Heterometathesis of diphosphanes ($R_2P–PR_2$) with dichalcogenides (R'E–ER', E = O, S, Se, Te)

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Electronic supplementary information

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ESI 1: Experimental

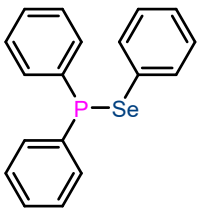
All manipulations were carried out under an inert atmosphere of nitrogen or argon using standard Schlenk and glovebox techniques. The solvents dichloromethane, tetrahydrofuran and toluene were collected from a Grubbs-type solvent delivery system, stored over 4 Å molecular sieves and degassed using the freeze-pump-thaw method. The deuterated solvents chloroform-d, methylene chloride-d2 and benzene-d6 were purchased from Sigma-Aldrich (Merck), dried over 4 Å molecular sieves and also degassed using the freeze-pump-thaw method. NMR spectra were acquired using either a Jeol ECS300, Jeol ECS400, Jeol ECZ400, Bruker Ascend 400 or Varian VNMRS500. ^{1}H and ^{13}C NMR are referenced to residual solvent and deuterated solvent respectively and ^{31}P and ^{77}Se to external standards, 85% H_3PO_4 and Me_2Se respectively. Mass spectrometry was performed by the University of Bristol Mass Spectrometry Service and X-ray crystallography by the University of Bristol X-ray Crystallography Service. FTIR spectroscopy was performed using a Perkin Elmer Spectrum 2 spectrometer.

The diphosphanes: tetraphenyldiphosphane, tetra(*p*-tolyl)diphosphane and tetra(*p*-anisyl)diphosphane were prepared via the Wurtz coupling–type method we reported previously, from their respective chlorophosphines and magnesium metal.[1]

1,2-dibutyldiselane (dibutyldiselenide) was prepared from bromobutane and sodium diselenide according to the literature method of J. Scianowski.[2] 3,3'-diselanediyldipropionic acid was prepared from 3-chloropropanoic acid and sodium diselenide according to the literature procedure of V. Nascimento *et al*.[3]

Unless otherwise specified all other reagents were purchased and used as received from the supplier without purification.

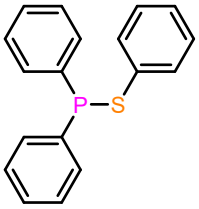
$^{31}P\{^{1}H\}$ NMR integrals were used throughout this study to approximate the relative concentrations of different phosphorus species present in solution. Relaxation effects were not accounted for in this work, which means that these integrations should be treated as approximations.



1

Diphenyl(phenylselanyl)phosphane (1):

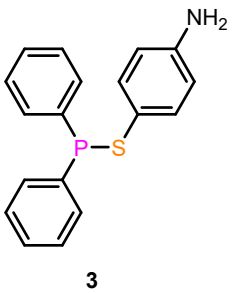
Tetraphenyldiphosphane (190 mg, 0.513 mmol) and diphenyl diselenide (160 mg, 0.513 mmol) were added to a Schlenk flask and dissolved in THF (10 ml), immediately creating a pale-yellow solution, which was left to stir for 10 min. The solvent was then removed *in vacuo* affording **1** as an almost-colourless oily solid (323 mg, 92% yield). After storage under argon overnight the oily solid partially crystallised. Crystals suitable for single-crystal X-ray crystallography were grown over 1 week via CH_2Cl_2/n-hexane vapour diffusion. ^{1}H NMR (400 MHz; $CDCl_3$): 7.57 (6H, m, Ar*H*), 7.34 (6H, m, Ar*H*), 7.22 (3H, m, Ar*H*). $^{31}P\{^{1}H\}$ NMR (162 MHz; $CDCl_3$): +30.5 (s, J_{PSe} = 229.0 Hz). $^{77}Se\{^{1}H\}$ NMR (76 MHz; $CDCl_3$): +309.7 (J_{SeP} = 229.0 Hz). $^{13}C\{^{1}H\}$ NMR (101 MHz; $CDCl_3$): 137.1 (d, J_{CP} = 27.4 Hz), 133.9 (d, J_{CP} = 5.8 Hz), 133.5 (s), 133.3 (s), 129.3 (s), 129.3 (s), 128.7 (d, J_{CP} = 6.3 Hz), 127.6 (s). HRMS (APCI+): Found $[M+H]^+$: m/z 343.0140 (343.0149).



