{-}I{-}I)I}]_2$ that are interconnected by additional Se···Se contacts.

Keywords: donor–acceptor interactions · iodine · iodophosphane selenides · selenium · supramolecular chemistry

Introduction

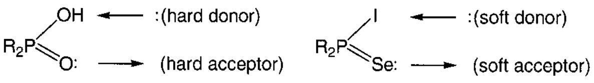
Iodine atoms adjacent to $\sigma^4\lambda^5$-phosphonium centres behave as soft electrophiles. With iodide anions as nucleophiles, anion–cation donor–acceptor I···I interactions of I^- with electrophilic iodine atoms of iodophosphonium ions $R_nPI^+_{4-n}$ lead—depending on the number of iodine atoms bound to phosphorus—to spoke structures with approximately linear P–I···I units ($n = 3$; R_3PI_2),[1–5] to rings, helices and zigzag chains ($n = 2$, R_2PI_3),[6–9] or to interpenetrating puckered layers and 3D networks ($n = 1$, RPI_4).[10] The above kind of cation–anion soft–soft donor–acceptor interactions could lead to a novel kind of soft–soft building blocks for supramolecular chemistry, when soft donor and acceptor functions are expressed in one type of molecule. Such bifunctional molecules should adopt properties related to base-pairing building blocks. Selenium is a suitable soft donor atom for designing such building blocks, because its electronegativity is very similar to that of iodine and because selenium ligands are better donors towards iodine than are related sulfur ligands.[11] We selected the phosphane selenide (P=Se) group as the first selenium donor function designed to coordinate to iodine atoms bonded to $\sigma^4\lambda^5$ phosphorus (Scheme 1). Phosphane selenides $R_3P{=}Se$ are known to react with molecular iodine,[11, 12] but structure determinations on products from such reactions have been carried out only recently.[13, 14]

A study of the structures of the products $t\mathrm{Bu_3PSe{-}I{-}I}$, $[(t\mathrm{Bu_3PSe})_2I]^+[I_3]^-$ and $[\{(t\mathrm{Bu_3PSe})_2I\}_2]^+[2/x\,(I_5)_x]^-$ from the reactions of tri-*tert*-butylphosphane selenide with varying amounts of iodine revealed that the ability of this phosphane selenide to act as a soft donor towards iodine is very similar to that of iodide ions.[13] Compared with $t\mathrm{Bu_3P{=}Se}$, $Ph_3P{=}Se$ is a slightly weaker donor towards molecular iodine, and aminophosphane selenides $(R_2N)_3P{=}Se$ are slightly better donors.[14]



Scheme 1. Se–I and I–I donor–acceptor interactions in the neighborhood of $\sigma^4\lambda^5$ phosphorus.

The simplest combination of a $\sigma^4\lambda^5$-P–I acceptor function and a P=Se donor function within one molecule should be expressed in iodophosphane selenides $R_nP({=}Se)I_{3-n}$; however, structures of this type of molecule have not yet been determined. As building blocks for intermolecular interactions, we regard compounds $R_2P({=}Se)I$ as soft–soft equivalents of phosphinic acids $R_2P({=}O)OH$ (Scheme 2). Depending on their organic substituents, the latter crystallise as P=O···H–O–P-bridged dimers or polymers.[15–17] Similarly, solid phosphoryl chloride and bromide exhibit weak inter



Scheme 2. Phosphinic acid derivatives interacting with hard and soft donors and acceptors.

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molecular P=O···X–P interactions (O···Cl 305 pm, O···Br 325 pm) leading to infinite chains.[18] For iodophosphane selenides, we expected a novel type of P=Se···I–P bridging. Like O···H–O bridges, Se···I–P bridges should be close to linear. In the following, syntheses and the first solid-state structures of iodophosphane selenides and of an iodophosphane selenide adduct with molecular iodine are presented.

