Sterically crowded *peri*-substituted naphthalene phosphines and their P^V derivatives

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Supporting Information Available

X-ray crystallographic files for **1**, **2**, **nO**, **nS**, **nSe** (**n**= 1-3).

Keywords: naphthalene, *peri*-substitution, intramolecular, chalcogen, phosphorus, X-Ray Structure, oxidation, DFT

INDEX ENTRY

Steric crowding whilst giving quasi linear E...P-C fragments does not result in 3c-4e bonds but calculations suggest these molecules are ideal precursors for radicals.

Abstract

Three sterically crowded *peri*-substituted naphthalene phosphines Nap[PPh₂][ER] (Nap = naphthalene-1,8-diyl; ER = SEt, SPh, SePh) **1-3** containing phosphorus and chalcogen functional groups at the *peri*-positions have been prepared. Each phosphine reacts to form a complete series of P^V chalcogenides Nap[P(E')(Ph₂)(ER)] (E' = O, S, Se). The novel compounds were fully characterised by X-ray crystallography and multinuclear NMR, IR and MS. X-ray data for **1**, **2**, **nO**, **nS**, **nSe** (**n** = **1-3**) are compared. Eleven molecular structures have been analysed by naphthalene ring torsions, *peri*-atom displacement, splay angle magnitude, X...E interactions, aromatic ring orientations and quasi-linear arrangements. An increase in the congestion of the *peri*-region following the introduction of heavy chalcogen atoms is accompanied by a general increase in naphthalene distortion. P...E distances increase for molecules containing bulkier atoms at the *peri*-positions and also when larger chalcogen atoms are bound to phosphorus. The chalcogenides adopt similar conformations containing a quasi-linear E...P-C fragment, except for **3O** which displays a twist-axial-twist conformation resulting in the formation of a linear O...Se-C alignment. *Ab initio* MO calculations performed on **2O**, **3O**, **3S** and **3Se** reveal Wiberg bond index values of 0.02-0.04 indicating only minor non-bonded interactions however, calculations on radical cations of **3O**, **3S** and **3Se** reveal increased values [0.14-0.19].

Introduction

Peri-substituted naphthalenes incorporating large heteroatoms, confined in close proximity with separations shorter than the sum of van der Waals radii, have received great attention.^[1] Un-substituted ('ideal') naphthalene is known to be rigidly planar with unequal bond lengths and bond angles.^[2] The *peri*-carbon atoms are separated by a distance of 2.44 Å,^[2] sufficient to accommodate two hydrogen atoms but it is reasonable to expect that with larger substituents occupying the *peri*-positions there will be considerable steric hindrance.^[3] Repulsive steric effects caused by the crowding of substituents can be overcome by attractive weak or strong intramolecular interactions, or by the deformation of the naphthalene skeleton away from 'ideal'.^[3,4] This gives rise to structurally distorted compounds with unusual bonding and geometry.^[3]

X-ray structural data has played a crucial role when analysing the extent of steric strain and the amount of distortion occurring in non-ideal naphthalenes and has helped to elucidate attractive effects between *peri*-atoms and verify the existence of weak intra- and intermolecular interactions.^[4] To quantify the extent of naphthalene distortion taking place in a given molecule, the naphthalene geometry is compared with that of 'ideal' or un-substituted naphthalene.^[2,5,6]

Steric strain operating between crowded *peri*-atoms can also be relieved by coordination of the bidentate ligand to a bridging metal center, forming a stable ring complex (chelate).^[7] Phosphines being neutral two electron donors are one of the most versatile ligands that can bind to late transition metals.^[8] The complexes they form are important in organic synthesis and have been shown to act as active homogeneous catalysts in reactions of industrial importance.^[9] The development of a novel class of 1,8-bisphosphine bidentate ligand utilising the rigid C₃-naphthalene backbone and positioning phosphino groups *peri*-substituted on the ring has received great attention over the last 30 years.^[10]

Extensive work has also been carried out on mixed donor phosphorus-nitrogen compounds.^[11] A leading topic of current research and one which has seen much controversy, concerns the possible occurrence of intramolecular dative bond formation leading to hypercoordination.^[11,12] Most of the pertinent work in this field has been investigated using 8-dimethylaminonaphth-1-yl (DAN) compounds where the nitrogen atom can donate a pair of electrons in the formation

of a coordination bond with acceptor heteroatoms such as Si or P.^[13] Upon bond formation the acceptor species finds itself with a greater than normal co-ordination number and is termed *hypercoordinate*.^[13]

Unlike bis-phosphines and DAN-phosphorus compounds, phosphorus-oxygen, phosphorus-sulfur and phosphorus-selenium *peri*-substituted naphthalenes have received limited attention in the literature. These exciting new phosphorus ligands provide good models with which to study naphthalene distortion, intramolecular interactions (including possible dative bonding and hypercoordination) and metal complexation. The difference in the electronic properties between the donor atoms of the new (P,O), (P,S) and (P,Se) systems means these compounds could also be of value as hemilabile ligands.^[14]

During our early studies of sterically crowded 1,8-disubstituted naphthalenes we investigated di-chalcogenide ligands^[15] and unusual phosphorus compounds.^[16] More recently we have reported the synthesis and structural study of mixed halogen-chalcogen^[5] and chalcogen-chalcogen^[6] systems and the preparation of a novel mixed donor phosphorus-oxygen ligand.^[17] A preliminary study of the coordination chemistry of a novel phosphorus-sulfur ligand **2** has also been presented.^[18]

Figure 1 Sterically crowded *peri*-substituted naphthalene phosphines **1-3** and their phosphorus(V) oxygen, sulfur and selenium derivatives **nO**, **nS**, **nSe** (**n** = **1-3**).

Here we report the synthesis and a comprehensive structural study of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine **2**,^[18] along with two analogous mixed phosphorus-chalcogen *peri*-substituted systems, (8-ethylsulfanylnaphth-1-yl)diphenylphosphine **1** and (8-phenylselanylnaphth-1-yl)diphenylphosphine **3**.^[19] **1-3** react to form complete series of monoxidised oxygen, sulfur and selenium derivatives and the synthesis and molecular study of these nine compounds is also presented (Figure 1).

Results and Discussion

Compounds **1-3** and their chalcogeno derivatives were synthesised and crystal structures were determined for **1**, **2**, **nO**, **nS** and **nSe** (**n** = **1-3**). All the derivatives were spectrally characterised by multinuclear NMR and IR spectroscopy and mass spectrometry and the homogeneity of the new compounds was, where possible, confirmed by microanalysis. ³¹P and ⁷⁷Se NMR spectroscopy data for all compounds is displayed in Table 1.

We have recently reported the synthesis of a series of 1-halo-8-(alkylchalcogeno)naphthalene derivatives **4-5** prepared from the stepwise halogen-lithium exchange reactions of analogous 1,8-dibromonaphthalene and 1,8-diiodonaphthalene.^[5] These compounds are ideal intermediates in the preparation of phosphorus-chalcogen *peri*-

substituted systems **1-3**. For their synthesis, the respective halogen-chalcogen compound was treated with a single equivalent of *n*-butyllithium in diethyl ether to afford the respective 1-lithio-8-(phenylchalcogeno)naphthalene precursor. Reaction with a single equivalent of chlorodiphenylphosphine, following standard reactions conditions,^[20] afforded the respective *peri*-substituted naphthalene phosphine **1-3** [**1** 11 %, 51 % based on the bromo and iodo starting material respectively, **2** 64 %, 74 %, **3** 40 %, 60 %] (Scheme 1).

Scheme 1 The preparation of (8-alkylchalcogenonaphth-1-yl)diphenylphosphines **1-3**.

1-3 were characterised by elemental analysis, infra red spectroscopy, ¹H, ¹³C and ³¹P NMR spectroscopy and mass spectrometry. **3** was analysed by ⁷⁷Se NMR spectroscopy. Similar chemical shifts were observed in the ³¹P NMR spectra of sulfur compounds **1** [δ_P = -5.24 ppm] and **2** [δ_P = -5.30 ppm]. ³¹P and ⁷⁷Se NMR spectroscopy for **3** was in accord with previous literature values [δ_P = -12.94 ppm (lit.,^[19] δ_P = -12.51 ppm); δ_{Se} = 439.6 ppm, $^4J(P,Se)$ = 391.0 Hz (lit.,^[19] δ_{Se} = 446.2 ppm, $^4J(P,Se)$ = 380.9 Hz)] (Table 1).

Phosphines **1-3** react to form a series of three phosphorus(V) chalcogenide derivatives. In each case, under atmospheric conditions, the three coordinate phosphorus atom is readily oxidised to four coordinate phosphine oxides **1O**, **2O** and **3O** (Scheme 2). Similarly, the treatment of **1-3** with stoichiometric amounts of sulfur and selenium powder under reflux, selectively affords the novel sulfides (**1S**, **2S**, **3S**) and selenides (**1Se**, **2Se**, **3Se**) respectively. Conversion of **1-3** to the respective P^V chalcogenide derivative was achieved in 100 % yield in each case, as seen by ¹H and ³¹P NMR.

Scheme 2 The preparation of the phosphorus(V) chalcogenide derivatives of **1-3**.

The P^V chalcogenides were characterised by elemental analysis, infra red spectroscopy, ¹H, ¹³C and ³¹P NMR spectroscopy and mass spectrometry. **1Se**, **2Se**, **3O**, **3S** and **3Se** were analysed by ⁷⁷Se NMR spectroscopy. Characterisation for **3O** was found to be in accord with the literature [δ_P = 37.99 ppm (lit.,^[19] δ_P = 37.47 ppm); δ_{Se} = 450.4 ppm (lit.,^[19] δ_{Se} = 457.9 ppm)].^[19]

A downfield shift was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the 4-coordinate phosphorus compounds compared to the chemical shifts of the three-coordinate phosphines **1-3**. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showed single peaks at comparable shifts for the oxides [$\delta_{\text{P}} = 36.34$ **1O**, 37.01 **2O**, 37.99 **3O**], sulfides [$\delta_{\text{P}} = 51.84$ **1S**, 52.52 **2S**, 51.01 **3Se**] and selenides [$\delta_{\text{P}} = 41.92$ **1Se**, 42.46 **2Se**, 40.50 **3Se**]. Expected 1J and 4J values for phosphorus-selenium coupling were observed in the spectra of **3Se** [$^1J(\text{P,Se}) = 715.3$ Hz, $^4J(\text{P,Se}) = 23.9$ Hz] though $^1J(\text{P,Se})$ coupling was not observed in the spectra of **1Se** or **2Se** and $^4J(\text{P,Se})$ coupling was not observed in the spectra of **3O** and **3S** (Table 1).

Single peaks in the ^{77}Se NMR spectra of **1Se**, **2Se** and **3O** displayed no $J(\text{Se,P})$ coupling. The ^{77}Se NMR spectrum for **3S** displayed a doublet at $\delta = 448.5$ ppm with a small value for $^4J(\text{Se,P})$ coupling [19.1 Hz]. Two sharp doublets were observed in the ^{77}Se NMR spectrum of **3Se** $\delta = 451.4$ ppm and $\delta = -162.8$ ppm, with 1J and 4J values for selenium-phosphorus coupling [$^1J(\text{Se,P}) = 715$ Hz, $^4J(\text{Se,P}) = 24$ Hz] (Table 1).

X-ray investigations

Compound **3** is an oil at room temperature though suitable single crystals were obtained for all other derivatives by diffusion of pentane into saturated solutions of the individual compound in dichloromethane. The molecular structures were analysed, although **2**^[18] and **3O**^[19] have been previously reported. Compound **1** crystallises with two nearly identical molecules in the asymmetric unit, all other compounds contain one molecule in the asymmetric unit. Selected interatomic distances, angles and torsion angles are listed in Table 2 and 3. Further crystallographic information can be found in Table 7 and the Supporting Information.

Figure 2 The crystal structure of (8-ethylsulfanylnaphth-1-yl)diphenylphosphine **1** showing two independent molecules in the asymmetric unit.

The molecular structures of **1** and **2** are shown in Figures 2 and 3 respectively. Overall, the degree of steric strain operating between the *peri*-atoms in S(ethyl) derivative **1** is notably reduced compared to the S(phenyl) analogue **2**. The displacement of the *peri*-atoms to opposite sides of the mean naphthalene plane occurs to a slightly unequal degree in the two independent molecules of **1** [-0.11 Å (0.05 Å), 0.16 Å (-0.03 Å)]. In compound **2** [0.007 Å, 0.13 Å]^[18] the phosphorus atom lies virtually on the naphthyl plane. Positive splay angles are observed for both compounds **1** [11.7° (11.4°)] and **2** [14.1°]^[18] but there is a notable increase in the splay of the P-C and S-C bonds in the S(phenyl) derivative to alleviate the greater “perispace crowding”.^[22]

Figure 3 The crystal structure of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine **2**.^[18]

The resulting geometry repels the P and S atoms to a greater non-bonded interatomic distance of 3.0330(7) Å in **2**^[18] compared with the S(ethyl) derivative **1** [2.9737(14) Å (2.9469(15) Å)]. The *peri*-gap in both cases is still 16-18 % shorter than the sum of their collective van der Waals radii. The naphthalene units for both derivatives show only minor deviations from planarity with maximum C-C-C-C central naphthalene ring torsion angles of *ca* 0-4°. **Repulsive forces acting between the P and S atoms are accompanied by C-C bond and C-C-C angle stretching in the naphthalene scaffold.** Bond lengths around C10, closer to the repulsive forces, are on average longer than those around C5 [average 1.45 Å and 1.42 Å respectively] and C(1)-C(10)-C(9) bond angles splay to a mean 127°, wider than the ‘ideal’ geometry observed for C(4)-C(5)-C(6) (average 119°).^[2] S-C [1.78-1.82 Å] and P-C [1.83-1.86 Å] bond lengths are within the usual ranges [1.77, 1.84 ± 0.05 Å respectively]^[23] in both cases.

The geometrical structures of compounds **1** and **2** can be described by the conformation and arrangement of the naphthyl ring and ethyl/phenyl groups, relative to the two C(ar)-P(1)-C(ar) planes and the C(ar)-S(1)-C(R) plane. This can be categorised from torsion angles θ and γ respectively (see Table 2). When θ and γ approach 90° the orientation is denoted axial and when the angles indicate a quasi-planar arrangement (close to 180°), they are termed equatorial.^[24] When angle θ is axial, the respective P-C_{Ph}/S-C_R bond lies perpendicular to the naphthyl plane whilst an equatorial conformation aligns the bond on or close to the plane. Based on the classification system presented by Nakanishi *et al.*,^[25] axial conformations of angle θ correspond to a type A structure and equatorial to type B. The twist conformation is thus type C.^[24,25] From the nomenclature reported by Nakanishi *et al.*,^[25] compounds **1** and **2** can thus be described as type BA-B and type BA-C-*c* (*c*-cis orientation of phenyl groups with respect to the naphthyl plane) respectively (Figure 4).^[25] One quasi-linear arrangement [S(1)⋯P(1)-C(11)] is observed in **2** with an angle of 174.5°, whilst two linear arrangements are observed in **1** [S(1)⋯P(1)-C(11), P(1)⋯S(1)-C(23)] with angles 163.3° (160.6°) and 161.1° (165.1°) respectively.

Figure 4 The orientation of the phenyl and ethyl groups, the type of structure and the quasi-linear arrangements of **1** and **2**.^[25]

The BA-C-c conformation in **2** places one of the P(phenyl) groups and the (S)phenyl group on the same side of the naphthyl plane and in close proximity (Figure 4).^[25] The mixed axial-twist conformation of the two phenyl rings [γ_1 92.6(11)°; γ_3 48.0(1)] results in no significant overlap and with a centroid-centroid distance of 4.32 Å, much higher than for known π - π stacking [3.3-3.8 Å],^[26] no π - π interactions are observed.