2

Diphenyl(phenylthiol)phosphane (2):

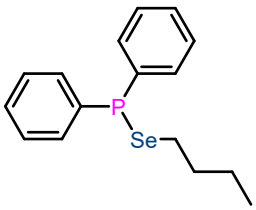
Tetraphenyldiphosphane (300 mg, 0.81 mmol) and diphenyl disulfide (219 mg, 0.81 mmol) were added to a Schlenk flask, dissolved in THF (15 ml) and then stirred for 2 h. The solution was then filtered through two basic alumina plugs to remove residual P(V) species. The solvent was removed under reduced pressure affording **2** as a colourless oily solid (205 mg, 40% yield). ^{1}H NMR (301 MHz; $CDCl_3$): 7.61 (m, 4H, Ar*H*), 7.53 (m, 2H, Ar*H*), 7.38 (m, 6H, Ar*H*), 7.24 (m, 3H, Ar*H*). $^{31}P\{^{1}H\}$ NMR (162 MHz; $CDCl_3$): +32.7 (s). $^{13}C\{^{1}H\}$ NMR (101 MHz; $CDCl_3$): 137.6 (d, J_{CP} = 23.2 Hz), 135.2 (d, J_{CP} = 14.1 Hz), 132.9 (d, J_{CP} = 20.9 Hz), 132.0 (d, J_{CP} = 7.9 Hz), 129.5 (s), 129.1 (s), 128.7 (d, J_{CP} = 6.5 Hz), 127.1 (d, J_{CP} = 1.7 Hz). HRMS (APCI+): Found $[M+H]^+$ m/z 295.0695 (295.0705).



3

4-((diphenylphosphanyl)thio)aniline (3):

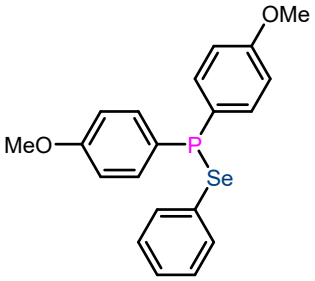
Tetraphenyldiphosphane (287 mg, 0.775 mmol) and 4,4'-dithioaniline (265 mg, 0.775 mmol) were added to a Schlenk flask, dissolved in CH_2Cl_2 and then the resultant lime green solution was stirred for 1.5 h. The solution was then filtered through a basic alumina plug and the solvent removed under reduced pressure affording **3** as an almost colourless oily solid (186 mg, 34% yield). ^{1}H NMR (400 MHz; CD_2Cl_2): 7.58 (m, 4H, Ar*H*), 7.37 (m, 6H, Ar*H*), 7.21 (m, 2H, Ar*H*), 6.56 (m, 2H, Ar*H*), 3.77 (bs, 2H, NH_2). $^{31}P\{^{1}H\}$ NMR (162 MHz; CD_2Cl_2): +37.2 (s). $^{13}C\{^{1}H\}$ NMR (101 MHz; CD_2Cl_2): 146.9 (s), 138.1 (d, J_{CP} = 25.2 Hz), 134.8 (s), 134.8 (s), 129.2 (s), 132.7 (d, J_{CP} = 20.8 Hz), 128.5 (d, J_{CP} = 6.4 Hz), 115.4 (s). HRMS (APCI+): Found $[M+H]^+$ m/z 310.0802 (310.0814).