Results and Discussion

Syntheses and NMR spectra: Crystalline iodophosphane selenides $(t\mathrm{Bu})_2\mathrm{P({=}Se)I}$ (**1**) and $c\text{-}\mathrm{C_6H_{11}P({=}Se)I_2}$ (**2**) were prepared from the related iodophosphanes with elemental selenium. It was sufficient to prepare the iodophosphanes in situ from chloro- or bromophosphanes with excess sodium iodide in toluene and to add selenium powder to the crude iodophosphanes. Yellow **1** was recrystallised from hexane, red-orange **2** crystallised from toluene solution. Addition of iodine to a toluene solution of **1** furnished the iodine adduct $[(t\mathrm{Bu})_2\mathrm{P(Se{-}I{-}I)I}]$ (**3**); diffusion of hexane into the toluene solution furnished brown-black single crystals of pure **3**. Similar reactions of **2** and the related compound $t\mathrm{BuP({=}Se)I_2}$ with iodine in dichloromethane led to insoluble, amorphous black solids that are apparently not straightforward 1:1 adducts.

In the ^{31}P-NMR spectra of **1**–**3**, satellites arising from $^1J(^{77}\mathrm{Se},^{31}\mathrm{P})$ are well-resolved. Compared with $t\mathrm{Bu_3P{=}Se}$,[19] the magnitude of $^1J(^{77}\mathrm{Se},^{31}\mathrm{P})$ of iodophosphane selenide **1** (775 Hz) is about 60 Hz larger. The couplings of diiodophosphane selenides **2** (755 Hz) and $t\mathrm{BuP({=}Se)I_2}$ (747 Hz), however, are about 20–30 Hz smaller than that of **1**. As in the case of the reactions of $\mathrm{R_3PSe}$ with iodine,[13, 14] coordination of **1** with iodine leads to a decrease of $^1J(^{77}\mathrm{Se},^{31}\mathrm{P})$ and to an upfield shift of δ^{31}P, and no separate signals of free and iodine-coordinated phosphane selenide were resolved in ^{31}P NMR spectrum at room temperature, that is, **3** is kinetically labile. The NMR parameters of **3** are solvent-dependent: the change from dichloromethane to benzene (in which it is less soluble) leads to a further significant decrease of $^1J(^{77}\mathrm{Se},^{31}\mathrm{P})$ and to a slight deshielding of the ^{31}P nucleus.

Structure determinations: Iodophosphane selenide **1** crystallises with two independent molecules in the unit cell. Bond angles and lengths within the two molecules of **1** are very similar; the most significant deviation between molecules I and II of **1** is the slightly larger P–Se distance in molecule II. (P1–Se1: 210.4(2) pm, P2–Se2: 212.1(2) pm). P–I bond lengths are very similar to those of $\{[(t\mathrm{Bu})_2\mathrm{PI_2}]^+[\mathrm{I}]^-\}_n$, which is a chain polymer as a result of P–I···I···I–P bridging.[7] Compound **1** can be described as a helical chainlike polymer if intermolecular P–Se···I–P contacts are taken into consideration (Figure 1). These secondary Se···I contacts (Se1–I2′ 369.04(9) and Se2–I1 384.38(9) pm; symmetry operator: $-x$, $y+0.5$, $-z+0.5$) are only slightly shorter than the sum of the van der Waals radii of selenium and iodine,[20] and are even longer than those found in the diselenide–diiodine intercalation compound $[(\mathrm{TIP_2Se_2})_2\mathrm{I_2}]$.[21] However, the L-shaped geometry of the P=Se···I–P bridges, with the iodine atoms being approximately linearly coordinated, is consistent with the expectations for typical Se(donor)→I(acceptor) interactions [$\sphericalangle$P1-I1-Se2 158.62(4)°, $\sphericalangle$P2-I2-Se1′ 167.68(4)°; symmetry operator: $-x$, $y-0.5$, $-z+0.5$].