Figure 5 Comparison of the *peri*-distances of phosphines **1-3** and their P^V chalcogenides.

All non-hydrogen atoms are larger in size than a lone-pair of electrons, thus perhaps not surprisingly, an increase in steric strain is observed in chalcogenide derivatives **nO**, **nS** and **nSe** (**n** = **1-3**) when O, S and Se atoms crowd the *peri*-space instead of the lone-pair in phosphanyl compounds **1-3**. The heavy chalcogen atoms are accommodated by a greater deformation of the naphthalene geometry via an increase in-plane and out-of-plane distortions and a significant twisting of the naphthalene skeleton.

The degree of distortion is generally related to the size of the atoms residing in the *peri*-region. This is best observed by comparing the magnitude of the *peri*-distance parameter (Table 2 and 3, Figure 5). In each set of chalcogenide derivatives there is a marked lengthening of the *peri*-gap as larger atoms bind to phosphorus. The separation of the *peri*-atoms in the selenium compounds **3O**, **3S** and **3Se** is also notably larger compared with the derivatives of sulfur compounds **1** and **2** (Figure 5). P...E distances [3.12-3.28 Å] are less than the respective sum of van der Waals radii for the two *peri*-atoms [3.60-3.70 Å],^[21] in all cases this is between 87-90 % of the vdW sum. For derivatives of **1** and **2** this is an increase in the length of the *peri*-distance by 4-8 % upon the exchange of the phosphorus lone-pair for a chalcogen atom. These short non-bonded *peri*-distances indicate the possible existence of weak intramolecular interactions.^[27]

The increased congestion of the *peri*-space in the P^V chalcogenide derivatives is accompanied by a significantly larger displacement of the *peri*-atoms to opposite sides of the naphthalene best plane [0.40-0.74 Å] compared with phosphines **1** and **2** [0.01-0.16 Å] (Figure 16). Considerable repulsion of the P-C and E-C bonds is also evident, with positive splay angles [11.9-17.3°] helping to alleviate the “perispace crowding” (Figure 15).^[22] The aforementioned distortions are insufficient to overcome the steric strain occurring in the bay region and are thus supplemented by major deformations of the naphthalene geometry. C-C bonds and C-C-C angles are stretched whilst a buckling of the naphthalene skeleton away from planarity takes place. Bond lengths around C10, closer to the repulsion, are on average longer than those around C5 [average 1.44 Å and 1.42 Å respectively] and C(1)-C(10)-C(9) bond angles splay to a mean 127°, away from the ‘ideal’ geometry observed for C(4)-C(5)-C(6) (average 119°). Central naphthalene ring C-C-C-C torsion angles [4.3-11.6°] illustrate the extent and variation of twisting occurring in the naphthalene framework of the nine chalcogenide derivatives (Figure 6) which are notably less planar compared with the backbones of phosphines **1** and **2** [0.2-3.5°]. S-C [1.77-1.83 Å], Se-C [1.92-1.94 Å], P-C [1.80-1.84 Å], P=O [1.48-1.49 Å], P=S [1.96-1.97 Å] and P=Se [2.11-2.12 Å] bond lengths are within the usual ranges [1.82, 1.93, 1.84, 1.49, 1.95, 2.09 ±0.05 Å respectively]^[23] in all nine compounds. The P-C distances are slightly shortened on oxidation from P^{III} in **1** and **2** to P^V in the chalcogenide derivatives.

Figure 6 The least **3Se** and most **1S** distorted naphthalene units for the P^V chalcogenides.

The molecular structures of **1O**, **1S** and **1Se** are shown in Figure 7. As expected, a general increase in the steric strain is observed when larger atoms occupy the *peri*-region. Non-covalent P...S *peri*-distances [3.1349(13) Å **1O**, 3.2083(14) Å **1S**, 3.2283(19) Å **1Se**] are significantly longer than the separation in **1** [2.9737(14) Å (2.9469(15) Å)], and lengthen with the increasing bulk of atoms bound to phosphorus. Nonetheless all distances are shorter than the sum of van der Waals radii for phosphorus and sulfur by 0.37-0.47 Å.

The displacement of the *peri*-atoms to opposite sides of the best naphthalene plane is significantly greater in the chalcogenides [0.40-0.74 Å] compared with **1** [0.03-0.16 Å] with the greatest out-of-plane distortion observed in **1S** [-0.62 Å, 0.74 Å]. Positive splay angles are comparable for **1O** [13.1°] and **1Se** [13.7°] implying the P-C and S-C bonds are tilted apart to a similar extent in order to minimise the steric repulsion acting in the *peri*-region. The splay angle of **1S** [11.9°] is notably smaller and similar to phosphine **1** [11.7°]. The naphthalene units of **1O** and **1Se** also show similar deviations from planarity with maximum C-C-C-C torsion angles in the range 5-6°. A major distortion of the naphthalene scaffold is observed in **1S** with the deviation from planarity more pronounced and larger than any of the chalcogenides reported here; the maximum C-C-C-C torsion angle is 11.6 for C(6)-C(5)-C(10)-C(1) (Figure 6).

Figure 7 The crystal structures of **1O**, **1S** and **1Se** showing the alignment of the S(ethyl) groups and CH- π interactions.

As with the structures of compounds **1** and **2**, the conformation and arrangement of the naphthyl rings and ethyl and phenyl groups for the P^V chalcogenides can be categorised relative to the two C(ar)-P(1)-C(ar) planes and the C(ar)-S(1)-C(R) plane (from torsion angles θ and γ respectively; see Table 5). The torsion angle conformations can be related to the A, B, C type classification system presented by Nakanishi *et al.*,^[25] which can be used to describe the geometry of the molecules [angle θ : axial = type A, equatorial = type B, twist = type C].^[24,25] Torsion angles θ , show the naphthalene units in **1O**, **1S** and **1Se** display the same equatorial/axial/axial conformation with respect to the C(ar)-P(1)-C(ar) and C(ar)-S(1)-C(R) planes. This arrangement corresponds to a BA-A-*c* type arrangement (Figure 8);^[24,25] one P-C_{Ph} bond and the S-C_{Et} bond align perpendicular to and on the same side of the naphthyl plane and the remaining P-C_{Ph} bond adopts a position close to/on the plane.^[25] One quasi-linear S...P-C_{Ph} interaction is observed in each compound with angles approaching linearity [174.3°, 175.4°, 170.9°] (Figure 8).

The BA-A-*c* conformation places one phenyl group and the ethyl group attached to S(1) on the same side of the naphthyl plane. The chalcogen bonded to P(1) is subsequently forced to reside in the *peri*-region and in close contact with S(1) (Figure 7). In all cases the chalcogen atom lies below the naphthyl plane, with distances as expected increasing from the plane with the increasing size of the atom [-1.7200(51) Å **1O**, -2.019(5) Å **1S**, -2.3022(69) Å **1Se**]. Non-covalent S(1)...E(2) separations [3.033(2) Å **1O**, 3.2951(15) Å **1S**, 3.43(1) Å **1Se**] are shorter than the sum of van der Waals radii for the two interacting atoms by 0.27-0.31 Å and close enough to suggest possible intramolecular interaction.^[27]

A large number of organosulfur compounds reported contain conformations considerably influenced by intramolecular sulfur-nucleophile interactions;^[27a] such as non-bonded S...O, S...N, S...S and S... π interactions. In these molecules the S...nucleophile distance is significantly shorter than the sum of the sulfur and nucleophile van der Waals radii.^[27] While the S(1)...E(2) distances **1O**, **1S** and **1Se** are in the range for intramolecular interaction, rotating around the C(1)-P(1)

bond would bring the two interacting moieties in closer contact and produce shorter separations in line with known non-bonded interaction values.^[27] If an S(1)⋯E(2) interaction takes place it is likely to be weak and not the fundamental influence on the geometry of the molecules.

Although all three chalcogenides adopt the BA-A-c conformation, torsion angles γ , show that the phenyl and ethyl moieties arranged *cis* to the naphthyl plane adopt different orientations and therefore interact slightly differently.^[24,25] In **1O** and **1Se** the ethyl group aligns with an axial conformation [γ_3 79.1(1)°; γ_3 -67.0(1) °] where the C(23)-C(24) bond points directly away from the closest phenyl ring (Figure 7). In both compounds the C(23)⋯centroid distance is small enough to suggest possible CH- π interaction [**1O** C(23)⋯Cg(17-22) 3.644(1) Å; **1Se** C(23)⋯Cg(17-23) 3.578(1) Å].^[28] These are weak non-covalent attractive ‘hydrogen bond type’ interactions between soft acids (CH) and soft bases (π -system) which have previously been shown to be important in self-assembly and molecular recognition processes, in determining conformations, selectivities of reactions and crystal structures.^[28] The ethyl group in **1S** aligns with an equatorial conformation [γ_3 179.4(1)°], the C(23)-C(24) bond lies parallel to the phenyl ring and close enough to envisage CH- π interaction [**1S** C(23)⋯Cg(17-23) 4.041(1) Å, C(24)⋯Cg(17-23) 3.790(1) Å] (Figure 7).^[28] CH- π Hydrogen bond distances are displayed in Table 6.

Figure 8 The orientation of the phenyl and ethyl groups, the type of structure and the quasi-linear arrangements of **nO**, **nS** and **nSe** (**n** = 1-3).^[25]

The molecular structures of **2O**, **2S** and **2Se** are shown in Figure 9. As expected, P and S *peri*-atoms are forced to lie further apart in the chalcogenides compared to phosphine **2**, with longer intramolecular *peri*-distances accommodating the greater steric congestion of the *peri*-region. Oxide **2O** and sulfide **2S** have lengths comparable to their S(ethyl) counterparts whilst the separation of the *peri*-atoms in selenide **2Se** is shorter than expected and similar in size to the sulfide compounds [2 3.0339(13) Å, **2O** 3.1489(9) Å, **2S** 3.1909(1) Å, **2Se** 3.190(1) Å]. The displacement of the *peri*-atoms to opposite sides of the least squares naphthalene plane is comparable throughout the series of compounds [0.43–0.63 Å] and more pronounced than phosphine **2** [0.01 Å, 0.13 Å]. Corresponding splay angles 13.7° and 14.1° implies distortion of the bay area geometry is also similar for **2S** and **2Se** whilst a smaller but still positive splay angle is observed in **2O** [12.4°]. **2O** exhibits the largest amount of buckling within the naphthalene unit with central naphthalene ring C-C-C-C torsion angles in the range 8–10°. The naphthalene scaffolds see a smaller deviation from planarity in **2S** and **2Se** [*ca* 5–7°].

Figure 9 The crystal structures of phosphorus(V) chalcogenides **2O**, **2S** and **2Se**.

The S(phenyl) chalcogenides display similar BA-A-*c* type structures to the S(ethyl) derivatives with the naphthalene units adopting equatorial/axial/axial conformations with respect to the C(ar)-P(1)-C(ar) and C(ar)-S(1)-C(R) planes (Figure 8).^[24,25] One quasi-linear S...P-C_{Ph} interaction is observed in each compound with angles 177.6°, 174.0°, 173.8° (Figure 8). The *cis*-orientation of phenyl groups again forces the extra chalcogen atom to reside in the *peri*-region and in close contact to S(1); in all cases lying above the naphthyl plane with distances from the plane increasing with the increasing size of the atom [1.6231(46) Å **2O**, 2.1977(43) Å **2S**, 2.3457(51) Å **2Se**] (Figure 9). Non-bonded interatomic S(1)···E(2) distances [2.9612(17) Å **2O**, 3.3142(11) Å **2S**, 3.3974(10) Å **2Se**] are comparable to those found for the S(ethyl) derivatives and shorter than the sum of van der Waals radii for the two interacting atoms by 9–12 %.^[21] This once again suggests the non-bonded distance is close enough for possible weak intramolecular interactions to occur.^[27]

Figure 10 The crystal structures of **2O**, **2S** and **2Se** showing the orientation and overlap of the phenyl rings.

Torsion angles (γ) show that the phenyl rings arranged *cis* to the naphthyl plane adopt equatorial conformations in all three compounds and thus overlap in a slipped packing arrangement.^[26] Variations in the twist of the phenyl groups however are observed. A greater overlap of the rings is found in **2S** [γ_1 160.9(1)°, γ_3 179.5(1)°] and **2Se** [γ_2 161.4(1)°, γ_3 178.6(1)°] which adopt a parallel alignment similar to the face-to-face offset arrangement (Figure 10).^[24,26] The phenyl rings in **2O** [γ_1 154.9(1)°, γ_3 170.0(1)°] twist in towards one another and thus do not align parallel (Figure 10). In all three compounds the distances between the two interacting centroids is longer than the range for typical centroid-centroid π -stacking [3.3–3.8 Å]^[26] and no π - π stacking is envisaged [Cg(17–22)⋯Cg(23–28): **2O** 4.397(1) Å; **2S** 3.955(1) Å, **2Se** 3.995(1) Å].^[26]

The molecular structures of **3O**, **3S** and **3Se** are shown in Figure 11. With the substitution of the larger Se(phenyl) moiety at the C(9) *peri*-position, congestion of the *peri*-region would be expected to increase compared with chalcogenides containing the S(ethyl) and the S(phenyl) functional groups. Greater deformation of the naphthalene geometry is observed in **3O**, **3S** and **3Se** compared with analogous sulfur compounds to alleviate the extra steric strain. An increase in the distortion is also observed within the group as the size of chalcogen bonded to P(1) increases.

Figure 11 The crystal structures of phosphorus(V) chalcogenides **3O**, **3S** and **3Se** showing the difference between the CA-C and BA-A type structures and overlap of phenyl rings.

Phosphorus and selenium functional groups lie in close proximity to each other, with non-bonded *peri*-distances [3.215(2) Å **3O**; 3.2803(8) Å **3S**; 3.278(2) Å **3Se**] showing a general increase with the increasing size of the chalcogen at P(1). The *peri*-separation in selenide **3Se**, like its sulfur analogue **2Se**, is shorter than expected and similar in size to the distance of sulfide **3S**. Unsurprisingly, the *peri*-gaps observed for the Se(phenyl) compounds are notably larger than those for analogous chalcogenides containing sulfur functional groups at the C(9) position. Nonetheless all P⋯Se separations are shorter than the sum of van der Waals radii for phosphorus and selenium [3.70 Å]^[21] by 0.42–0.49 Å.

A similar displacement of the *peri*-atoms to either side of the naphthalene least-squares plane is observed throughout the series of Se(phenyl) chalcogenides [0.40–0.60 Å] and comparable to the out-of-plane distortion for the S(phenyl) analogues [0.43–0.63 Å]. Distortion within the naphthyl plane however, is much more pronounced in the selenium compounds and increases significantly from oxide **3O** to selenide **3Se**. Large and positive splay angles of the magnitude 15.5° **3O**, 16.8° **3S**, 17.3° **3Se**, illustrate a major tilt of the *peri*-bonds in opposite directions to reduce the greater steric repulsion acting between the heavy atoms in the bay region. The displacement of the phosphorus and selenium substituents within and out of the plane is accompanied by a distortion of the usually planar and rigid C₁₀-unit by a twist into a non-planar conformation. The deformation of the naphthalene skeleton in selenium compounds **3O**, **3S** and **3Se**

corresponds to the distortion occurring in the S(phenyl) chalcogenides **2O**, **2S** and **2Se**. Oxide **3O** shows the greatest deviation from planarity with central naphthalene ring torsion angles of magnitude 6-10°, whilst a smaller contortion of the scaffold is observed for **3S** and **3Se** [*ca* 4-6°]. In fact the naphthalene unit of **3Se** is the most planar of the chalcogenides reported here (Figure 6).