4

(Butylselanyl)diphenylphosphane (4):

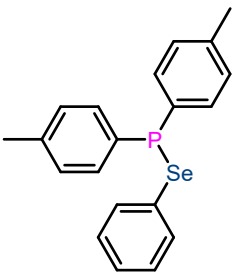
Tetraphenyldiphosphane (166 mg, 0.488 mmol) and di(*n*-butyl) diselenide (122 mg, 0.488 mmol) were added to a Schlenk and dissolved in THF (15 ml), which gave a pale-yellow solution that was left to stir for 20 min. The reaction mixture was then filtered through a basic alumina plug. The solvent was removed under reduced pressure affording **4** as a colourless oil (138 mg, 48% yield). ^{1}H NMR (301 MHz; $CDCl_3$): 7.55 (m, 4H, Ar*H*), 7.31 (m, 5H, Ar*H*), 2.79 (q, 2H, J_{HH} = 7.72 Hz, CH_2), 1.69 (m, 2H, CH_2), 1.37 (m, 2H, CH_2), 0.86 (t, 3H, J_{HH} = 7.38 Hz, CH_3). ^{31}P{^{1}H} NMR (162 MHz; $CDCl_3$): +22.1 (s, J_{PSe} = 241.8 Hz). ^{77}Se{^{1}H} NMR (76 MHz; toluene): +169.5 (d, J_{SeP} = 243.3 Hz). ^{13}C{^{1}H} NMR (101 MHz; $CDCl_3$): 138.5 (d, J_{CP} = 26.02 Hz), 133.4 (d, J_{CP} = 20.61 Hz), 129.2 (s), 128.8 (d, J_{CP} = 6.27 Hz), 34.4 (d, J_{CP} = 4.45 Hz), 27.0 (d, J_{CP} = 20.61 Hz), 23.2 (s), 13.7 (s). HRMS (APCI+): Found $[M+H]^+$ m/z 322.0450 (323.0462).



5

Bis(4-methoxyphenyl)(phenylselanyl)phosphane (5):

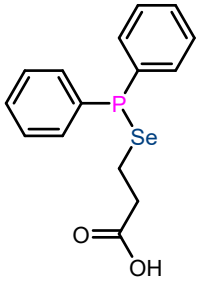
Tetra(*p*-anisyl)diphosphane (150 mg, 0.305 mmol) and diphenyl diselenide (95 mg, 0.305 mmol) were added to a Schlenk flask, dissolved in THF (10 ml), and stirred for 10 min. The solvent was removed under reduced pressure affording **5** as a yellow oil (114 mg, 79% yield). ^{1}H NMR (400 MHz; $CDCl_3$): 7.54 (m, 6H, Ar*H*), 7.23 (m, 3H, Ar*H*), 6.91 (m, 4H, Ar*H*), 3.82 (s, 6H, CH_3). ^{31}P{^{1}H} NMR (162 MHz; $CDCl_3$): +29.8 (s, J_{PSe} = 223.2 Hz). ^{77}Se{^{1}H} NMR (57 MHz; $CDCl_3$): +317.1 (d, J_{SeP} = 223.4 Hz). ^{13}C{^{1}H} NMR (100 MHz; $CDCl_3$): 160.8 (s), 134.8 (d, J_{CP} = 22.2 Hz), 133.8 (d, J_{CP} = 5.0 Hz), 131.7 (s), 129.2 (s), 128.1 (d, J_{CP} = 25.6 Hz), 127.3 (s), 114.4 (d, J_{CP} = 7.1 Hz), 55.4 (s). HRMS (APCI+): Found $[M+H]^+$ m/z 403.0362 (403.0361)).