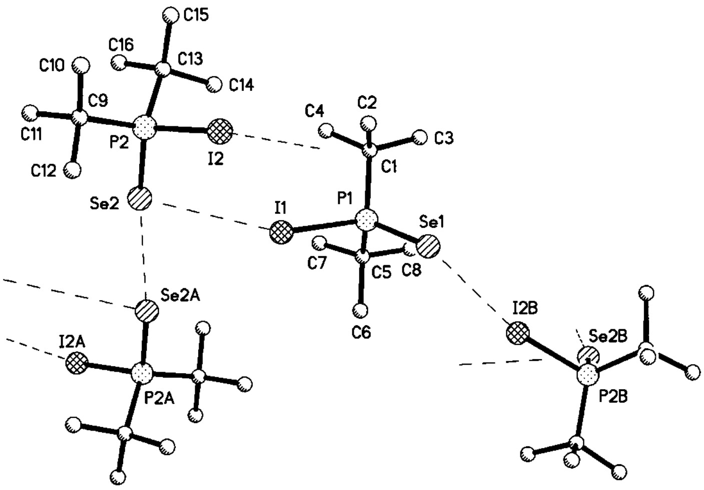

Figure 1. Molecular structure and secondary contacts of **1** (H atoms are omitted). Symmetry operators for equivalent atoms: $-x$, $y-0.5$, $-z+0.5$ (A); $-x$, $y+0.5$, $-z+0.5$ (B).

A surprising feature of the structure of **1** are additional intermolecular contacts between the two symmetry-equivalent selenium atoms Se2 and Se2′ (Se2···Se2′ 359.4(2) pm; symmetry operator: $-x$, $y+1$, $-z+1$); the P–Se···Se–P arrangement is not far from linear [$\sphericalangle$P–Se–Se 173.73(6)°]. This additional secondary cross-link between the chains arising from PSe···IP interactions is associated with the above-mentioned slight elongation of d(P2–Se2) compared with d(P1–Se1): Se1 does not participate in intermolecular Se···Se interactions (Figure 1). Cross-linking of the PSe···IP chains by PSe···SeP interactions leads to layers that are separated by regions containing the *tert*-butyl groups from adjacent layers (Figure 2).

Because crystals of the related diiodophosphane selenide $t\mathrm{BuP({=}Se)I_2}$ were not suitable for a structure determination, the comparable *c*-hexyl compound **2** was isolated and investigated. Like **1**, compound **2** contains a P=Se donor function [**2**: d(P=Se) 209.2(2) pm: shorter than both P=Se bonds in **1**]; however, two electrophilic iodine atoms are attached to the phosphorus atom of **2**. As in compound **1**, L-shaped P–Se···I–P donor–acceptor interactions (Se···I: 347.59(8) pm) form one motif of the supramolecular structure of **2** and P–Se···Se–P contacts (361.23(14) pm) the other (Figure 3).

Interconnection of two stacks of molecules of **2** by L-shaped P–Se···I–P bridges leads to staircaselike helices; layers are built up by connection of these helices through Se···Se contacts. In contrast to **1**, all selenium atoms of **2**, but only one iodine atom of each molecule participate in building up layers from helices. The stacking of these layers allows cyclohexyl groups and iodine atoms from terminal P–I groups to approach in a herringbone pattern, creating domains of iodine atoms and of cyclohexyl groups from two adjacent layers (Figure 4, p. 388).

As expected, iodophosphane selenides exhibit intermolecular L-shaped P–Se···I–P donor–acceptor interactions;