3S and **3Se** adopt the same BA-A-*c* type structure as the S(ethyl) and S(phenyl) chalcogenides where the conformation of the naphthalene unit is equatorial/axial/axial with respect to the C(ar)-P(1)-C(ar) and C(ar)-S(1)-C(R) planes (Figure 8, 13).^[24,25] One quasi-linear Se...P-C_{Ph} interaction exists in each compound with angles 173.5° and 172.9° respectively (Figure 8). Oxide **3O** adopts a similar but notably different structural arrangement to the other chalcogenides reported here (Figure 11). Relative to the C(ar)-P(1)-C(ar) and C(ar)-S(1)-C(R) planes, the naphthalene unit now assumes a twist/axial/twist arrangement [θ_1 146.5(1)°, θ_2 -99.7(1)°, θ_3 134.5(1)°] which corresponds to a CA-C type structure (Figure 8).^[24,25] The P-C_{Ph} bond and the Se-C_{Ph} bond which align along the naphthyl plane and perpendicular to the plane respectively in **3S** and **3Se** are rotated in **3O** and lie at an intermediate angle [~45°] (Figure 11). With this conformation, the linearity of the Se...P-C_{Ph} interaction in **3O** is reduced [167.9°] however, the twist conformation of the Se(phenyl) moiety promotes the formation of a quasi-linear O...Se-C_{Ph} arrangement [178.1°] (Figure 8).^[24,25]

Both the BA-A and CA-C type structures position the chalcogen atom bonded to P(1) in the *peri*-region and in close contact with Se(1). E(2)...Se(1) non-bonded interatomic distances [2.770(3) Å **3O**; 3.3490(7) Å **3S**; 3.4217(8) Å **3Se**] increase across the series with separations shorter than the sum of van der Waals radii of the interacting atoms in all cases.^[21] The O(1)...Se(1) contact in **3O** is notably close with a distance 19 % shorter than the vdW sum of oxygen and selenium. This distance is shorter than expected when compared with the E(2)...E(1) distances observed in the remaining chalcogenides reported here which contain relatively longer distances (7-11% of the vdW sum). These distances are short enough for the existence of non-bonded weak intramolecular interactions to occur.^[27]

The parallel alignment of phenyl groups arranged *cis* to the naphthyl plane in **3S** and **3Se** is confirmed by torsion angles (γ) which show both rings adopt equatorial conformations [**3S** γ_2 164.2(1)°, γ_3 -176.5(1)°; **3Se** γ_2 -20.4(1)°, γ_3 -2.2(1)°]. Although the rings adopt a parallel displacement, the distance between the two interacting centroids is longer than the range for typical centroid-centroid π -interaction [3.3-3.8 Å]^[26] in both cases so no π - π stacking is envisaged [Cg(17-22)...Cg(23-28): **3S** 4.034(1) Å, **3Se** 4.075(1) Å] (Figure 11).

Compound **3** and its oxide **3O**, were previously reported by Nakanishi *et al* whilst studying non-bonded lone-pair interactions in *peri*-substituted naphthalenes.^[19] Quantum-chemical calculations performed on optimised structures of models **A** and **B** (Figure 12) were used to reproduce the structure around P and Se in **3O** and investigate the role of lone-pair orbitals in the non-bonded P...Se interaction on the structure of the molecule. Based on their MO calculations the 3c-4e type interaction was reported to induce a linear O...Se-H alignment in the models, and the structure of **3O** with its linear O...Se-C arrangement was therefore reported to originate from the 3c-4e type interaction of the linear O...Se-C atoms.^[19]

Figure 12 *Ab initio* MO calculations were performed by Nakanishi *et al* on models A and B.^[19]

To try and assess the possibility of direct P...Se and E(2)...Se bonding interactions that would indicate an onset of 3c-4e bonding, density functional theory computations were performed for derivatives **2O**, **3O**, **3S** and **3Se** at the B3LYP/6-31+G* level. For each compound both linear type arrangements [E(2)...E(1)-C and E(1)...P-C] were evaluated (Figure 13). The Wiberg bond index (WBI),^[29] which measures the covalent bond order, was calculated for each linear arrangement, both for the structures found in the solid and for the minima resulting from full geometry optimisations in the gas phase. WBI values of 0.02-0.04 are obtained throughout, indicating a very minor interaction between non-bonded atoms in these compounds. For comparison, the fully covalent S-S single bond in naphtho(1,8-cd)(1,2-dithiole) has a WBI of 0.99 at the same level. For **3S** and **3Se**, the aromatic π -stacking between phenyl groups at P and the chalcogen that is found in the solid is lost upon optimisation (due to the missing dispersion interaction at that level), but this affects the computed WBIs only slightly. When the "equatorial" Ph group on Se(1) in 1,8-bis(phenylselanyl)naphthalene is replaced with Br, Se-Se distances as short as 2.516 Å have been observed.^[30] A B3LYP computation for the latter molecule from the X-ray structure affords a WBI of 0.55, suggesting a large extent of 3c-4e bonding in this case. Judging from the refined phosphorus-chalcogen and chalcogen-chalcogen distances, none of the species in the present study comes close to such a bonding situation.

Figure 13 DFT calculations performed on chalcogenides **2O**, **3O**, **3S** and **3Se** and their radical cations (B3LYP/6-31+G* level).

Further calculations were performed on the radical cations of chalcogenides **2O**, **3O**, **3S**, and **3Se** (Figure 13). Whilst the Wiberg bond index values for the phosphorus-chalcogen interactions showed little change, the values for the E(2)...Se(1) interaction in the radical cations of selenium compounds **3O**, **3S**, and **3Se** increased to 0.14-0.19 indicating a greater interaction compared to the neutral species. This increase is a consequence of the nature of the HOMO in the

latter species, which consists essentially of p-orbitals on E(2) and Se(1) in an antibonding combination (see Figure 1 for **3Se**). As MOs with the corresponding bonding combination are lower in energy, removal of an electron from the HOMO increases the net bond order between these atoms. No similar increase was observed for the O(1)⋯S(1) interaction in **2O** upon oxidation.

For each of the radical cations the adiabatic and vertical ionisation potentials were calculated. The values of 6.84-6.20 and 7.05-6.70 eV, respectively (Figure 13), are comparable to those of the known compound naphtho[1,8-*cd*]-1,2-dithiole, which has adiabatic and vertical IP values of 7.82 and 8.03 eV, respectively, computed at the same level. From previous unpublished work from the Woollins group it was shown that naphtho[1,8-*cd*]-1,2-dithiole can undergo one-electron oxidation and forms crystals of $[\text{C}_{10}\text{H}_6\text{S}_2^+]_3[\text{BF}_4^-]_3$ using electrocrystallisation techniques.^[31] Judging from the computed IP values, the four chalcogenides **2O**, **3O**, **3S** and **3Se**, could exhibit similar electrochemical reactivity to naphtho[1,8-*cd*]-1,2-dithiole and may be able to form charge transfer compounds.

Figure 14 Selected molecular orbitals of the neutral and radical cation species of **3Se** (B3LYP level) showing bonding (bottom) and antibonding (top) combinations of p-orbitals on the Se atoms.

Conclusion

Phosphorus-chalcogen naphthalenes **1-3** have been prepared via standard halogen-lithium exchange reactions of 1-halo-8-(alkylchalcogeno)naphthalene derivatives,^[5] followed by treatment with dichlorodiphenylphosphine. **1-3** react to form complete series of P^V chalcogenides which exhibit greater steric crowding due to the added presence of the extra chalcogen atom in the *peri*-region and by inference a greater deformation of the naphthalene geometry. The presence of quasi-linear three body fragments in the chalcogenides [O...Se-C_{Ph}/E...P-C_{Ph}: 171-178°] accompanied by O...Se and E...P distances shorter than the sum of van der Waals radii suggests attractive 3c-4e interactions could be operating. To try and assess the possibility of direct O...Se/E...P bonding interactions that would indicate an onset of 3c-4e bonding in the chalcogenides, density functional theory computations were performed for derivatives **2O**, **3O**, **3S** and **3Se**. Judging from the Wiberg bond index (WBI)^[29] values of 0.02-0.04, none of the species in the present study comes close to such a bonding situation and instead steric affects dominate the overall geometry of the molecules.

We have recently reported a preliminary study of the coordination chemistry of the novel phosphorus-sulfur ligand **2**^[18] showing the potential of these ligands towards specific metal coordination. The difference in electronic properties between donor atoms (P,S) and (P,Se) gives these compounds added value as hemilabile ligands^[14] and the presence of the extra chalcogen atom in the chalcogenides adds the potential to form extended 7-membered chelate complexes upon coordination with transition metals.^[32]

Experimental Section

All experiments were carried out under an oxygen- and moisture-free nitrogen atmosphere using standard Schlenk techniques and glassware. Reagents were obtained from commercial sources and used as received. Dry solvents were collected from a MBraun solvent system. 1-halo-8-(phenylchalcogeno)naphthalene derivatives^[5] were prepared from 1,8-dibromonaphthalene **11**^[33] and 1,8-diiodonaphthalene **12**.^[34] Elemental analyses were performed by the University of St. Andrews School of Chemistry Microanalysis Service. Infra-red spectra were recorded as KBr discs in the range 4000-300 cm⁻¹ on a Perkin-Elmer System 2000 Fourier transform spectrometer. ¹H and ¹³C NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with δ (H) and δ (C) referenced to external tetramethylsilane. ³¹P and ⁷⁷Se NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with δ (P) and δ (Se) referenced to external phosphoric acid and dimethylselenide respectively. Assignments of ¹³C and ¹H NMR spectra were made with the help of H-H COSY and HSQC experiments. All measurements were performed at 25 °C. All values reported for NMR spectroscopy are in parts per million (ppm). Coupling constants (*J*) are given in Hertz (Hz). Mass spectrometry was performed by the University of St. Andrews Mass Spectrometry Service. Electron impact mass spectrometry (EIMS) and Chemical Ionisation Mass Spectrometry (CIMS) was carried out on a Micromass GCT orthogonal acceleration time of flight mass spectrometer. Electrospray Mass Spectrometry (ESMS) was carried out on a Micromass LCT orthogonal accelerator time of flight mass spectrometer.

(8-ethylsulfanylnaphth-1-yl)diphenylphosphine Nap[PPh₂][SEt] (1) from (4Br): A solution of 2.5 M *n*-butyllithium in hexane (0.5 mL, 1.1 mmol) was transferred dropwise to a freshly prepared solution of 1-bromo-8-(ethylsulfanyl)naphthalene (0.3 g, 1.1 mmol) in diethyl ether (10 mL) at -10-0°C (salted ice bath). The bright mixture was stirred for 2 h at this temperature, after which chlorodiphenylphosphine (0.24 g, 0.2 mL, 1.1 mmol) was added slowly. The addition coloured the reaction mixture first bright yellow and finally a pale yellow. Stirring was continued for a further 2 h at -10-0°C. The mixture was allowed to warm to room temperature. The solvent was removed *in vacuo*

and hexane (40 mL) was added to precipitate out unwanted salts. The solution was filtered under nitrogen and the solvent removed *in vacuo*. The yellow solid obtained was recrystallised from toluene to give colourless crystals (0.2 g, 40 %); ^1H NMR (270 MHz, CDCl_3 , 25 °C, TMS) δ = 7.82-7.63 (m, 5 H; nap 4,5,7-H, 2 x PPh_2 4-H), 7.39-7.30 (m, 2 H; nap 3,6-H), 7.28-7.10 (m, 9 H; nap 2-H, 2 x PPh_2 2,3,5,6-H), 2.64 (q, 3J (H,H) = 7.4 Hz, 2 H; SCH_2), 0.91 (t, 3J (H,H) = 7.4 Hz, 3 H; SCH_2CH_3); ^{13}C NMR (67.9 MHz, CDCl_3 , 25 °C, TMS): δ = 137.0(s), 136.0(s), 134.1(d, J (C,P) = 19.7 Hz), 130.8 (s), 130.0(s), 128.6(s), 128.4(d, J (C,P) = 7.2 Hz), 125.6(d, J (C,P) = 5.8 Hz), 125.5(s), 35.2 (s; CH_2), 13.3 (s; CH_3); ^{31}P NMR (109.4 MHz, CDCl_3 , 25 °C, H_3PO_4): δ = -5.26; IR (KBr disk): ν_{max} cm^{-1} : 3430br, 3054s, 2919s, 2227s, 1587s, 1480s, 1434vs, 1308s, 1261s, 1185s, 1096vs, 1021s, 997s, 910s, 820s, 725vs, 690vs, 528vs, 321s, 294s; MS (ES^+): m/z (%): 411.18 (100) [$\text{M}^+ + \text{K}$]; elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{21}\text{PS}$: C 74.2, H 5.5; found: C 74.5, H 6.1.

Nap[PPh₂][SEt] (1) from (4I): A solution of 2.5 M *n*-butyllithium in hexane (0.4 mL, 1.0 mmol) was transferred dropwise to a freshly prepared solution of 1-iodo-8-ethylsulfanylnaphthalene (0.3 g, 1.0 mmol) in diethyl ether (10 mL) at -10-0°C (salted ice bath). The bright mixture was stirred for 2 h at this temperature, after which chlorodiphenylphosphine (0.23 g, 0.2 mL, 1.0 mmol) was added slowly. The addition coloured the reaction mixture first bright yellow and finally a pale yellow. Stirring was continued for a further 2 h at -10-0°C. The mixture was allowed to warm to room temperature. The solvent was removed *in vacuo* and hexane (40 mL) was added to precipitate out unwanted salts. The solution was filtered under nitrogen and the solvent removed *in vacuo* (0.2 g, 52 %). The product was identified by ^1H and ^{31}P NMR spectroscopy.

(8-ethylsulfanylnaphth-1-yl)diphenylphosphine oxide Nap[O:PPh₂][SEt] (10): (8-ethylsulfanylnaphth-1-yl)diphenylphosphine **3** readily oxidised in contact with the atmosphere to produce (8-ethylsulfanylnaphth-1-yl)diphenylphosphine oxide **16** with 100 % conversion as seen by ^{31}P NMR spectroscopy. Colourless crystals were obtained by diffusion of pentane into a saturated solution of the white solid obtained in dichloromethane; ^1H NMR (270 MHz, CDCl_3 , 25 °C, TMS) δ = 7.92 (d, 3J (H,H) = 8.2 Hz, 1 H; nap 4-H), 7.82-7.76 (m, 2 H; nap 5,7-H), 7.59-7.51 (m, 4 H; 2 x PPh_2 2,6-H), 7.51-7.44 (m, 1 H; nap 2-H), 7.44-7.30 (m, 7 H; nap 6-H, 2 x PPh_2 3-5-H), 7.28-7.22 (m, 1 H; nap 3-H), 2.32 (q, 3J (H,H) = 7.4 Hz, 2 H; SCH_2), 0.65 (t, 3J (H,H) = 7.4 Hz, 3 H; SCH_2CH_3); ^{13}C NMR (67.9 MHz, CDCl_3 , 25 °C, TMS): δ = 138.7(d, J (C,P) = 12.5 Hz), 137.7(s), 134.4(d, J (C,P) = 3.1 Hz), 131.3(d, J (C,P) = 9.3 Hz), 130.7(d, J (C,P) = 2.1 Hz), 128.4(d, J (C,P) = 12.4 Hz), 126.5(s), 124.1(d, J (C,P) = 14.6 Hz), 33.9(s; CH_2), 13.5(s; CH_3); ^{31}P NMR (109.4 MHz, CDCl_3 , 25 °C, H_3PO_4): δ = 36.34; IR (KBr disk): ν_{max} cm^{-1} : 3406w, 3050w, 2924w, 2360vs, 2341vs, 1815w, 1765w, 1726w, 1710w, 1961w, 1658s, 1641s, 1592vs, 1548s, 1536s, 1482s, 1438vs, 1316s, 1187vs, 1112s, 1096s, 994s, 885s, 818vs, 761vs, 730s, 715w, 690s, 562vs, 539vs, 524s, 507vs, 434s, 403w, 389w, 363w; MS (ES^+): m/z (%): 411.00 (100) [$\text{M}^+ + \text{Na}$]; elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{21}\text{POS}$: C 74.2, H 5.5; found: C 74.5, H 6.1.