6

(Phenylselanyl)di-*p*-tolylphosphane (6):

Tetra(*p*-tolyl)diphosphane (150 mg, 0.350 mmol) and diphenyl diselenide (110 mg, 0.350 mmol) were added to a Schlenk flask, dissolved in THF (10 ml) and then stirred for 20 min. The solvent was removed under reduced pressure affording **6** as a yellow oil (221 mg, 90% yield). ^{1}H NMR (400 MHz; $CDCl_3$): 7.50 (m, 6H, Ar*H*), 7.19 (m, 7H, Ar*H*), 2.36 (s, 6H, CH_3). ^{31}P{^{1}H} NMR (162 MHz; $CDCl_3$): +30.2 (s, J_{PSe} = 225.2 Hz). ^{77}Se{^{1}H} NMR (57 MHz; $CDCl_3$): +311.4 (d, J_{SeP} = 225.4 Hz). ^{13}C{^{1}H} NMR (101 MHz; $CDCl_3$): 139.4 (s), 133.9 (s), 133.7 (d, J_{CP} = 5.9 Hz), 133.6 (s), 133.3 (d, J_{CP} = 21.0 Hz), 129.5 (d, J_{CP} = 6.65 Hz), 129.2 (s), 127.3 (s), 21.5 (s). HRMS (APCI+): Found $[M+H]^+$ m/z 371.0468 (371.0462).



7

3-((diphenylphosphanyl)selanyl)propanoic acid (7):

Tetraphenyldiphosphane (100 mg, 0.270 mmol) and 3,3'-diselanediyldipropionic acid (82 mg, 0.270 mmol) were added to a Schlenk flask, dissolved in THF (10 ml) and then stirred for 20 min. The solvent was removed under reduced pressure affording **7** as a colourless oil (93 mg, 51% yield). ^{1}H NMR (400 MHz; $CDCl_3$): 10.6 (bs, COO*H*), 7.19–7.51 (m, 10H, Ar*H*), 2.91 (q, 2H, J_{HH} = 7.7 Hz), 2.75 (t, 2H, J_{HH} = 7.3 Hz). $^{31}P\{^{1}H\}$ NMR (162 MHz; $CDCl_3$): +23.0 (s, J_{PSe} = 235.7 Hz). $^{77}Se\{^{1}H\}$ NMR (57 MHz; $CDCl_3$): +394.3 (d, J_{SeP} = 237.8 Hz). $^{13}C\{^{1}H\}$ NMR (101 MHz; $CDCl_3$): 177.8 (s), 137.25 (d, J_{CP} = 25.6 Hz), 133.2 (d, J_{CP} = 20.6 Hz), 129.2 (s), 128.7 (d, J_{CP} = 6.3 Hz), 36.5 (d, J_{CP} = 4.8 Hz), 19.7 (d, J_{CP} = 22.5 Hz). HRMS (APCI+): Found $[M+H]^+$ m/z 339.0034 (339.0048).