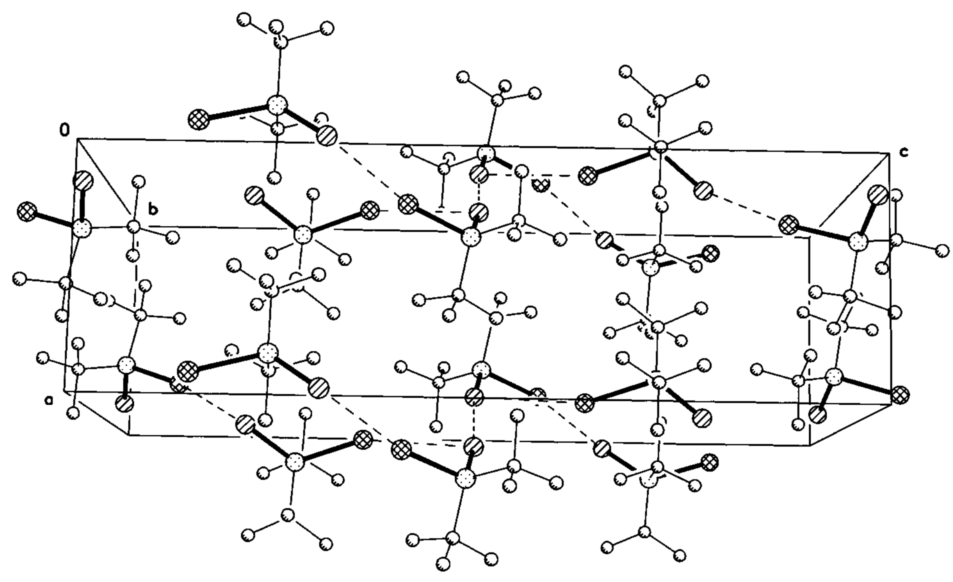

Figure 2. Packing diagram of **1**.

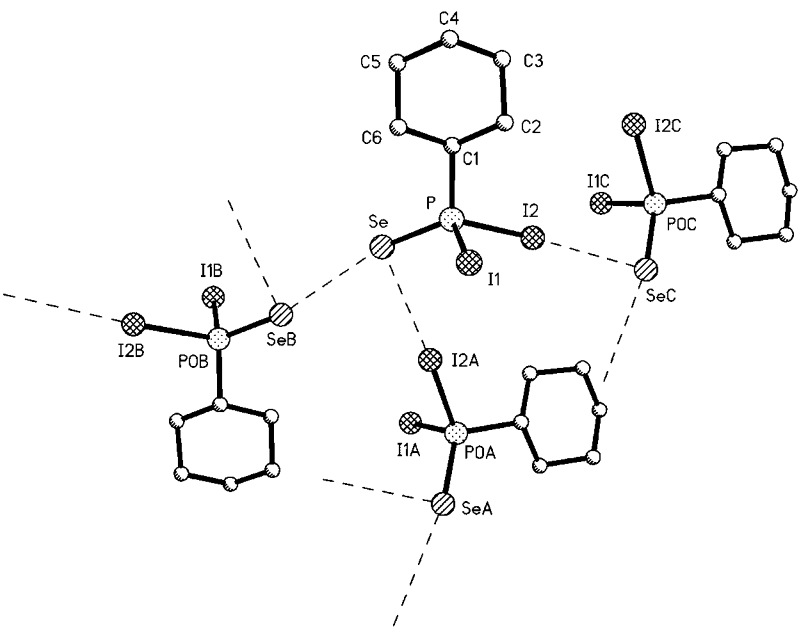

Figure 3. Molecular structure and secondary contacts of **2** (H atoms are omitted). Symmetry operators for equivalent atoms: $x-0.5$, $-y+1.5$, $-z$ (A); $-x+0.5$, $y+0.5$, z (B); $x+0.5$, $-y+1.5$, $-z$ (C).

however, in the case of **1** and **2** these interactions do not lead to base-pair-like dimers, but to chains. If the factor preventing dimers in solid **1** and **2** were unfavourable steric interactions between linearly coordinated acceptor iodine atoms of two adjacent L-shaped moieties, relief from this kind of strain might be provided by increasing the distance between the two donor–acceptor systems. Such an increase of distance should be achieved by inserting iodine molecules between two molecules of **1**. From the solid-state structures of iodine[22] and of the dimeric adduct of Ph_2Se_2 with I_2[23] it is known that I_2 molcules may act as both acceptor and donor at the same time: when one iodine atom behaves as electrophile, the donor properties of the other iodine atom become more pronounced.