(8-ethylsulfanylnaphth-1-yl)diphenylphosphine sulfide Nap[S:PPh₂][SEt] (1S): To a solution of (8-ethylsulfanylnaphth-1-yl)diphenylphosphine **3** (0.10 g, 0.27 mmol) in toluene (10 mL) powdered sulfur (9 mg, 0.27 mmol) was added in small batches at 0°C. The mixture was stirred for ½ h at 0°C and another 2 h at ambient temperature. The resulting cloudy solution was filtered, the solvent was removed *in vacuo* and the remaining oil vigorously stirred with hexane (10 mL) over night, which resulted in a thick suspension. The yellow solid product was collected by filtration and colourless crystals were obtained by diffusion of pentane into a saturated solution of the solid in dichloromethane, recrystallised from dichloromethane/hexane (0.02 g, 72 %); ^1H NMR (270 MHz, CDCl_3 , 25 °C,

TMS) δ = 7.98-7.89 (m, 2 H; nap 4,5-H), 7.89-7.65 (m, 5 H; nap 7-H, 2 x *PPh*₂ 2,6-H), 7.54-7.33 (m, 8 H; nap 3,6-H, 2 x *PPh*₂ 3-5-H), 7.32-7.21 (m, 1 H; nap 2-H), 2.18-2.04 (m, 2 H; *SCH*₂), 0.54 (t, ³*J* (H,H) = 7.4 Hz, 3 H; *SCH*₂*CH*₃); ¹³C NMR (67.9 MHz, CDCl₃, 25 °C, TMS): δ = 138.1(s), 137.8(d, *J* (C,P) = 10.4 Hz), 134.0(d, *J* (C,P) = 3.1 Hz), 131.5(d, *J* (C,P) = 2.1 Hz), 131.2(d, *J* (C,P) = 10.4 Hz), 130.5(d, *J* (C,P) = 2.1 Hz), 130.3(s), 128.7(d, *J* (C,P) = 12.4 Hz), 128.4(d, *J* (C,P) = 12.4 Hz), 126.7(s), 124.0(d, *J* (C,P) = 14.5 Hz), 35.2(s; CH₂), 13.2(s; CH₃); ³¹P NMR (109.4 MHz, CDCl₃, 25 °C, H₃PO₄): δ = 51.84; IR (KBr disk): ν_{max} cm⁻¹: 3048w, 2957s, 2923vs, 2851s, 1987w, 1962w, 1896w, 1820w, 1737w, 1666w, 1585w, 1476w, 1433s, 1370w, 1320w, 1260s, 1183w, 1092s, 1019w, 991w, 968w, 920w, 880w, 849w, 820vs, 801vs, 765s, 746s, 718s, 690s, 645s, 609w, 576w, 546w, 512w, 490w, 442w, 407s; MS (EI⁺): *m/z* (%): 374.98 (28) [M⁺-Et], 342.99 (100) [M⁺-SEt], 188.96 (63) [M⁺-SPPH₂]; elemental analysis calcd (%) for C₂₄H₂₁PS₂: C 71.3, H 5.2; found: C 70.1, H 5.7.

(8-ethylsulfanylnaphth-1-yl)diphenylphosphine selenide Nap[Se:PPh₂][SEt] (1Se): (8-ethylsulfanylnaphth-1-yl)diphenylphosphine **3** (0.62 g, 1.5 mmol) and Se (0.12 g, 1.5 mmol) were heated under reflux in toluene (10 mL) for 2 h. The resulting cloudy solution was filtered, the solvent was removed *in vacuo* and the remaining oil vigorously stirred with hexane (10 mL) over night, which resulted in a thick suspension. The yellow solid product was collected by filtration and colourless crystals were obtained by diffusion of pentane into a saturated solution of the solid in dichloromethane. (0.18 g, 65 %); ¹H NMR (270 MHz, CDCl₃, 25 °C, TMS) δ = 7.84-7.82 (m, 2 H; nap 4,5-H), 7.81-7.60 (m, 5 H; nap 7-H, 2 x *PPh*₂ 2,6-H), 7.42-7.40 (m, 1 H; nap 6-H), 7.40-7.19 (m, 8 H; nap 2,3-H, 2 x *PPh*₂ 3-5-H), 2.09-1.92 (m, 2 H; *SCH*₂), 0.48 (t, ³*J* (H,H) = 7.4 Hz, 3 H; *SCH*₂*CH*₃); ¹³C NMR (67.9 MHz, CDCl₃, 25 °C, TMS): δ = 138.3(s), 137.5(dd, *J* (C,P) = 10.4 Hz), 134.1(d, *J* (C,P) = 3.1 Hz), 133.4-131.4(br m), 130.6(d, *J* (C,P) = 2.0 Hz), 130.4(s), 128.4(d, *J* (C,P) = 12.4 Hz), 126.8(s), 124.0(d, *J* (C,P) = 13.5 Hz), 35.9(s; CH₂), 13.8(s; CH₃); ³¹P NMR (109.4 MHz, CDCl₃, 25 °C, H₃PO₄): δ = 41.92; ⁷⁷Se NMR (51.5 MHz, CDCl₃, 25 °C, PhSeSePh): δ = -172.3; IR (KBr disk): ν_{max} cm⁻¹: 3047w, 2952w, 2922s, 2851w, 2360vs, 2336vs, 1475w, 1435s, 1318w, 1247w, 1180w, 1096s, 1088s, 1023w, 994w, 973w, 917w, 880w, 820s, 764s, 746s, 690vs, 615w, 587s, 565s, 533s, 508s, 489w, 442w, 409w; MS (EI⁺): *m/z* (%): 343.07 (100) [M⁺-Se], 188.99 (15) [M⁺-SePPh₂]; elemental analysis calcd (%) for C₂₄H₂₁PSSe: C 63.9, H 4.7; found: C 63.4, H 4.7.

(8-phenylsulfanylnaphth-1-yl)diphenylphosphine Nap[PPh₂][SPh] (2) from (5Br): A solution of 2.5 M *n*-butyllithium in hexane (1.3 mL, 3.2 mmol) was transferred dropwise to a freshly prepared solution of 1-bromo-8-(phenylsulfanyl)naphthalene (1.02 g, 3.2 mmol) in diethyl ether (30 mL) at -10-0°C (salted ice bath). The bright mixture was stirred for 2 h at this temperature, after which chlorodiphenylphosphine (0.71 g, 0.6 mL, 3.2 mmol) was added slowly. Stirring was continued for a further 2 h at -10-0°C. The mixture was allowed to warm to room temperature. The solvent was removed *in vacuo* and hexane (40 mL) was added to precipitate out unwanted salts. The solution was filtered under nitrogen and the solvent removed *in vacuo*. The crude yellow solid obtained was recrystallised from hexane to give colourless crystals (0.9 g, 64 %); ¹H NMR (270 MHz, CDCl₃, 25 °C, TMS) δ = 7.93-7.81 (m, 2 H; nap 4,5-H), 7.71 (d, ³*J* (H,H) = 1.5 Hz, 1 H; nap 2-H), 7.45-7.36 (m, 1 H; nap 3-H), 7.36-7.28 (m, 1 H; nap 6-H), 7.26-7.13 (m, 11 H; nap 2-H, 2 x *PPh*₂ 2-6-H), 7.09-6.97 (m, 3 H; *SPh* 3-5-H), 6.77-6.70 (m, 2 H; *SPh* 2,6-H); ¹³C NMR (67.9 MHz, CDCl₃, 25 °C, TMS): δ = 140.0(q), 139.8(q), 137.6(s), 137.0(s), 135.6(q), 134.1(d, *J* (C,P) = 19.8 Hz), 132.2(q), 131.3(d, *J* (C,P) = 9.4 Hz), 130.9(s), 130.6(s), 128.6(s), 128.4(d, *J* (C,P) = 7.3 Hz), 128.1(d, *J* (C,P) = 3.1 Hz), 126.4(q), 125.9(s), 125.8(s), 125.4(s); ³¹P NMR (109.4 MHz, CDCl₃, 25 °C, H₃PO₄): δ = -5.30; IR (KBr disk): ν_{max} cm⁻¹: 3050s, 2963s, 1949w, 1884w, 1828w, 1579s, 1544s, 1472s, 1432vs, 1352w, 1308w, 1261vs, 1197s,

1092vs, 1021vs, 864w, 817vs, 801vs, 767vs, 740vs, 691vs, 592w, 539w, 499s, 474s, 424w, 387s; MS (ES⁺): *m/z* (%): 459.20 (100) [M⁺+K]; elemental analysis calcd (%) for C₂₈H₂₁PS: C 79.9, H 5.0; found: C 79.7, H 5.0.

Nap[PPh₂][SPh] (2) from (5I): A solution of 1.6 M *n*-butyllithium in hexane (1.9 mL, 3.0 mmol) was transferred dropwise to a freshly prepared solution of 1-iodo-8-(phenylsulfanyl)naphthalene (1.10 g, 3.0 mmol) in diethyl ether (30 mL) at -10-0°C (salted ice bath). The bright yellow mixture was stirred for 2 h at this temperature, after which chlorodiphenylphosphine (0.67 g, 0.5 mL, 3.0 mmol) was added slowly. Stirring was continued for a further 2 h at -10-0°C. The mixture was allowed to warm to room temperature. The solvent was removed *in vacuo* and hexane (40 mL) was added to precipitate out unwanted salts. The solution was filtered under nitrogen and the solvent removed *in vacuo*. The crude yellow solid obtained was recrystallised from hexane (0.9 g, 74 %). The product was identified by ¹H and ³¹P NMR spectroscopy.

(8-phenylsulfanylnaphth-1-yl)diphenylphosphine oxide Nap[O:PPh₂][SPh] (2O): (8-phenylsulfanylnaphth-1-yl)diphenylphosphine **19** oxidised in contact with the atmosphere to produce (8-phenylsulfanylnaphth-1-yl)diphenylphosphine oxide **21** with 100 % conversion as seen by ³¹P NMR spectroscopy. Colourless crystals were obtained by diffusion of pentane into a saturated solution of the white solid product obtained in dichloromethane; m.p./b.p. 50-52°C; ¹H NMR (270 MHz, CDCl₃, 25 °C, TMS) δ = 7.97 (d, ³*J* (H,H) = 8.2 Hz, 1 H; nap 4-H), 7.90 (d, ³*J* (H,H) = 8.1 Hz, 1 H; nap 5-H), 7.83 (dd, ³*J* (H,H) = 7.2 Hz, ⁴*J* (H,H) = 1.3 Hz, 1 H; nap 7-H), 7.52-7.40 (m, 6 H; nap 2,6-H, 2 x PPh₂ 2,6-H), 7.32-7.23 (m, 3 H; nap 3-H, 2 x PPh₂ 4-H), 7.23-7.15 (m, 4 H; 2 x PPh₂ 3,5-H), 6.84-6.72 (m, 3 H; SPh 3-5-H), 6.18-6.12 (m, 2 H; SPh 2,6-H); ¹³C NMR (67.9 MHz, CDCl₃, 25 °C, TMS): δ = 139.8(s), 138.4(d, *J* (C,P) = 12.4 Hz), 134.2(d, *J* (C,P) = 4.1 Hz), 131.2(d, *J* (C,P) = 9.3 Hz), 130.6(d, *J* (C,P) = 2.1 Hz), 128.2(s), 128.1(d, *J* (C,P) = 3.8 Hz), 127.1(s), 126.3(s), 124.6(s), 124.3(d, *J* (C,P) = 14.5 Hz); ³¹P NMR (109.4 MHz, CDCl₃, 25 °C, H₃PO₄): δ = 37.01; IR (KBr disk): ν_{max} cm⁻¹: 3393w, 3051w, 2360vs, 2339vs, 1954w, 1868w, 1843w, 1769w, 1716w, 1699w, 1651w, 1581w, 1557w, 1539w, 1519w, 1507w, 1475s, 1435vs, 1357w, 1321w, 1259w, 1211w, 1181vs, 1153s, 1111s, 1097s, 1067s, 1024w, 993s, 930w, 886s, 827vs, 770s, 734vs, 715s, 689vs, 632w, 614w, 587w, 563vs, 540vs, 507s, 455s, 419w; MS(CI⁺): *m/z* (%): 437.12 (100) [M⁺+H], 327.09 (32) [M⁺-SPh]; elemental analysis calcd (%) for C₂₈H₂₁PSO: C 77.0, H 4.9; found: C 77.7, H 5.0.

(8-phenylsulfanylnaphth-1-yl)diphenylphosphine sulfide Nap[S:PPh₂][SPh] (2S): To a solution of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine **19** (0.239 g, 0.569 mmol) in toluene (10 mL) powdered sulfur (18.2 mg, 0.569 mmol) was added in small batches at 0°C. The mixture was stirred for ½ h at 0°C and another 2 h at ambient temperature. The resulting cloudy solution was filtered, the solvent was removed *in vacuo* and the remaining oil vigorously stirred with hexane (10 mL) over night, which resulted in a thick suspension. The yellow solid product was collected by filtration and colourless crystals were obtained by diffusion of pentane into a saturated solution of the solid dichloromethane. (0.1 g, 44 %); ¹H NMR (270 MHz, CDCl₃, 25 °C, TMS) δ = 7.99-7.88 (m, 3 H; nap 4,5,7-H), 7.54-7.48 (m, 1 H; nap 6-H), 7.32-7.10 (m, 12 H; nap 2,3-H, 2 x PPh₂ 2-6-H), 6.81-6.69 (m, 3 H; SPh 3-5-H), 5.93-5.87 (m, 2 H; SPh 2,6-H); ¹³C NMR (67.9 MHz, CDCl₃, 25 °C, TMS): δ = 140.7(s), 137.7(d, *J* (C,P) = 11.4 Hz), 134.2(d, *J* (C,P) = 3.1 Hz), 131.8(s), 130.5(s), 128.3(d, *J* (C,P) = 12.5 Hz), 128.1(s), 127.4(s), 125.3(s), 124.4(s), 124.2(s); ³¹P NMR (109.4 MHz, CDCl₃, 25 °C, H₃PO₄): δ = 52.52; IR (KBr disk): ν_{max} cm⁻¹: 3446br, 3062w, 1966w, 1847w, 1579s, 1543w, 1473s, 1430s, 1381w, 1357w, 1321s, 1302s, 1272w, 1199w, 1177s, 1150s, 1089s, 1022w, 989s, 916w, 882w, 824s,

766vs, 736vs, 687s, 642vs, 611s, 547s, 578w, 547s, 523s, 511vs, 492s, 468s, 447w, 407s; MS(ES⁺): *m/z* (%): 474.97 (100) [M⁺+Na]; elemental analysis calcd (%) for C₂₈H₂₁PS₂: C 74.3, H 4.7; found: C 73.3, H 4.7.