Molybdenum complexation studies

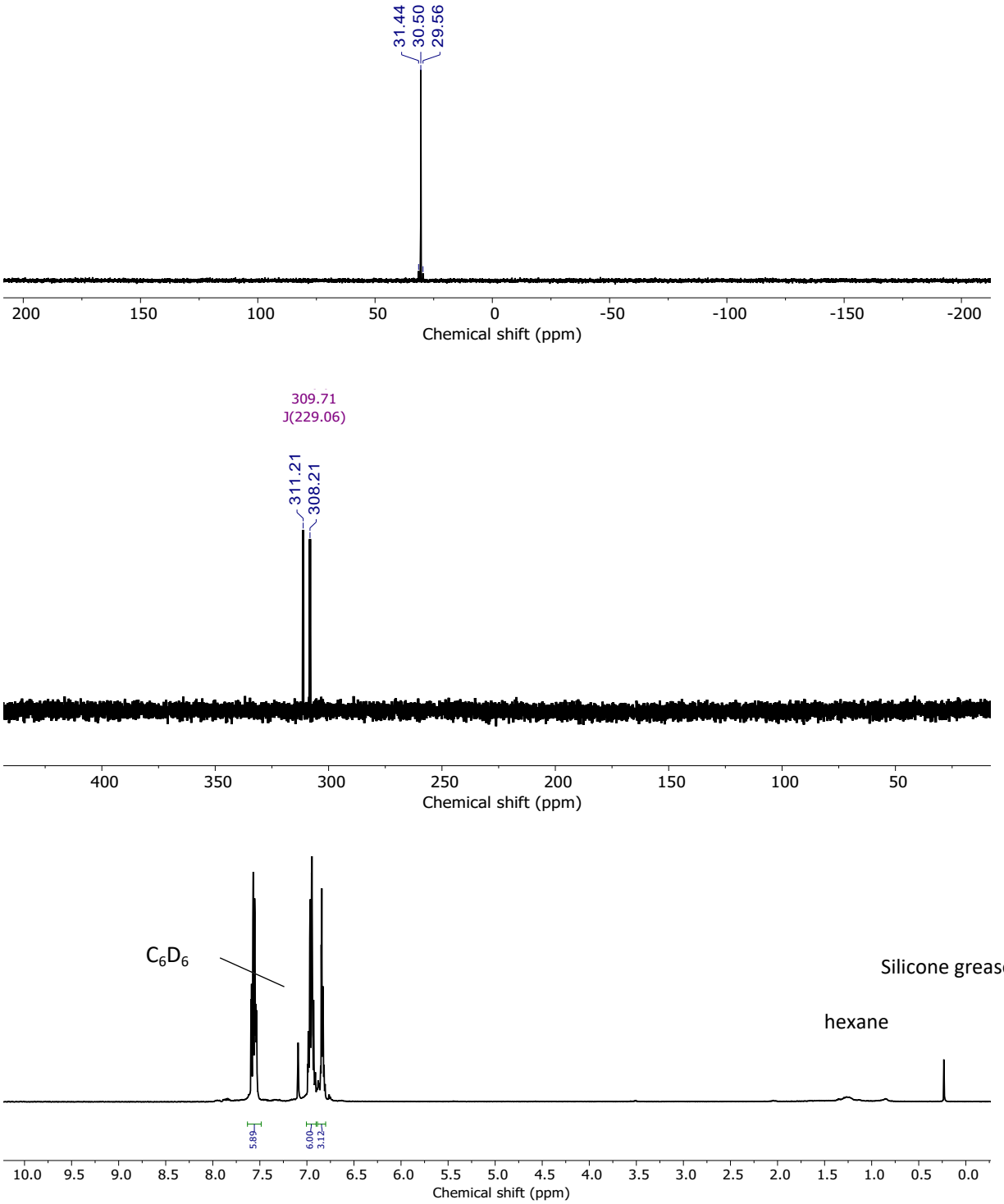
$[Mo(CO)_4(nbd)]$ (15 mg, 0.050 mmol) and either **1** or **7** (34 mg, 0.10 mmol) were added to a J Young's NMR tube, CD_2Cl_2 (2 ml) was added and the mixture shaken vigorously for 5 min. In this time most of the reactants dissolved forming a pale yellow solution, although some $[Mo(CO)_4(nbd)]$ remained undissolved as a dark green powder. The NMR reaction was then left for 17 h, prior to the removal of volatiles under reduced pressure affording a yellow-brown residue. The residue was then divided into two portions, one that was redissolved prior to further NMR analysis and the second portion analysed by FTIR. Multiple attempts to obtain single crystals suitable for X-ray crystallography from mixtures of **8/9** via vapour diffusion were unsuccessful.

TEMPO inhibition of $Ph_2P–PPh_2$ / PhE–EPh (E = Se or S)