The structure of the iodine adduct **3** can to a first approximation be described as a molecular 1:1 complex of the iodophosphane selenide **1** donor with iodine as acceptor. Compared with tBu$_3$PSe–I–I, the Se–I bond length within the monomeric unit of **3** is slightly longer and the I–I bond length is slightly shorter, that is, **1** is a somewhat weaker donor than tBu$_3$PSe[13] towards molecular iodine and should be compared with Ph_3PSe[14] (Table 1, p. 388). However, the monomeric units of **3** exhibit secondary I⋯I contacts [d(I1–I3′) 370.32(11) pm; symmetry operator: $-x+1$, $-y+1$, $-z$] that lead to the formation of dimeric units, which can alternatively be regarded as two molecules of **1** bridged by two molecules of molecular iodine (Figure 5, p. 388). In this respect, the resulting ten-membered ring of 2**1** and 2I_2 molecules, all acting as donors *and* as acceptors, shows a coordination pattern that is very similar to that of the dimeric adduct of Ph_2Se_2 with I_2.[23]

Between the ten-membered cyclic dimers, additional PSe⋯SeP contacts (382.9(2) pm, resembling those in **1** and **2**) and further I⋯I contacts [d(I3-I3′) 379.83(14) pm; symmetry operator: $-x+2$, $-y+1$, $-z$] lead to a layer structure through the base-pair-like dimers (Figure 6, p. 388).

Conclusion

Addition of selenium to alkyl(iodo)phosphanes R_nPI_{3-n} led to the isolation of the first iodophosphane selenides $R_nP({=}Se)I_{3-n}$ (**1**: R = tBu, $n=2$; and **2**: R = c-Hex, $n=1$) and the determination of their structures. Increasing the number of iodine atoms bonded to phosphorus (at the expense of alkyl groups) from one to two leads to a slight decrease of the P=Se bond length. Solid **1** and **2** exhibit intermolecular P=Se(donor) →I–P(acceptor) [$n\rightarrow\sigma^*$] interactions leading to infinite chains. Addition of iodine to **1** can be understood as insertion of an iodine molecule into such a donor–acceptor system, leading to Se(donor) →I–I →I–P-(acceptor) brigding. From two such bridges, a novel soft–soft base pair (dimeric **3**) is built up. Becoming two-coordinate by

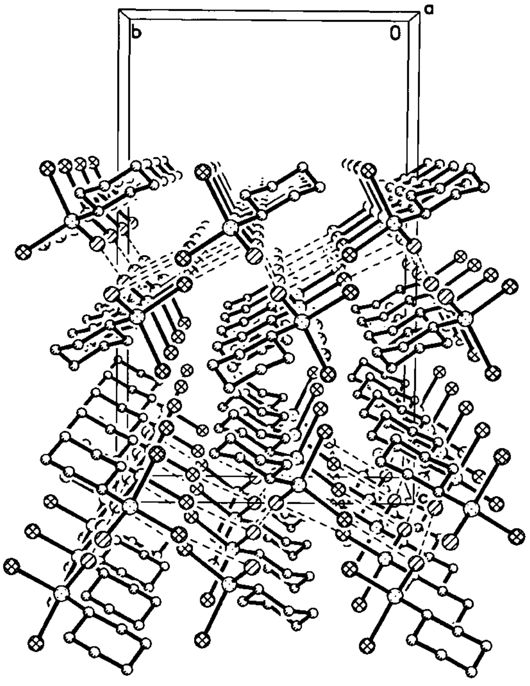

Figure 4. Packing diagram of **2**.