(8-phenylsulfanylnaphth-1-yl)diphenylphosphine selenide Nap[Se:PPh₂][SPh] (2Se): (8-phenylsulfanylnaphth-1-yl)diphenylphosphine **19** (0.23 g, 0.55 mmol) and Se (0.047 g, 0.55 mmol) were heated under reflux in toluene (10 mL) for 2 h. The resulting cloudy solution was filtered, the solvent was removed *in vacuo* and the remaining oil vigorously stirred with hexane (10 mL) over night, which resulted in a thick suspension. The yellow solid product was collected by filtration and recrystallised by diffusion of pentane into a saturated solution of the compound to give yellow crystals. from dichloromethane/hexane (0.2 g, 85 %); ¹H NMR (270 MHz, CDCl₃, 25 °C, TMS) δ = 8.00-7.91 (m, 3 H; nap 4,5,7-H), 7.56-7.49 (m, 1 H; nap 6-H), 7.30-7.10 (m, 12 H; nap 2,3-H, 2 x PPh₂ 2-6-H), 6.77-6.67 (m, 3 H; SPh 3-5-H), 5.86-5.81 (m, 2 H; SPh 2,6-H); ¹³C NMR (67.9 MHz, CDCl₃, 25 °C, TMS): δ = 140.7(s), 137.3(d, *J* (C,P) = 10.4 Hz), 134.2(d, *J* (C,P) = 3.2 Hz), 131.9(s), 130.6(d, *J* (C,P) = 3.1 Hz), 128.3(d, *J* (C,P) = 12.4 Hz), 128.1(s), 127.6(s), 125.0(s), 124.3(s), 124.2(s); ³¹P NMR (109.4 MHz, CDCl₃, 25 °C, H₃PO₄): δ = 42.46 (*J* (P,Se) = 722.4 Hz); ⁷⁷Se NMR (51.5 MHz, CDCl₃, 25 °C, PhSeSePh): δ = -341.0 (*J* (Se,P) = 722.4 Hz); IR (KBr disk): ν_{max} cm⁻¹: 2856vs, 2395w, 1718w, 1646s, 1542w, 1461vs, 1378vs, 1308w, 1181w, 1120w, 973w, 886w, 809s, 722s, 691w, 616w, 562w, 539w, 506w; MS(CI⁺): *m/z* (%): 501.04 (4) [M⁺+H], 421.12 (75) [M⁺-Se], 391.02 (12) [M⁺-SPh], 343.08 (100) [M⁺-SePh]; elemental analysis calcd (%) for C₂₈H₂₁PSSe: C 67.3, H 4.2; found: C 65.9, H 4.4.

(8-phenylselanylnaphth-1-yl)diphenylphosphine Nap[PPh₂][SePh] (3) from (6Br): A solution of 2.5 M *n*-butyllithium in hexane (1.1 mL, 2.8 mmol) was transferred dropwise to a freshly prepared solution of 1-bromo-8-(phenylselanyl)naphthalene (1.02 g, 2.8 mmol) in diethyl ether (30 mL) at -10-0°C (salted ice bath). The bright yellow mixture was stirred for 2 h at this temperature, after which chlorodiphenylphosphine (0.62 g, 0.5 mL, 2.8 mmol) was added slowly. Stirring was continued for a further 2 h at -10-0°C. The mixture was allowed to warm to room temperature. The solvent was removed *in vacuo* and hexane (40 mL) was added to precipitate out unwanted salts. The solution was filtered under nitrogen and the solvent removed *in vacuo* to give a yellow oil (0.5 g, 40 %); ¹H NMR (270 MHz, CDCl₃, 25 °C, TMS) δ = 7.76 (dd, ³*J* (H,H) = 7.9 Hz, ⁴*J* (H,H) = 1.5 Hz, 1 H; nap 4-H), 7.66 (d, ³*J* (H,H) = 8.1 Hz, 1 H; nap 5-H), 7.52 (dd, ³*J* (H,H) = 7.4 Hz, ⁴*J* (H,H) = 1.2 Hz, 1 H; nap 7-H), 7.35-7.30 (m, 1 H; nap 2-H), 7.30-7.05 (m, 17 H; nap 2,3-H, SPh 2-6-H, 2 x PPh₂ 2-6-H); ¹³C NMR (67.9 MHz, CDCl₃, 25 °C, TMS): δ = 137.7(s), 135.0(s), 133.9(d, *J* (C,P) = 5.2 Hz), 133.7(s), 131.2(s), 129.2(s), 128.9(s), 128.5(d, *J* (C,P) = 6.2 Hz), 128.3(s), 127.4(s), 126.1(s), 125.6(s); ³¹P NMR (109.4 MHz, CDCl₃, 25 °C, H₃PO₄): δ = -12.94 (*J* (P,Se) = 386.2.0 Hz); ⁷⁷Se NMR (51.5 MHz, CDCl₃, 25 °C, PhSeSePh): δ = 439.6 (*J* (Se,P) = 386.2.0 Hz); IR (KBr disk): ν_{max} cm⁻¹: 3853w, 3735w, 3673w, 3649w, 3628w, 3049w, 2911w, 2851w, 2360vs, 2340vs, 1734w, 1699w, 1651w, 1558w, 1541w, 1474w, 1433s, 1310w, 1259w, 1193w, 1153w, 1088w, 1021w, 996w, 971w, 911w, 815s, 765s, 739s, 690s, 669s, 538w, 504w, 420w, 397w, 352w; MS(CI⁺): *m/z* (%): 469.06 (65) [M⁺+H], 391.02 (98) [M⁺+H-Ph]; elemental analysis calcd (%) for (C₂₈H₂₁PSe)₄CDCl₃: C 68.2, H 4.4; found: C 68.4, H 4.6.

Nap[PPh₂][SePh] (3) from (6I): A solution of 2.5 M *n*-butyllithium in hexane (0.5 mL, 1.2 mmol) was transferred dropwise to a freshly prepared solution of 1-iodo-8-(phenylselanyl)naphthalene (0.50 g, 1.2 mmol) in diethyl ether (30 mL) at -10-0°C (salted ice bath). The bright yellow mixture was stirred for 2 h at this temperature, after which chlorodiphenylphosphine (0.27 g, 0.2 mL, 1.2 mmol) was added slowly. Stirring was continued for a further 2 h at -10-0°C. The mixture was allowed to warm to room temperature. The solvent was removed *in vacuo* and hexane (40 mL)

was added to precipitate out unwanted salts. The solution was filtered under nitrogen and the solvent removed *in vacuo* to give a yellow oil (0.5 g, 89 %); The product was identified by ^1H and ^{31}P NMR spectroscopy.

(8-phenylselanylnaphth-1-yl)diphenylphosphine oxide Nap[O:PPh₂][SePh] (3O): (8-phenylselanylnaphth-1-yl)diphenylphosphine **32** readily oxidised in contact with the atmosphere to produce (8-phenylselanylnaphth-1-yl)diphenylphosphine oxide **35** with 100 % conversion as seen by ^{31}P NMR spectroscopy. The orange solid product obtained was recrystallised by diffusion of pentane into a saturated solution of the compound to give colourless crystals; m.p./b.p. 50-52°C; ^1H NMR (270 MHz, CDCl_3 , 25 °C, TMS) δ = 7.92 (d, 3J (H,H) = 8.2 Hz, 1 H; nap 4-H), 7.88 (d, 3J (H,H) = 6.4 Hz, 1 H; nap 5-H), 7.79 (d, 3J (H,H) = 8.1 Hz, 1 H; nap 7-H), 7.57-7.48 (m, 4 H; 2 x PPh₂ 2,6-H), 7.40-7.32 (m, 3 H; nap 2-H, 2 x PPh₂ 4-H), 7.30-7.21 (m, 6 H; nap 3,6-H, 2 x PPh₂ 3,5-H), 6.97-6.90 (m, 1 H; SPh 4-H), 6.90-6.81 (m, 2 H; SPh 3,5-H), 6.59 (d, 3J (H,H) = 7.2 Hz, 2 H; SPh 2,6-H); ^{13}C NMR (67.9 MHz, CDCl_3 , 25 °C, TMS): δ = 140.3(s), 137.6(q), 137.3(q), 135.6(q), 134.3(s), 131.8(d, J (C,P) = 9.4 Hz), 131.1(s), 130.3(s), 128.6(s), 128.4(s), 128.2(s), 127.1(s), 126.1(s), 123.8(d, J (C,P) = 15.5 Hz); ^{31}P NMR (109.4 MHz, CDCl_3 , 25 °C, H_3PO_4): δ = 37.99; ^{77}Se NMR (51.5 MHz, CDCl_3 , 25 °C, PhSeSePh): δ = 450.4; IR (KBr disk): ν_{max} cm^{-1} : 3423br, 3053s, 2924w, 1960w, 1893w, 1809w, 1589w, 1472s, 1436vs, 1314s, 1176vs, 1115vs, 1068w, 1022w, 997w, 981w, 923w, 866w, 821s, 763vs, 744vs, 721vs, 693vs, 541vs, 505s, 469w, 447w, 426w; MS(ES⁺): m/z (%): 507.02 (100) [M^+ +Na]; elemental analysis calcd (%) for $\text{C}_{28}\text{H}_{21}\text{PSeO}$: C 69.4, H 4.4; found C 68.5, H 4.6.

(8-phenylselanylnaphth-1-yl)diphenylphosphine sulfide Nap[S:PPh₂][SePh] (3S): To a solution of (8-phenylselanylnaphth-1-yl)diphenylphosphine **32** (0.086 g, 0.21 mmol) in toluene (10 mL) powdered sulfur (0.065 g, 0.21 mmol) was added in small batches at 0°C. The mixture was stirred for ½ h at 0°C and another 2 h at ambient temperature. The resulting cloudy solution was filtered, the solvent was removed *in vacuo* and the remaining oil vigorously stirred with hexane (10 mL) over night, which resulted in a thick suspension. The yellow solid product was collected by filtration and recrystallised by diffusion of pentane into a saturated solution of the compound to give colourless crystals 0.05 g, 54 %; m.p./b.p. 51-53°C; ^1H NMR (270 MHz, CDCl_3 , 25 °C, TMS) δ = 8.12 (dd, 3J (H,H) = 7.1 Hz, 4J (H,H) = 1.4 Hz, 1 H; nap 5-H), 8.00-7.88 (m, 2 H; nap 4,7-H), 7.76-7.62 (m, 4 H; 2 x PPh₂ 2,6-H), 7.48-7.22 (m, 9 H; nap 2,3,6-H, 2 x PPh₂ 3-5-H), 6.97-6.81 (m, 3 H; SPh 3-5-H), 6.43-6.35 (m, 2 H; SPh 2,6-H); ^{13}C NMR (67.9 MHz, CDCl_3 , 25 °C, TMS): δ = 141.2(s), 137.9(s), 134.3(d, J (C,P) = 3.1 Hz), 132.0(d, J (C,P) = 10.4 Hz), 131.1(s), 130.8(d, J (C,P) = 2.0 Hz), 129.4(s), 128.5(d, J (C,P) = 4.2 Hz), 128.3(s), 127.3(s), 125.6(s), 123.9(s); ^{31}P NMR (109.4 MHz, CDCl_3 , 25 °C, H_3PO_4): δ = 51.01; ^{77}Se NMR (51.5 MHz, CDCl_3 , 25 °C, PhSeSePh): δ = 448.5(d, J (Se,P) = 19.1 Hz); IR (KBr disk): ν_{max} cm^{-1} : 2925vs, 1871vs, 1574w, 1474s, 1434vs, 1375w, 1317w, 1260s, 1192w, 1177w, 1095s, 1064w, 1021s, 994w, 936s, 863w, 797vs, 769s, 732vs, 718vs, 690vs, 639s, 539s, 509s, 454w, 414w; MS(Cl⁺): m/z (%): 501.04 (3) [M^+ +H], 419.10 (11) [M^+ -Ph], 345.08 (100) [M^+ -Ph₂]; elemental analysis calcd (%) for $\text{C}_{28}\text{H}_{21}\text{PSSe}$: C 67.2, H 4.2; found C 66.7, H 3.9.

(8-phenylselanylnaphth-1-yl)diphenylphosphine selenide Nap[Se:PPh₂][SePh] (3Se): (8-phenylselanylnaphth-1-yl)diphenylphosphine **32** (1.09 g, 2.3 mmol) and Se (0.18 g, 2.3 mmol) were heated under reflux in toluene (20 mL) for 2 h. The resulting cloudy solution was filtered, the solvent was removed *in vacuo* and the remaining oil vigorously stirred with hexane (10 mL) over night, which resulted in a thick suspension. The yellow solid product was collected by filtration and recrystallised by diffusion of pentane into a saturated solution of the compound to give yellow crystals (0.8 g, 60 %); ^1H NMR (270 MHz, CDCl_3 , 25 °C, TMS) δ = 8.11 (dd, 3J (H,H) = 7.2 Hz, 4J (H,H) = 1.3 Hz, 1 H; nap 5-

H), 7.94-7.83 (m, 2 H; nap 4,7-H), 7.43-7.14 (m, 13 H; nap 2,3,6-H, 2 x *PPh*₂ 2-6-H), 6.88-6.74 (m, 3 H; *SPh* 3-5-H), 6.27-6.19 (m, 2 H; *SPh* 2,6-H); ¹³C NMR (67.9 MHz, CDCl₃, 25 °C, TMS): δ = 141.4(s), 137.4(d, *J* (C,P) = 9.4 Hz), 134.4(d, *J* (C,P) = 3.1 Hz), 131.2(s), 130.8(d, *J* (C,P) = 3.1 Hz), 128.8(s), 128.6(s), 128.5(s), 128.4(s), 128.3(s), 127.4(s), 125.5(s), 123.9(d, *J* (C,P) = 13.5 Hz); ³¹P NMR (109.4 MHz, CDCl₃, 25 °C, H₃PO₄): δ = 40.50 (¹*J* (P,Se) = 715.3 Hz, ⁴*J* (P,Se) = 23.9 Hz); ⁷⁷Se NMR (51.5 MHz, CDCl₃, 25 °C, PhSeSePh): δ = 451.4(d, ⁴*J* (Se,P) = 23.9 Hz), -162.8(d, ¹*J* (Se,P) = 715.3 Hz); IR (KBr disk): ν_{max} cm⁻¹: 2018vs, 1954vs, 1918vs, 1732w, 1651s, 1574w, 1473s, 1433s, 1316w, 1261s, 1197w, 1178w, 1156w, 1096s, 1019w, 995w, 978w, 905w, 862w, 824s, 800s, 774w, 765s, 748s, 735s, 686s, 662w, 615w, 583s, 557s, 524s, 505s, 486s, 458s, 443s, 413s; MS(EI⁺): *m/z* (%): 390.01 (5) [M⁺-SePh], 311.10 (18) [M⁺-Se₂Ph], 236.94 (12) [M⁺-Ph₃Se], 233.04 (100) [M⁺-Se₂Ph₂]; elemental analysis calcd (%) for C₂₈H₂₁PSe₂: C 61.6, H 3.9; found C 61.4, H 3.3.

Crystal structure analyses

X-ray crystal structures for compounds **1** and **2** were collected at -180(1) °C by using a Rigaku MM007 High brilliance RA generator (Mo Kα radiation, confocal optic) and Mercury CCD system. At least a full hemisphere of data was collected using ω scans. Intensities were corrected for Lorentz, polarisation and absorption. Data for the chalcogenide compounds **nO**, **nS**, **nSe** (**n** = **1-3**) were collected at -148(1) °C on a Rigaku ACTOR-SM, Saturn 724 CCD area detector with confocal optic Mo-Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz, polarisation and absorption. The data for the complexes analysed was collected and processed using CrystalClear (Rigaku).^[35] The structure was solved by direct methods^[36] and expanded using Fourier techniques.^[37] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure^[38] crystallographic software package except for refinement, which was performed using SHELXL-97.^[39] These X-ray data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html CCDC 737039 for **2**^[18] and 766917 - 766926 or from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

Computational Details

Geometries were fully optimised in the gas phase at the B3LYP level^[40] using Curtis and Binning's 962(d) basis^[41] on Se and 6-31+G(d) elsewhere, followed by calculation of the harmonic frequencies to confirm the minimum character of each stationary point and evaluation of Wiberg bond indices,^[29] obtained in a natural bond orbital^[42] analysis. The optimisations were started from the experimental structures available from X-ray crystallography, for which the WBIs were calculated as well. Radical cations were re-optimised from the closed-shell minima using the unrestricted Kohn-Sham formalism (spin contamination was negligible in all cases). The computations were performed using the Gaussian 03 suite of programs.^[43]

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Supporting Information Available

X-ray crystallographic files for **1**, **2**, **nO**, **nS**, **nSe** (**n**= 1-3).