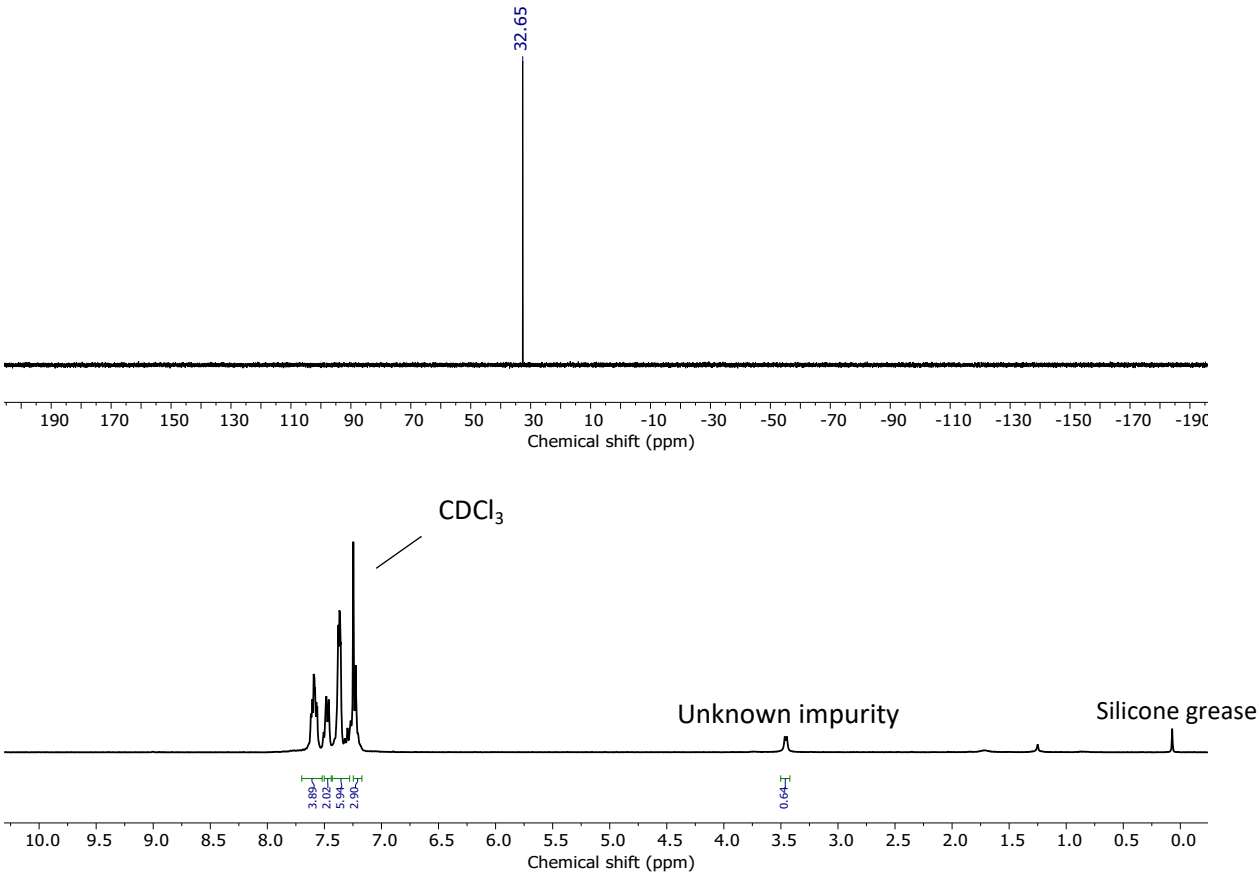
Tetraphenyldiphosphane (6 mg, 0.016 mmol), diphenyl diselenide (5 mg, 0.016 mmol) and 2,2,6,6-tetramethylpiperidine- 1-oxyl (TEMPO, 10 mg, 0.064 mmol) were added to an NMR tube prior to the addition of tetrahydrofuran (0.5 ml). The tube was then shaken until complete dissolution was observed and monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy after 1.5 h.

Tetraphenyldiphosphane (10 mg, 0.027 mmol), diphenyl disulfide (6.2 mg, 0.028 mmol) and 2,2,6,6-tetramethylpiperidine- 1-oxyl (TEMPO, 16.9 mg, 0.108 mmol) were added to an NMR tube prior to the addition of $CDCl_3$ (0.5 ml). The tube was shaken until complete dissolution was observed and then left to stand, with monitoring by $^{31}P\{^{1}H\}$ NMR spectroscopy over a 24 h period. A control experiment under the same conditions but without added TEMPO was monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy at the same intervals over 24 h.