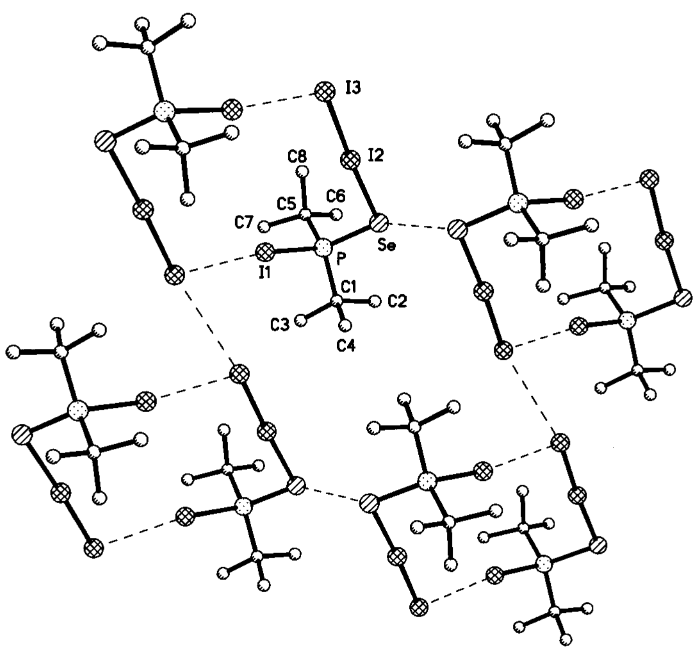

Figure 5. Molecular structure and secondary contacts of **3** (H atoms are omitted).

Table 1. Selected bond lengths and secondary contacts (< 400 pm) of compounds with C–P–Se–I moieties.

	d(P–Se)	d(P–I)	d(I–I)	d(Se–I)	d(Se–Se)
tBu$_2$P(Se)I (**1**)	210.4(2)	245.35(14)		369.04(9)	
	212.1(2)	244.6(2)		384.38(9)	359.4(2)
c-HexP(Se)I$_2$ (**2**)	209.2(2)	244.3(2)		347.59(8)	361.23(14)
		243.9(2)			
tBu$_2$P(SeI–I)I (**3**)	217.3(2)	243.1(2)	287.83(9)	278.19(11)	382.9(2)
			379.83(14)		
			370.32(11)		
tBu$_3$PSeI–I[13]	219.50(10)		291.44(8)	276.02(8)	352.70(12)
[(tBu$_3$PSe)$_2$I]$^+$[I$_3$]$^-$[13]	219.39(11)		291.42(10)	276.51(11)	
Ph$_3$PSeI–I[14]	215.6(4)		288.1(2)	280.3(3)	

weak P=Se → I interactions, selenium atoms of **1** and **2** tend to exhibit further weak P=Se ··· Se=P interactions that link the base-pair dimers of **3** and cross-link the chains of **1** and **2.** In compound **1**, the Se ··· Se interaction is associated with slight elongation of the participating P=Se bonds. This type of Se ··· Se interaction, which is not observed in ordinary phosphane selenides, indicates a certain electrophilicity of two-coordinate selenium atoms bonded to phosphonium centres; it is also related to Se ··· Se interactions in trigonal selenium and in certain solid diselenides.[21, 24] For future molecular architecture with iodophosphane selenides, besides packing of the organic substituents, directed L-type P=Se → I–P and approximately linear P=Se ··· Se=P interactions should be taken into consideration.

Experimental Section

^{31}P NMR spectra were run on a Bruker AM 200 spectrometer (81.0 MHz) with CH$_2$Cl$_2$ as solvent, if not otherwise specified. J values are given in Hz. Melting points were determined on a Kofler hot-stage microscope. All values are uncorrected. Elemental analyses were carried out by the Analytisches Laboratorium des Instituts für Anorganische und Analytische Chemie, Technische Universität Braunschweig. Solvents were dried by distillation under nitrogen from the appropriate drying agent, glassware was flame-dried and cooled under a stream of nitrogen.