References

- [1] a) H. E. Katz, *J. Am. Chem. Soc.* **1985**, *107*, 1420; b) R. W. Alder, P. S. Bowman, W. R. S. Steel, D. R. Winterman, *Chem. Commun.* **1968**, 723; c) T. Costa, H. Schmidbaur, *Chem. Ber.* **1982**, *115*, 1374; d) A. Karacar, M. Freytag, H. Thönnessen, J. Omelanczuk, P. G. Jones, R. Bartsch, R. Schmutzler, *Heteroat. Chem.* **2001**, *12*, 102; e) J. Meinwald, D. Dauplaise, F. Wudl, J. J. Hauser, *J. Am. Chem. Soc.* **1977**, *99*, 255; f) R. S. Glass, S. W. Andruski, J. L. Broeker, H. Firouzabadi, L. K. Steffen, G. S. Wilson, *J. Am. Chem. Soc.* **1989**, *111*, 4036; g) T. Fuji, T. Kimura and N. Furukawa, *Tetrahedron Lett.* **1995**, *36*, 1075; h) W. Nakanishi, S. Hayahi, S. Toyota, *Chem. Comm.* **1996**, 371; i) G. P. Schiemenz, *Z. Anorg. All. Chem.* **2002**, 628, 2597; j) R. J. P. Corriu, J. C. Young, *Hypervalent Silicon Compounds*, in *The Chemistry of Organic Silicon Compounds*, (Eds. S. Patai, Z. Rappoport), Wiley, New York, **1989**, p. 1242.
- [2] a) C. A. Coulson, R. Daudel, J. M. Robertson, *Proc. R. Soc. London, Ser. A.* **1951**, A207, 306; b) D. W. J. Cruickshank, *Acta Crystallogr.* **1957**, *10*, 504; c) C. P. Brock, J. D. Dunitz, *Acta Crystallogr., Sect. B.* **1982**, B38, 2218; d) J. Oddershede, S. Larsen, *J. Phys. Chem. A* **2004**, *108*, 1057.
- [3] V. Balasubramaniyan, *Chem. Rev.* **1966**, *66*, 567.
- [4] a) H. Schmidbaur, H.-J. Öller, D. L. Wilkinson, B. Huber, G. Müller, *Chem. Ber.* **1989**, *122*, 31; b) H. Fujihara, N. Furukawa, *J. Mol. Struct.* **1989**, *186*, 261; c) H. Fujihara, R. Akaishi, T. Erata, N. Furukawa, *J. Chem. Soc., Chem. Commun.* **1989**, 1789; d) J. Handal, J. G. White, R. W. Franck, Y. H. Yuh, N. L. Allinger, *J. Am. Chem. Soc.* **1977**, *99*, 3345; e) J. F. Blount, F. Cozzi, J. R. Damewood, D. L. Iroff, U. Sjöstrand, K. Mislow, *J. Am. Chem. Soc.* **1980**, *102*, 99; f) F. A. L. Anet, D. Donovan, U. Sjöstrand, F. Cozzi and K. Mislow, *J. Am. Chem. Soc.* **1980**, *102*, 1748; g) W. D. Hounshell, F. A. L. Anet, F. Cozzi, J. R. Damewood Jr., C. A. Johnson, U. Sjöstrand, K. Mislow, *J. Am. Chem. Soc.* **1980**, *102*, 5941; h) R. Schröck, K. Angermaier, A. Sladek, H. Schmidbaur, *Organometallics* **1994**, *13*, 3399.
- [5] F. R. Knight, A. L. Fuller, A. M. Z. Slawin, J. D. Woollins, *Chem. Eur. J.* accepted, chem.200903523.
- [6] F. R. Knight, A. L. Fuller, A. M. Z. Slawin and J. D. Woollins, *Chem. Eur. J.*, accepted, chem.201000435.
- [7] P. Kilian, A. M. Z. Slawin, J. D. Woollins, *Dalton Trans.* **2003**, 3876.
- [8] E. Valls, J. Suades, *Organometallics* **1999**, *18*, 5475.
- [9] a) *Homogeneous Hydrogenation*, (Ed. B. R. James), Wiley-Interscience, New York, **1973**; b) B. R. James, *Adv. Organomet. Chem.* **1979**, *17*, 319; c) *Organic Syntheses with Noble Metal Catalysts*, (Ed. P. N. Rylander), Academic Press, New York, **1973**; d) J. L. Spencer, *Adv. Organomet. Chem.* **1979**, *17*, 407; e) A. J. Chalk, J. F. Harrod, *Adv. Organomet. Chem.* **1968**, *6*, 119; f) R. L. Pruett, *Adv. Organomet. Chem.* **1979**, *17*, 1; g) F. R. Hartley, *Chem. Rev.* **1969**, *69*, 799; h) P. M. Henry, in *Palladium Catalysed Oxidation of Hydrocarbons*, (Ed. D. Reidel), Dordrecht, Holland, **1979**; i) J. F. Roth, J. H. Craddock, A. Hershman, F. E. Paulik, *Chem. Technol.* **1971**, 600; j) D. Foster, *Adv. Organomet. Chem.* **1979**, *17*, 255.
- [10] a) T. Costa, H. Schmidbaur, *Chem. Ber.* **1982**, *115*, 1374; b) R. D. Jackson, S. James, A. G. Orpen, P. G. Pringle, *J. Organomet. Chem.* **1993**, 458, C3; c) S. L. James, A. G. Orpen, P. G. Pringle, *J. Organomet. Chem.* **1996**, 525, 299; d) J. van Soolingen, R.-J. de Lang, R. den Besten, P. A. A. Klusener, N. Veldman, A. L. Spek, L. Brandsma, *Synth. Commun.* **1995**, *25*, 1741; e) E. Drent, J. A. M. van Broekhaven, M. J. Doyle, *J. Organomet. Chem.* **1991**, 417, 235; f) G. P. C. M. Dekker, C. J. Elsevier, K. Vrieze, P. W. N. M. van Leeuwen,

- Organometallics* **1992**, *11*, 1598; g) G. P. C. M. Dekker, C. J. Elsevier, K. Vrieze, P. W. N. M. van Leeuwen, C. F. Roobeek, *J. Organomet. Chem.* **1992**, *430*, 357; h) J. K. Hogg, S. L. James, A. G. Orpen, P. G. Pringle, *J. Organomet. Chem.* **1994**, *480*, C1; i) A. Karacar, H. Thonnessen, P. G. Jones, R. Bartsch, R. Schmutzler, *Chem. Ber. Rec.* **1997**, *130*, 1485; j) A. Karacar, H. Thonnessen, P. G. Jones, R. Bartsch, R. Schmutzler, *Heteroat. Chem.* **1997**, *8*, 539; k) H. B. Kagan, *Asymmetric Synthesis using Organometallic Catalysts*, in *Comprehensive Organometallic Chemistry*, (Ed. G. Wilkinson), Pergamon Press, Oxford, **1982**, vol. 8, pp. 463-498; l) H. B. Kagan, *Chiral Ligands for Asymmetric Catalysis in Asymmetric Synthesis*, (Ed. J. D. Morrison), Academic Press, Orlando San Diego, New York, London, Toronto, Montreal, Sydney, Tokyo, **1985**, vol. 5, pp. 1-39; m) *Catalytic Asymmetric Synthesis*, (Ed. I. Ojima), VCH Publishers, New York, Weinheim, Cambridge, **1993**; n) *Asymmetric Catalysis in Organic Synthesis*, (Ed. R. Noyori), John Wiley and Sons, New York, Chichester, Brisbane, Toronto, Singapore, **1994**; o) R. Noyori, S. Hashiguchi, in *Applied Homogenous Catalysis with Organometallic Compounds*, (Eds. B. Cornils, W. A. Hermann), VCH, Weinheim, New York, Basel, Cambridge, Tokyo, **1996**, vol. 1, p. 552; p) K. M. Pietrusiewicz, M. Zablocka, *Chem. Rev.* **1994**, *94*, 1375; q) A. Karacar, M. Freytag, H. Thönnessen, J. Omelanczuk, P. G. Jones, R. Bartsch, R. Schmutzler, *Heteroat. Chem.* **2001**, *12*, 102; r) W.-W. du Mont, R. Hensel, S. Kubiniok, L. Lange, in *The Chemistry of Organic Selenium and Tellurium Compounds*, (Ed. S. Patai), Wiley, New York, **1987**, vol. 2, ch. 15; s) A. Karacar, M. Freytag, P. G. Jones, R. Bartsch, R. Schmutzler, *Z. Anorg. Chem.* **2001**, 627, 1571.
- [11] a) G. P. Schiemenz, B. Schiemenz, S. Petersen, C. Wolff, *Chirality* **1998**, *10*, 180; b) D. Hellwinkel, W. Lindner, H.-J. Wilfinger, *Chem. Ber.* **1974**, *107*, 1428; c) D. Hellwinkel, W. Krapp, *Chem. Ber.* **1977**, *110*, 693; d) R. O. Day, R. R. Holmes, *Inorg. Chem.* **1980**, *19*, 3609; e) A. Chandrasekaran, P. Sood, R. R. Holmes, *Inorg. Chem.* **1998**, *37*, 459; f) N. V. Timosheva, A. Chandrasekaran, R. O. Day, R. R. Holmes, *Inorg. Chem.* **1998**, *37*, 4945; g) C. Chuit, R. J. P. Corriu, P. Montfort, C. Réyé, J. -P. Declercq, A. Dubourg, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1430; h) M. Chauhan, C. Chiut, R. J. P. Corriu, C. Reyé, J.-P. Declercq, A. Dubourg, *J. Organomet. Chem.* **1996**, *510*, 173; i) C. Chuit, R. J. P. Corriu, P. Montfort, C. Reyé, J.-P. Declercq, A. Dubourg, *J. Organomet. Chem.* **1996**, *511*, 171; j) C. Chuit, C. Reyé, *Eur. J. Inorg. Chem.* **1998**, 1847; k) G. P. Schiemenz, *Phosphorus, Sulfur Silicon Relat. Elem.* **2000**, *163*, 185; l) G. Wittig, M. Rieber, *Liebigs Ann. Chem.* **1949**, 562, 187; m) P. J. Wheatley, *J. Chem. Soc.* **1964**, 2206; n) G. P. Schiemenz, R. Bukowski, L. Eckholt, B. Varnskühler, *Z. Naturforsch.* **2000**, *55b*, 12; o) A. G. Ekstrand, J. Prakt, *Chem. N. F.* **1888**, *38*, 139; p) F. Dannerth, *J. Am. Chem. Soc.* **1907**, *29*, 1319; q) G. P. Schiemenz, S. Pörksen, C. Näther, *Z. Naturforsch.* **2000**, *55b*, 841; r) G. Dyker, M. Hagel, G. Henkel, M. Köckerling, C. Näther, S. Peterson, G. P. Schiemenz, *Z. Naturforsch.* **2001**, *56b*, 1109; s) G. P. Schiemenz, C. Näther, S. Pörksen, *Z. Naturforsch.* **2003**, *58b*, 663.
- [12] a) C. Chuit, R. J. P. Corriu, C. Reyé, J. C. Young, *Chem. Rev.* **1993**, *93*, 1371; b) C. Brelière, F. Carré, R. J. P. Corriu, M. Poirier, G. Royo, J. Zwecker, *Organometallics* **1989**, *8*, 1831; c) R. J. P. Corriu, J. C. Young, *Hypervalent Silicon Compounds*, in *The Chemistry of Organic Silicon Compounds*, (Eds. S. Patai, Z. Rappoport), Wiley, New York, **1989**, p. 1242; d) S. N. Tandura, M. G. Voronkov, N. V. Alekaev, *Top. Curr. Chem.* **1986**, *131*, 99; e) G. Sawiski, J. von Schnering, *Chem. Ber.* **1976**, *109*, 3728; f) C. Brelière, R. J. P. Corriu, G. Royo, J. Zwecker, *Organometallics* **1989**, *8*, 1834.
- [13] V. I. Minkin, *Pure Appl. Chem.* **1999**, *71*(10), 1919.
- [14] a) C. S. Slone, D. A. Weinberger, C. A. Mirkin, *Prog. Inorg. Chem.* **1999**, *48*, 233; b) P. Braunstein, F. Naud, *Angew. Chem., Int. Ed.* **2001**, *40*, 680; c) P. Espinet, K. Soulantica, *Coord. Chem. Rev.* **1999**, *195*, 499; d) J. C.

-
- Jeffrey, T. B. Rauchfuss, *Inorg. Chem.* **1979**, *18*, 2658; e) J. A. Davies, F. R. Hartley, *Chem. Rev.* **1981**, *81*, 79; f) T. B. Rauchfuss, F. T. Patino, D. M. Roundhill, *Inorg. Chem.* **1975**, *4*, 652.
- [15] a) S. M. Aucott, H. L. Milton, S. D. Robertson, A. M. Z. Slawin, G. D. Walker, J. D. Woollins, *Chemistry Eur. J.* **2004**, *10*, 1666-1676; b) S. M. Aucott, H. L. Milton, S. D. Robertson, A. M. Z. Slawin, J. D. Woollins, *Heteroat. Chem.* **2004**, *15*, 531-542; c) S. M. Aucott, H. L. Milton, S. D. Robertson, A. M. Z. Slawin, J. D. Woollins, *Dalton Trans.* **2004**, 3347-3352; d) S. M. Aucott, P. Kilian, H. L. Milton, S. D. Robertson, A. M. Z. Slawin, J. D. Woollins, *Inorg. Chem.* **2005**, *44*, 2710-2718; e) S. M. Aucott, P. Kilian, S. D. Robertson, A. M. Z. Slawin, J. D. Woollins, *Chem. Eur. J.* **2006**, *12*, 895-902; f) S. M. Aucott, D. Duerden, Y. Li, A. M. Z. Slawin, J. D. Woollins, *Chem. Eur. J.* **2006**, *12*, 5495-5504.
- [16] a) P. Kilian, D. Philp, A. M. Z. Slawin, J. D. Woollins, *Eur. J. Inorg. Chem.* **2003**, 249-254; b) P. Kilian, A. M. Z. Slawin, J. D. Woollins, *Chem. Eur. J.* **2003**, *9*, 215-222; c) P. Kilian, A. M. Z. Slawin, J. D. Woollins, *Chem. Commun.* **2003**, 1174-1175; d) P. Kilian, A. M. Z. Slawin, J. D. Woollins, *Dalton Trans.* **2003**, 3876-3885; e) P. Kilian, H. L. Milton, A. M. Z. Slawin, J. D. Woollins, *Inorg. Chem.* **2004**, *43*, 2252-2260; f) P. Kilian, A. M. Z. Slawin, J. D. Woollins, *Inorg. Chim. Acta* **2005**, *358*, 1719-1713; g) P. Kilian, A. M. Z. Slawin, J. D. Woollins, *Dalton Trans.* **2006**, 2175-2183.
- [17] F. R. Knight, A. L. Fuller, A. M. Z. Slawin, J. D. Woollins, *Polyhedron* accepted, [doi:10.1016/j.poly.2010.02.033](https://doi.org/10.1016/j.poly.2010.02.033).
- [18] a) F. R. Knight, A. L. Fuller, A. M. Z. Slawin, J. D. Woollins, *Dalton Trans.* **2009**, 8476-8478; b) F. R. Knight, A. L. Fuller, A. M. Z. Slawin, J. D. Woollins, *Polyhedron* accepted, [doi:10.1016/j.poly.2010.03.006](https://doi.org/10.1016/j.poly.2010.03.006).
- [19] W. Nakanishi, S. Hayashi, *Phosphorus, Sulfur Silicon Relat. Elem.* **2002**, *177*, 1833.
- [20] H. Riihimäki, P. Suomalainen, H. K. Reinius, J. Suutari, S. Jääskeläinen, A. O. I. Krause, T. A. Pakkanen, J. T. Pursiainen, *J. Mol. Catal. A: Chem.* **2003**, *200*, 69.
- [21] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.
- [22] S. A. Reiter, S. D. Nogai, K. Karaghiosoff, H. Schmidbaur, *J. Am. Chem. Soc.* **2004**, *126*, 15833.
- [23] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1987**, *12*, S1.
- [24] P. Nagy, D. Szabó, I. Kapovits, Á. Kucsman, G. Argay, A. Kálmán, *J. Mol. Struct.* **2002**, *606*, 61.
- [25] a) W. Nakanishi, S. Hayashi, *J. Org. Chem.*, **2002**, *67*, 38; b) S. Hayashi, K. Yamane, W. Nakanishi, *J. Org. Chem.* **2007**, *72*, 7587; c) W. Nakanishi, S. Hayashi, S. Toyota, *J. Am. Chem. Soc.* **1998**, *63*, 8790; d) W. Nakanishi, S. Hayashi, T. Uehara, *J. Phys. Chem.* **1999**, *103*, 9906; e) W. Nakanishi, S. Hayashi, T. Uehara, *Eur. J. Org. Chem.* **2001**, 3933.
- [26] a) H. W. Roesky, M. Andruh, *Coord. Chem., Rev.* **2003**, *236*, 91; b) T. Koizumi, K. Tsutsui, K. Tanaka, *Eur. J. Org. Chem.* **2003**, 9(18), 4528; c) C. Janiak, *J. Chem. Soc., Dalton Trans.* **2000**, 3885.
- [27] a) I. Vargas-Baca, T. Chivers, *Phosphorus, Sulfur Silicon Relat. Elem.* **2000**, *164*, 207-227; b) N. Lozac'h, *Adv. Heterocycl. Chem.* **1971**, *13*, 161; c) R. E. Rosenfield, Jr., R. Parthasarathy, J. D. Dunitz, *J. Am. Chem. Soc.* **1977**, *99*, 4860; d) A. Kálmán, L. Párkányi, *Acta Crystallogr., Sect. B* **1980**, *B36*, 2372; e) Á. Kucsman, I. Kapovits, in *Organic Sulfur Chemistry: Theoretical and Experimental Advances*, (Eds. I. G. Csizmadia, A. Mangini, F. Bernardi), Elsevier, Amsterdam, **1985**, p. 191; f) J. G. Ángyán, R. A. Poirier, Á. Kucsman, I. G. Csizmadia, *J. Am. Chem. Soc.* **1987**, *109*, 2237; g) R. S. Glass, L. Adamowicz, J. L. Broeker, *J. Am. Chem. Soc.* **1991**, *113*, 1065; h) F. T. Burling, B. M. Goldstein, *Acta Crystallogr., Sect. B* **1993**, *B49*, 738; i) Y.
-