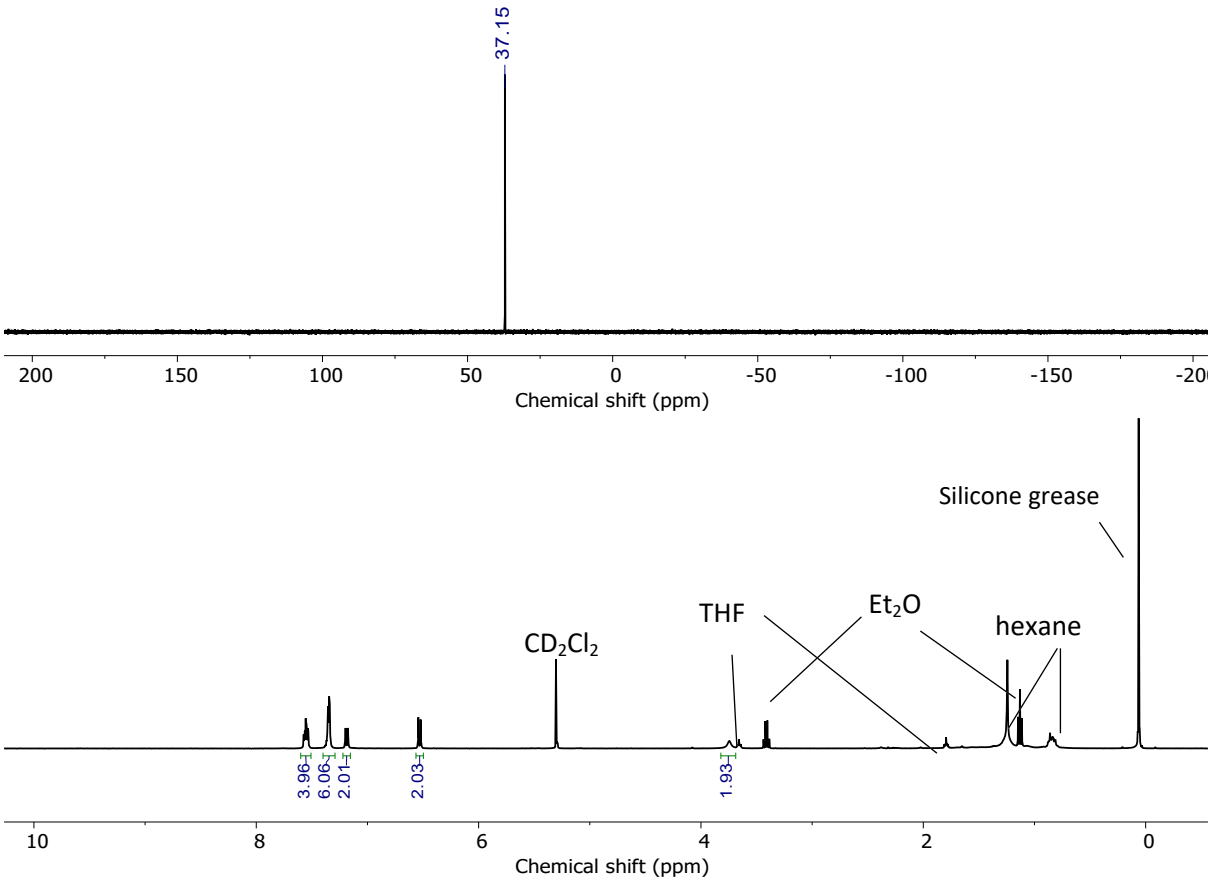
ESI 2: $^{31}P\{^{1}H\}$, $^{77}Se\{^{1}H\}$ and ^{1}H NMR spectra of isolated products **1–7**.