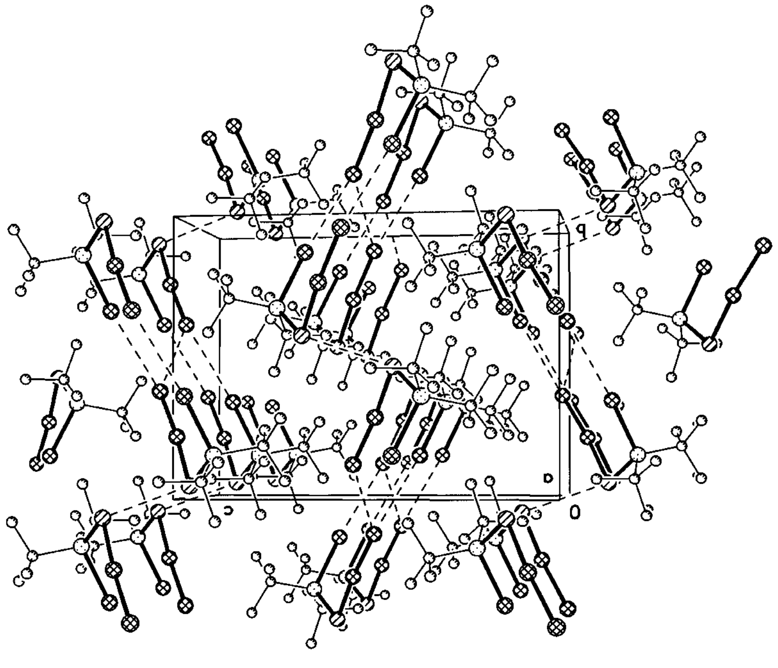

Figure 6. Packing diagram of **3**.

Di-*tert*-butyliodophosphane selenide (**1**): Di-*tert*-butylchlorophosphane (9.03 g 50 mmol) was added to a suspension of sodium iodide (14.9 g, 100 mmol) in toluene (50 mL). After stirring for 4 d the solid was removed by filtration, half of the solvent was evaporated under reduced pressure, and powdered grey selenium (3.20 g, 40 mmol) was added. After stirring for 3 d unconsumed selenium was removed by filtration, the solvent was evaporated under reduced pressure, and the yellowish residue was recrystallised from hexane. Compound **1** (11.45 g, 65 %) was isolated as yellow crystals. M.p. 83 °C; ^{31}P NMR: $\delta = 126$ (s, $^{1}J(^{77}\text{Se},^{31}\text{P}) = \pm 775$ Hz); $C_8H_{18}PSeI$ (351.07): calcd C 27.37, H 5.17; found C 29.11, H 5.28.

*Crystal structure determination of **1***:[24] $C_8H_{18}IPSe$, $M = 351.05$, $P2_1/c$, $a = 756.9(2)$, $b = 1375.7(4)$, $c = 2388.1(2)$ pm, $\beta = 90.334(10)°$, $V = 2.4864(9)$ nm^3, $Z = 8$, $\rho_{\text{calcd}} = 1.876$ Mg m^{-3}, $\mu = 5.583$ mm^{-1}, $T = 143$ K. A yellow prism ($0.75 \times 0.40 \times 0.30$ mm) was mounted in inert oil. 4517 reflections were measured (2Θ 6–50°, ω/Θ scans, $-9 < h < 9$, $-16 < k < 12$, $-28 < l < 28$; index ranges not complete, data are composed of independent set plus some Friedel pairs) with $Mo_{K\alpha}$ radiation (graphite monochromator) on a Stoe STADI-4 diffractometer. After absorption correction (psi scans, min. and max. transmission: 0.386, 0.646), 4372 reflections were unique ($R_{\text{int}} = 0.0279$) and 4368 were used for all calculations (program SHELXL-93[26]). The structure was solved by direct methods and refined anisotropically by full-matrix least squares on $|F|^2$. Rigid methyl groups were employed. The final $wR(F^2)$ was 0.0942, with conventional $R(F)$ 0.0396, for 211 parameters and 96 restraints (highest peak 1399, deepest hole -1556 e pm^{-3}).

***c*-Hexyldiiodophosphane selenide** (**2**): A bromochlorocyclo-*c*-hexylphosphane mixture (18.36 g, about 80 mmol, Cl:Br ratio about 2:1), which had been obtained by distillation from the reaction of *c*-hexylmagnesium bromide with phosphorus trichloride, was added to a suspension of sodium iodide (30 g, 200 mmol) in toluene (40 mL). The mixture was heated under reflux for 1 h. After further 18 h at room temperature, the solid was removed by filtration, and powdered grey selenium (6.40 g, 80 mmol) was added. After 1 d at room temperature, the mixture was heated to 90 °C for 30 min to complete the reaction. After filtration of the hot solution, slow cooling led to crystallisation of 18.23 g (about 50 %) **2** as red-orange prisms. M.p. 74 °C; ^{31}P NMR: $\delta = -79$ (s, $^{1}J(^{77}\text{Se},^{31}\text{P}) = \pm 755$ Hz); $C_6H_{11}PSeI_2$ (446.90): calcd C 16.13, H 2.48; found C 17.84, H 2.66.