- Nagao, T. Hirata, S. Goto, S. Sano, A. Kakehi, K. Iizuka, M. Shiro, *J. Am. Chem. Soc.* **1998**, *120*, 3104; j) K. Ohkata, M. Ohsugi, K. Yamamoto, M. Ohsawa, K. Akiba, *J. Am. Chem. Soc.* **1996**, *118*, 6355.
- [28] a) M. Nishio, *CrystEngComm*. **2004**, *6*(27), 130; b) C. Fischer, T. Gruber, W. Seichter, D. Schindler, E. Weber, *Acta Crystallogr. Sect. E* **2008**, *E64*, o673; c) M. Hirota, K. Sakaibara, H. Suezawa, T. Yuzuri, E. Ankai, M. Nishio, *J. Phys. Org. Chem.* **2000**, *13*, 620; d) H. Tsubaki, S. Tohyama, K. Koike, H. Saitoh, O. Ishitani, *Dalton Trans.* **2005**, 385.
- [29] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083.
- [30] 1,6-dibromo-2-phenyl-1,2-diselenaacenaphthylene (two molecules in the unit cell with Se-Se distances of 2.516 Å and 2.542 Å): E. Horn, T. Nakahodo, N. Fukurawa, *Z. Kristallogr. -New Cryst. Struct.* **2000**, *215*, 23.
- [31] S. D. Robertson, Ph.D. Thesis, University of St Andrews, **2005**.
- [32] A. Karaçar, M. Freytag, H. Thönnessen, J. Omelanczuk, P. G. Jones, R. Bartsch, R. Schmutzler, *Z. Anorg. Allg. Chem.* **2000**, *626*, 2361.
- [33] D. Seyferth, S. C. Vick, *J. Organomet. Chem.* **1977**, *141*, 173.
- [34] H. O. House, D. G. Koeppell, W. J. Campbell, *J. Org. Chem.* **1972**, *37*(7), 1003.
- [35] CrystalClear 1.6: Rigaku Corporation, 1999. CrystalClear Software User's Guide, Molecular Structure Corporation, (c) 2000. J. W. P. Flugrath, *Acta Crystallogr., Sect. D* **1999**, *D55*, 1718.
- [36] SIR97: A. Altomare, M. Burla, M. Camalli, G. Casciarano, C. Giacovazzo, A. Guagliardi, A. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115.
- [37] DIRDIF99: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, **1999**. The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
- [38] CrystalStructure 3.8.1: Crystal Structure Analysis Package, Rigaku and Rigaku/MS (2000-2006). 9009 New Trails Dr. The Woodlands TX 77381 USA.
- [39] SHELX97: G.M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.
- [40] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
- [41] R. C. Binning, L. A. Curtiss, *J. Comput. Chem.* **1990**, *11*, 1206.
- [42] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.
- [43] M. J. Frisch *et al*, Gaussian 03, Gaussian, Inc., Pittsburgh PA, 2003.

Table 1 Phosphorus-31 and selenium-77 NMR spectroscopic data for phosphines **1-3** and related chalcogeno derivatives [δ (ppm), J (Hz)]

Compound	1	1O	1S	1Se
δ_P	-5	36	52	42
δ_{Se}	n/a	n/a	n/a	-172
Compound	2	2O	2S	2Se
δ_P	-5	37	53	42
δ_{Se}	n/a	n/a	n/a	-341
$^1J_{PSe}$	n/a	n/a	n/a	722
Compound	3	3O	3S	3Se
δ_P	-13	38	51	41
δ_{Se}	n/a	n/a	n/a	-163
δ_{Se}	440	450	449	451
$^4J_{PSe}$	391	-	19	24
$^1J_{PSe}$	n/a	n/a	n/a	715

Table 2 Selected interatomic distances [$\text{\AA}$] and angles [$^\circ$] for **1**, **1O**, **1S** and **1Se** [values in parentheses are for independent molecules]

Compound	1	1O	1S	1Se
<i>Peri-region distances and sub-van der Waals contacts in peri-region</i>				
P(1)···S(1)	2.9737(14) [2.9469(15)]	3.1349(13)	3.2083(14)	3.2283(19)
$\Sigma r_{\text{vdW}} - \text{P} \cdots \text{S}; \% \Sigma r_{\text{vdW}}^{[a]}$	0.6263; 83 [0.6531; 82]	0.4651; 87	0.3917; 89	0.3717; 90
P(1)-C(1)	1.838(4) [1.848(3)]	1.832(3)	1.837(3)	1.843(5)
S(1)-C(9)	1.779(4) [1.776(4)]	1.772(3)	1.783(4)	1.771(6)
P(1)=E(2)	-	1.487(2)	1.9550(14)	2.1103(17)
S(1)···E(2)	-	3.033(2)	3.2951(15)	3.43(1)
$\Sigma r_{\text{vdW}} - \text{S} \cdots \text{E}; \% \Sigma r_{\text{vdW}}^{[a]}$	-	0.287; 91	0.305; 92	0.270; 93
<i>Naphthalene bond lengths</i>				
C(1)-C(2)	1.383(4) [1.373(5)]	1.382(5)	1.384(5)	1.364(6)
C(2)-C(3)	1.406(5) [1.416(5)]	1.387(5)	1.411(5)	1.408(8)
C(3)-C(4)	1.367(5) [1.355(5)]	1.369(5)	1.360(5)	1.358(7)
C(4)-C(5)	1.413(5) [1.413(5)]	1.418(5)	1.412(5)	1.417(6)
C(5)-C(10)	1.445(5) [1.438(5)]	1.426(5)	1.430(5)	1.434(7)
C(5)-C(6)	1.424(5) [1.416(6)]	1.411(5)	1.420(5)	1.401(7)
C(6)-C(7)	1.356(5) [1.338(6)]	1.368(5)	1.365(6)	1.373(7)
C(7)-C(8)	1.400(5) [1.410(6)]	1.386(6)	1.408(6)	1.397(8)
C(8)-C(9)	1.367(5) [1.379(5)]	1.379(5)	1.377(5)	1.378(7)
C(9)-C(10)	1.461(5) [1.438(5)]	1.439(5)	1.443(5)	1.443(6)
C(10)-C(1)	1.442(5) [1.466(5)]	1.444(4)	1.438(5)	1.456(6)

^[a] van der Waals radii used for calculations: $r_{\text{vdW}}(\text{P})$ 1.80 $\text{\AA}$, $r_{\text{vdW}}(\text{O})$ 1.52 $\text{\AA}$, $r_{\text{vdW}}(\text{S})$ 1.80 $\text{\AA}$, $r_{\text{vdW}}(\text{Se})$ 1.90.^[21]

Table 2 Continued - Selected interatomic distances [$\text{\AA}$] and angles [$^\circ$] for **1**, **10**, **1S** and **1Se** [values in parentheses are for independent molecules]

Compound	1	10	1S	1Se
<i>Peri-region bond angles</i>				
P(1)-C(1)-C(10)	123.6(3) [122.4(3)]	123.9(2)	124.5(2)	124.2(3)
C(1)-C(10)-C(9)	126.9(3) [126.0(3)]	126.5(3)	126.0(3)	127.2(4)
S(1)-C(9)-C(10)	121.2(3) [123.0(3)]	122.7(2)	121.4(2)	122.4(4)
Σ of bay angles	$\Sigma = 371.7$ [$\Sigma = 371.4$]	$\Sigma = 373.1$	$\Sigma = 371.9$	$\Sigma = 373.8$
Splay angle^[b]	11.7 [11.4]	13.1	11.9	13.8
C(4)-C(5)-C(6)	118.1(4) [118.9(4)]	118.2(3)	119.4(3)	118.7(5)
S(1)···P(1)-C(11)	163.3(1) [160.6(1)]	174.3(1)	175.4(1)	170.9(1)
<i>Out-of-plane displacement</i>				
P(1)	-0.11(1) [0.05(1)]	-0.566(4)	-0.620(4)	-0.599(7)
S(1)	0.16(1) [-0.03(1)]	0.404(4)	0.744(4)	0.527(6)
E(2)	-	-1.720(5)	-2.019(5)	-2.302(7)
<i>Central naphthalene ring torsion angles</i>				
C:(6)-(5)-(10)-(1)	-177.1(3) [179.8(4)]	175.4(3)	-168.4(3)	-173.7(6)
C:(4)-(5)-(10)-(9)	-176.5(3) [-177.2(4)]	175.0(3)	-171.0(3)	-175.3(6)

^[b]**Splay angle:** Σ of the three bay region angles – 360.

Table 3 Selected interatomic distances [Å] and angles [°] for **2**, **2O**, **2S**, **2Se**, **3O**, **3S** and **3Se**

Compound	2	2O	2S	2Se	3O	3S	3Se
<i>Peri-region distances and sub-van der Waals contacts in peri-region</i>							
P(1)···E(1)	3.0330(7)	3.1489(9)	3.191(1)	3.190(1)	3.215(2)	3.2803(8)	3.278(2)
$\Sigma r_{vdW} - P \cdots E$; % $\Sigma r_{vdW}^{[a]}$	0.567; 84	0.4511; 87	0.409; 89	0.410; 89	0.485; 89	0.4197; 89	0.422; 89
P(1)-C(1)	1.8548(19)	1.835(3)	1.837(3)	1.836(4)	1.826(5)	1.837(3)	1.825(6)
E(1)-C(9)	1.785(2)	1.777(3)	1.779(3)	1.782(4)	1.937(4)	1.916(3)	1.917(6)
P(1)=E(2)	-	1.492(2)	1.9585(12)	2.1181(11)	1.476(4)	1.9567(10)	2.1165(16)
E(1)···E(2)	-	2.9612(17)	3.3142(11)	3.3974(10)	2.770(3)	3.3490(7)	3.4217(8)
$\Sigma r_{vdW} - E \cdots E$; % $\Sigma r_{vdW}^{[a]}$	-	0.3588; 89	0.2858; 92	0.3026; 92	0.65; 81	0.351; 91	0.3783; 90
<i>Naphthalene bond lengths</i>							
C(1)-C(2)	1.376(3)	1.380(5)	1.376(5)	1.385(5)	1.358(7)	1.385(4)	1.387(8)
C(2)-C(3)	1.404(3)	1.400(5)	1.414(5)	1.400(6)	1.423(7)	1.397(4)	1.417(9)
C(3)-C(4)	1.353(3)	1.365(5)	1.352(4)	1.363(6)	1.344(8)	1.354(4)	1.341(9)
C(4)-C(5)	1.415(3)	1.419(5)	1.422(5)	1.422(6)	1.410(8)	1.413(4)	1.416(9)
C(5)-C(10)	1.442(3)	1.430(5)	1.435(4)	1.431(6)	1.439(7)	1.429(4)	1.441(9)
C(5)-C(6)	1.420(3)	1.420(4)	1.419(4)	1.411(5)	1.425(8)	1.418(4)	1.419(8)
C(6)-C(7)	1.358(3)	1.355(5)	1.345(5)	1.356(7)	1.368(8)	1.347(4)	1.359(10)
C(7)-C(8)	1.399(3)	1.408(5)	1.401(5)	1.390(6)	1.398(7)	1.402(4)	1.387(10)
C(8)-C(9)	1.377(3)	1.376(4)	1.372(4)	1.372(5)	1.384(7)	1.389(4)	1.396(8)
C(9)-C(10)	1.437(3)	1.432(4)	1.433(4)	1.431(5)	1.409(6)	1.433(4)	1.437(9)
C(10)-C(1)	1.448(3)	1.443(4)	1.452(4)	1.454(5)	1.455(7)	1.450(3)	1.437(8)

^[a] van der Waals radii used for calculations: $r_{vdW}(P)$ 1.80 Å, $r_{vdW}(O)$ 1.52 Å, $r_{vdW}(S)$ 1.80 Å, $r_{vdW}(Se)$ 1.90.^[21]

Table 3 Continued - Selected interatomic distances [Å] and angles [°] for **2**, **2O**, **2S**, **2Se**, **3O**, **3S** and **3Se**

Compound	2	2O	2S	2Se	3O	3S	3Se
<i>Peri-region bond angles</i>							
P(1)-C(1)-C(10)	124.07(13)	124.6(2)	124.2(2)	125.0(3)	123.6(3)	125.4(2)	126.5(4)
C(1)-C(10)-C(9)	126.90(17)	126.2(3)	127.3(3)	126.6(3)	126.8(4)	126.7(2)	126.3(5)
E(1)-C(9)-C(10)	123.11(13)	121.6(2)	122.2(2)	122.5(3)	125.1(3)	124.7(2)	124.5(4)
Σ of bay angles	Σ = 374.1	Σ = 372.4	Σ = 373.7	Σ = 374.1	Σ = 375.5	Σ = 376.8	Σ = 377.3
Splay angle^[b]	14.1	12.4	13.7	14.1	15.5	16.8	17.3
C(4)-C(5)-C(6)	118.60(18)	119.6(3)	118.9(3)	119.0(4)	119.8(4)	118.6(2)	118.9(6)
E(1)···P(1)-C(11)	174.5(1)	177.6(1)	174.0(1)	173.8(1)	167.9(1)	173.5(1)	172.9(1)
E(2)···E(1)-C(23)	-	145.4(1)	145.8(1)	149.1(1)	178.1(1)	145.0(1)	148.4(1)
<i>Out-of-plane displacement</i>							
P(1)	0.007(1)	0.6312(37)	0.633(4)	0.621(47)	-0.578(6)	0.601(3)	0.578(7)
E(1)	0.127(1)	-0.582(4)	-0.451(4)	-0.433(5)	0.450(6)	-0.420(3)	-0.397(7)
E(2)	-	1.6231(46)	2.1977(43)	2.3457(51)	-1.458(8)	2.179(4)	2.314(8)
<i>Central naphthalene ring torsion angles</i>							
C:(6)-(5)-(10)-(1)	178.49(16)	171.7(2)	173.7(2)	175.4(3)	174.4(5)	174.9(2)	175.7(5)
C:(4)-(5)-(10)-(9)	-179.5(2)	170.3(2)	173.4(2)	173.1(3)	170.5(5)	173.6(2)	175.1(5)