*Crystal structure determination of **2***:[24] $C_6H_{11}I_2PSe$, $M = 446.88$, $Pbca$, $a = 812.3(2)$, $b = 1289.9(2)$, $c = 2143.7(3)$ pm, $V = 2.2460(6)$ nm^3, $Z = 8$, $\rho_{\text{calcd}} = 2.643$ Mg m^{-3}, $\mu = 8.925$ mm^{-1}, $T = 173$ K. A orange prism ($0.38 \times 0.28 \times 0.20$ mm) was mounted in inert oil. 3442 reflections were measured (2Θ 6–50°, ω scan, $-9 < h < 6$, $-15 < k < 13$, $-3 < l < 25$; index ranges not complete, data are composed of independent set plus some Friedel pairs) with $Mo_{K\alpha}$ radiation (graphite monochromator) on a Siemens P4 diffractometer. After absorption correction (psi scans, min. and max. transmission: 0.411, 0.953), 1976 reflections were unique ($R_{\text{int}} = 0.0373$) and were used for all calculations (program SHELXL-93[26]). The structure was solved by direct methods and refined anisotropically by full-matrix least squares on $|F|^2$. All hydrogen atoms were refined with a riding model. The final $wR(F^2)$ was 0.0731, with conventional $R(F)$ 0.0296, for 92 parameters and 48 restraints (highest peak 858, deepest hole -681 e pm^{-3}).

Di-*tert*-butyliodophosphane selenide-diiodine (**3**): Iodine (0.76 g, 3.0 mmol) was added to a solution of **1** (1.20 g, 3.4 mmol) in toluene (10 mL). Stirring was continued until all iodine had dissolved. Subsequently 10 mL of hexane were carefully added and allowed to diffuse into the toluene solution. This led to the separation of black-brown crystals of **3** (1.45 g, 80 %). M.p. 96 °C (decomp); ^{31}P NMR (CH_2Cl_2): $\delta = 117$ (s, $^{1}J(^{77}\text{Se},^{31}\text{P}) = \pm 696$ Hz), ^{31}P NMR (C_6H_6): $\delta = 129$ (s, $^{1}J(^{77}\text{Se},^{31}\text{P}) = \pm 600$ Hz); $C_8H_{18}PSeI_3$ (604.88): calcd C 15.89, H 3.00; found C 15.23, H 2.83.

*Crystal structure determination of **3***:[24] $C_8H_{18}I_3PSe$, $M = 604.85$, $P2_1/c$, $a = 926.6(2)$, $b = 1132.8(3)$, $c = 1512.3(3)$ pm, $\beta = 91.165(8)°$, $V = 1.5870(6)$ nm^3, $Z = 4$, $\rho_{\text{calcd}} = 2.532$ Mg m^{-3}, $\mu = 8.271$ mm^{-1}, $T = 173$ K. A brown plate ($0.75 \times 0.38 \times 0.03$ mm) was mounted in inert oil. 4022 reflections were measured (2Θ 6–55°, ω scans, $-11 < h < 12$, $-14 < k < 11$, $-19 < l < 19$; index ranges not complete, data are composed of independent set plus some Friedel pairs) with $Mo_{K\alpha}$ radiation (graphite monochromator) on a Siemens P4 diffractometer. After absorption correction (psi scans, min. and max. transmission: 0.313, 0.818), 3384 reflections were unique ($R_{\text{int}} = 0.0319$) and 3379 reflections were used for all calculations (program SHELXL-93[26]). The structure was solved by direct methods and refined anisotropically by full-matrix least squares on $|F|^2$. Rigid methyl groups were employed. The final $wR(F^2)$ was 0.1167, with conventional $R(F)$ 0.0426, for 124 parameters (highest peak 1633, deepest hole -1626 e pm^{-3}).

Acknowledgements

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[24] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101426. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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