^[b]**Splay angle:** Σ of the three bay region angles – 360.**Table 4** Torsion angles [°] categorising the naphthalene and ethyl/phenyl ring conformations in **1** and **2** [values in parentheses are for independent molecules]

Compound	1		2	
	Torsion angle	Conformation	Torsion angle	Conformation
<i>Naphthalene ring conformations</i>				
C(10)-C(1)-P(1)-C(11)	θ ₁ 167.8(1) [162.6(1)]	Nap ₁ : ^[a] equatorial ^[i]	θ ₂ 177.0(1)	Nap ₁ : equatorial
C(10)-C(1)-P(1)-C(17)	θ ₂ -87.3(1) [-92.5(1)]	Nap ₂ : ^[b] axial ^[h]	θ ₂ 78.6(1)	Nap ₂ : axial
C(10)-C(9)-S(1)-C(23)	θ ₃ 168.3(1) [169.5(1)]	Nap ₃ : ^[c] equatorial	θ ₁ -129.2(1)	Nap ₃ : twist ^[j]
<i>Ethyl/Phenyl group conformations</i>				
C(1)-P(1)-C(11)-C(12)	γ ₁ 109.9(1) [96.1(1)]	Ph ₁ : ^[d] axial	γ ₁ 92.6(11)	Ph ₁ : axial
C(1)-P(1)-C(17)-C(18)	γ ₂ 158.1(1) [158.5(1)]	Ph ₂ : ^[e] equatorial	γ ₂ 17.8(1)	Ph ₂ : equatorial
C(9)-S(1)-C(23)-C(24)	γ ₃ -174.4(1) [-174.7(1)]	Et ₁ : ^[g] equatorial	γ ₃ 48.0(1)	Ph ₃ : ^[f] twist

^[a]**Nap₁**: naphthalene ring P(1) relative to C₁-P₁-C₁₁; ^[b]**Nap₂**: naphthalene ring P(1) relative to relative to C₁-P₁-C₁₇; ^[c]**Nap₃**: naphthalene ring S(1);^[d]**Ph₁**: P(1) phenyl ring 11-16; ^[e]**Ph₂**: P(1) phenyl ring 17-22; ^[f]**Ph₃**: S(1) phenyl ring; ^[g]**Et₁**: S(1) ethyl group; ^[h]**axial**: perpendicular to C(ar)-Z-C(R) plane; ^[i]**equatorial**: coplanar with C(ar)-Z-C(R) plane; ^[j]**twist**: intermediate between equatorial and axial.

Table 5 Torsion angles [°] categorising the naphthyl ring and phenyl/ethyl group conformations in **nO**, **nS** and **nSe** (**n** = **1-3**)

<i>Naphthalene ring conformations</i>			
Compound	C(10)-C(1)-P(1)-C(11)	C(10)-C(1)-P(1)-C(17)	C(10)-C(9)-E(1)-C(23)
1O	θ_1 -161.4(1); equatorial ^[b]	θ_2 -89.3(1); axial	θ_3 93.4(1); axial
1S	θ_1 -158.2(1); equatorial	θ_2 92.6(1); axial	θ_3 -89.1(1); axial
1Se	θ_1 -164.9(1); equatorial	θ_2 85.3(1); axial	θ_3 -90.9(1); axial
2O	θ_1 95.9(1); axial ^[a]	θ_2 152.7(1); equatorial	θ_3 95.3(1); axial
2S	θ_1 -89.5(1); axial	θ_2 162.0(1); equatorial	θ_3 90.6(1); axial
2Se	θ_1 162.4(1); equatorial	θ_2 -88.3(1); axial	θ_3 92.0(1); axial
3O	θ_1 146.5(1); twist ^[c]	θ_2 -99.7(1); axial	θ_3 134.5(1); twist
3S	θ_1 162.4(1); equatorial	θ_2 -88.8(1); axial	θ_3 91.7(1); axial
3Se	θ_1 162.9(1); equatorial	θ_2 -88.5(1); axial	θ_3 93.6(1); axial
<i>Phenyl ring conformations</i>			
Compound	C(1)-P(1)-C(11)-C(12)	C(1)-P(1)-C(17)-C(18)	C(9)-E(1)-C(23)-C(24)
1O	γ_1 -105.7(1); axial	γ_2 -24.8(1); equatorial	γ_3 79.1(1); axial
1S	γ_1 -98.7(1); axial	γ_2 -160.7(1); equatorial	γ_3 179.4(1); equatorial
1Se	γ_1 74.2(1); axial	γ_2 28.9(1); equatorial	γ_3 -67.0(1); axial
2O	γ_1 154.9(1); equatorial	γ_2 96.5(1); axial	γ_3 -170.0(1); equatorial
2S	γ_1 160.9(1); equatorial	γ_2 -81.4(1); axial	γ_3 179.5(1); equatorial
2Se	γ_1 -77.9(1); axial	γ_2 161.4(1); equatorial	γ_3 -178.6(1); equatorial
3O	γ_1 -86.3(1); axial	γ_2 -7.2(1); equatorial	γ_3 -56.1(1); twist
3S	γ_1 -79.4(1); axial	γ_2 164.2(1); equatorial	γ_3 -176.5(1); equatorial
3Se	γ_1 102.5(1); axial	γ_2 -20.4(1); equatorial	γ_3 -2.2(1); equatorial

^[a]axial: perpendicular to C(ar)-Z-C(R) plane; ^[b]equatorial: coplanar with C(ar)-Z-C(R) plane; ^[c]twist: intermediate between equatorial and axial.

Table 6 Non-bonded intramolecular ethyl- π interactions [$\text{\AA}$] and angles [°] for chalcogenides **1O**, **1S** and **1Se**.

Hydrogen bond geometry [$\text{\AA}$, °]				
Compound	D-H...A	H...A	D...A	D-H...A
1O	C(23)-H(23a)...Cg(17-23) ^[a]	3.09(1)	3.64(1)	117.2(1)
	C(23)-H(23b)...Cg(17-23)	3.59(1)	3.64(1)	85.4(1)
1S	C(23)-H(23b)...Cg(17-23)	3.83(1)	4.04(1)	94.9(1)
	C(24)-H(24b)...Cg(17-23)	2.90(1)	3.79(1)	151.5(1)
1Se	C(23)-H(23a)...Cg(17-23)	3.42(1)	3.58(1)	91.0(1)
	C(23)-H(23b)...Cg(17-23)	3.16(1)	3.58(1)	106.8(1)

^[a]Cg(17-23) is the centroid of atoms C(17)-C(22); ^[b]all CH bonds have been refined to 0.99(1) $\text{\AA}$.

Table 7 Crystallographic data for compounds **1**, **1O**, **1S** and **1Se**

Compound	1	1O	1S	1Se
Empirical Formula	C ₂₄ H ₂₁ PS	C ₂₄ H ₂₁ OPS	C ₂₄ H ₂₁ PS ₂	C ₂₄ H ₂₁ PSSe
Formula Weight	372.44	388.46	404.52	451.42
Temperature (°C)	-180(1)	-148(1)	-148(1)	-148(1)
Crystal Colour, Habit	colourless, prism	colourless, prism	colourless, prism	colourless, prism
Crystal Dimensions (mm³)	0.06 X 0.06 X 0.03	0.21 X 0.21 X 0.03	0.21 X 0.18 X 0.15	0.12 X 0.09 X 0.06
Crystal System	triclinic	monoclinic	monoclinic	monoclinic
Lattice Parameters	a = 8.6734(17) Å b = 13.165(3) Å c = 17.525(4) Å α = 102.307(6)° β = 96.444(6)° γ = 93.395(4)°	a = 12.851(3) Å b = 10.384(3) Å c = 29.473(8) Å - β = 91.689(8)° -	a = 11.652(2) Å b = 9.6047(18) Å c = 18.293(3) Å - β = 92.268(5)° -	a = 13.622(3) Å b = 9.3562(18) Å c = 17.224(4) Å - β = 112.028(4)° -
Volume (Å³)	V = 1935.7(7)	V = 3931.5(18)	V = 2045.6(6)	V = 2034.9(8)
Space Group	P-1	C2/c	P2 ₁ /c	P2 ₁ /n
Z value	4	8	4	4
Dcalc (g/cm³)	1.278	1.312	1.313	1.473
F000	784	1632	848	920
m(MoKa) (cm⁻¹)	0.254	2.57	3.446	20.33
No. of Reflections Measured	12531	10443	12018	11654
Rint	0.0595	0.044	0.06	0.075
Min and Max Transmissions	0.5879 – 1.000	0.946 - 0.992	0.928 - 0.950	0.779 - 0.885
Independent Reflections	6626	3418	3571	3570
Observed Reflection (No. Variables)	3809(470)	3044 (246)	3334 (246)	3162 (246)
Reflection/Parameter Ratio	14.1	13.89	14.52	14.51
Residuals: R₁ (I>2.00σ(I))	0.0614	0.0677	0.0658	0.069
Residuals: R (All reflections)	0.1131	0.0844	0.0735	0.0808
Residuals: wR₂ (All reflections)	0.1245	0.2324	0.1767	0.1172
Goodness of Fit Indicator	0.952	1.183	1.274	1.209
Flack Parameter	-	-	-	-
Maximum peak in Final Diff. Map	0.382 e-/Å ³	0.75 e-/Å ³	0.46 e-/Å ³	0.49 e-/Å ³
Minimum peak in Final Diff. Map	-0.332 e-/Å ³	-0.84 e-/Å ³	-0.42 e-/Å ³	-0.51 e-/Å ³

Table 7 Continued - Crystallographic data for compounds **2**, **2O**, **2S** and **2Se**

Compound	2	2O	2S	2Se
Empirical Formula	C ₂₈ H ₂₁ PS	C ₂₉ H ₂₃ OPSCl ₂	C ₂₈ H ₂₁ S ₂ P	C ₂₈ H ₂₁ PSSe
Formula Weight	420.48	521.44	452.57	499.47
Temperature (°C)	-180(1)	-148(1)	-148(1)	-148(1)
Crystal Colour, Habit	colourless, platelet	colourless, prism	colourless, platelet	yellow, block
Crystal Dimensions (mm³)	0.10 X 0.10 X 0.10	0.09 X 0.09 X 0.09	0.18 X 0.12 X 0.06	0.15 X 0.12 X 0.12
Crystal System	monoclinic	triclinic	monoclinic	monoclinic
Lattice Parameters	a = 11.1461(12) Å b = 8.8914(10) Å c = 21.587(2) Å - β = 90.837(4)° -	a = 9.2265(17) Å b = 11.6406(16) Å c = 13.239(3) Å α = 102.74(2)° β = 98.54(2)° γ = 112.23(2)°	a = 9.3241(13) Å b = 17.769(2) Å c = 13.7930(19) Å - β = 97.328(3)° -	a = 9.432(4) Å b = 17.849(6) Å c = 13.701(4) Å - β = 96.511(7)° -
Volume (Å³)	V = 2139.1(4)	V = 1240.7(5)	V = 2266.6(5)	V = 2291.8(13)
Space Group	P2 ₁ /c	P-1	P2 ₁ /n	P2 ₁ /n
Z value	4	2	4	4
Dcalc (g/cm³)	1.306	1.396	1.326	1.447
F000	880	540	944	1016
m(MoKa) (cm⁻¹)	0.239	4.313	3.191	18.131
No. of Reflections Measured	13424	12814	12358	12375
Rint	0.0325	0.041	0.054	0.04
Min and Max Transmissions	0.8678 – 1.000	0.961 - 0.962	0.943 - 0.981	0.757 - 0.804
Independent Reflections	3774	4275	3948	4012
Observed Reflection (No. Variables)	3348(272)	3896 (308)	3521(281)	3694(281)
Reflection/Parameter Ratio	13.88	13.88	14.05	14.28
Residuals: R₁ (I>2.00σ(I))	0.0408	0.0508	0.0582	0.0427
Residuals: R (All reflections)	0.0462	0.061	0.0694	0.0504
Residuals: wR₂ (All reflections)	0.1049	0.1469	0.123	0.1537
Goodness of Fit Indicator	1.042	1.203	1.201	1.231
Flack Parameter	-	-	-	-
Maximum peak in Final Diff. Map	0.906 e-/Å ³	0.51 e-/Å ³	0.29 e-/Å ³	0.56 e-/Å ³
Minimum peak in Final Diff. Map	-0.314 e-/Å ³	-0.51 e-/Å ³	-0.36 e-/Å ³	-0.53 e-/Å ³

Table 7 Continued - Crystallographic data for compounds **3O**, **3S** and **3Se**

Compound	3O	3S	3Se
Empirical Formula	C ₂₈ H ₂₁ PSeO	C ₂₈ H ₂₁ PSeS	C ₂₈ H ₂₁ PSe ₂
Formula Weight	483.41	499.47	546.37
Temperature (°C)	-148(1)	-148(1)	-148(1)
Crystal Colour, Habit	colourless, chunk	colourless, block	yellow, prism
Crystal Dimensions (mm³)	0.30 X 0.15 X 0.12	0.15 X 0.15 X 0.15	0.18 X 0.15 X 0.09
Crystal System	monoclinic	monoclinic	monoclinic
Lattice Parameters	a = 10.1430(16) Å b = 10.6578(17) Å c = 10.6907(19) Å - β = 100.935(4)° -	a = 9.3748(15) Å b = 17.820(3) Å c = 13.847(2) Å - β = 97.820(5)° -	a = 9.4797(12) Å b = 17.844(2) Å c = 13.7175(16) Å - β = 96.789(3)° -
Volume (Å³)	V = 1134.7(3)	V = 2291.7(6)	V = 2304.1(5)
Space Group	P2 ₁	P2 ₁ /n	P2 ₁ /n
Z value	2	4	4
Dcalc (g/cm³)	1.415	1.448	1.575
F000	492	1016	1088
m(MoKa) (cm⁻¹)	17.43	18.132	32.93
No. of Reflections Measured	6648	13337	12528
Rint	0.029	0.034	0.051
Min and Max Transmissions	0.588 - 0.811	0.756 - 0.762	0.543 - 0.744
Independent Reflections	3674	4607	4046
Observed Reflection (No. Variables)	3611(281)	4279(281)	3691(281)
Reflection/Parameter Ratio	13.07	16.4	14.4
Residuals: R₁ (I>2.00σ(I))	0.0374	0.0431	0.0553
Residuals: R (All reflections)	0.0406	0.0486	0.065
Residuals: wR₂ (All reflections)	0.1131	0.087	0.1585
Goodness of Fit Indicator	1.203	1.14	1.291
Flack Parameter	0.022(13)	-	-
Maximum peak in Final Diff. Map	0.69 e / Å ³	0.41 e / Å ³	0.71 e / Å ³
Minimum peak in Final Diff. Map	-0.67 e / Å ³	-0.45 e / Å ³	-0.67 e / Å ³