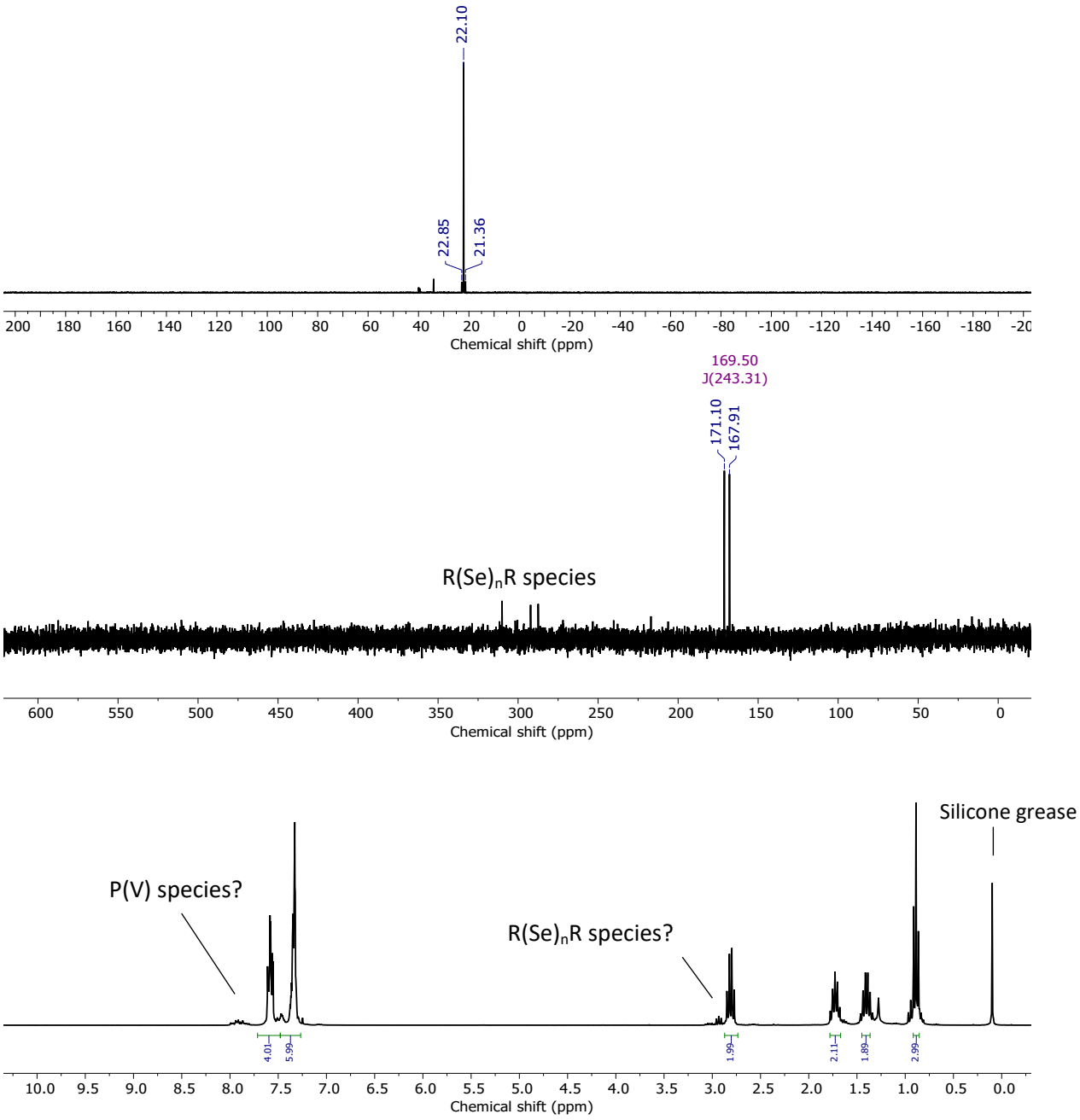
ESI 2.1. $^{31}P\{^{1}H\}$ (tetrahydrofuran), $^{77}Se\{^{1}H\}$ ($CDCl_3$) and ^{1}H (C_6D_6) NMR spectra of **1**. Small quantities of grease are observed.



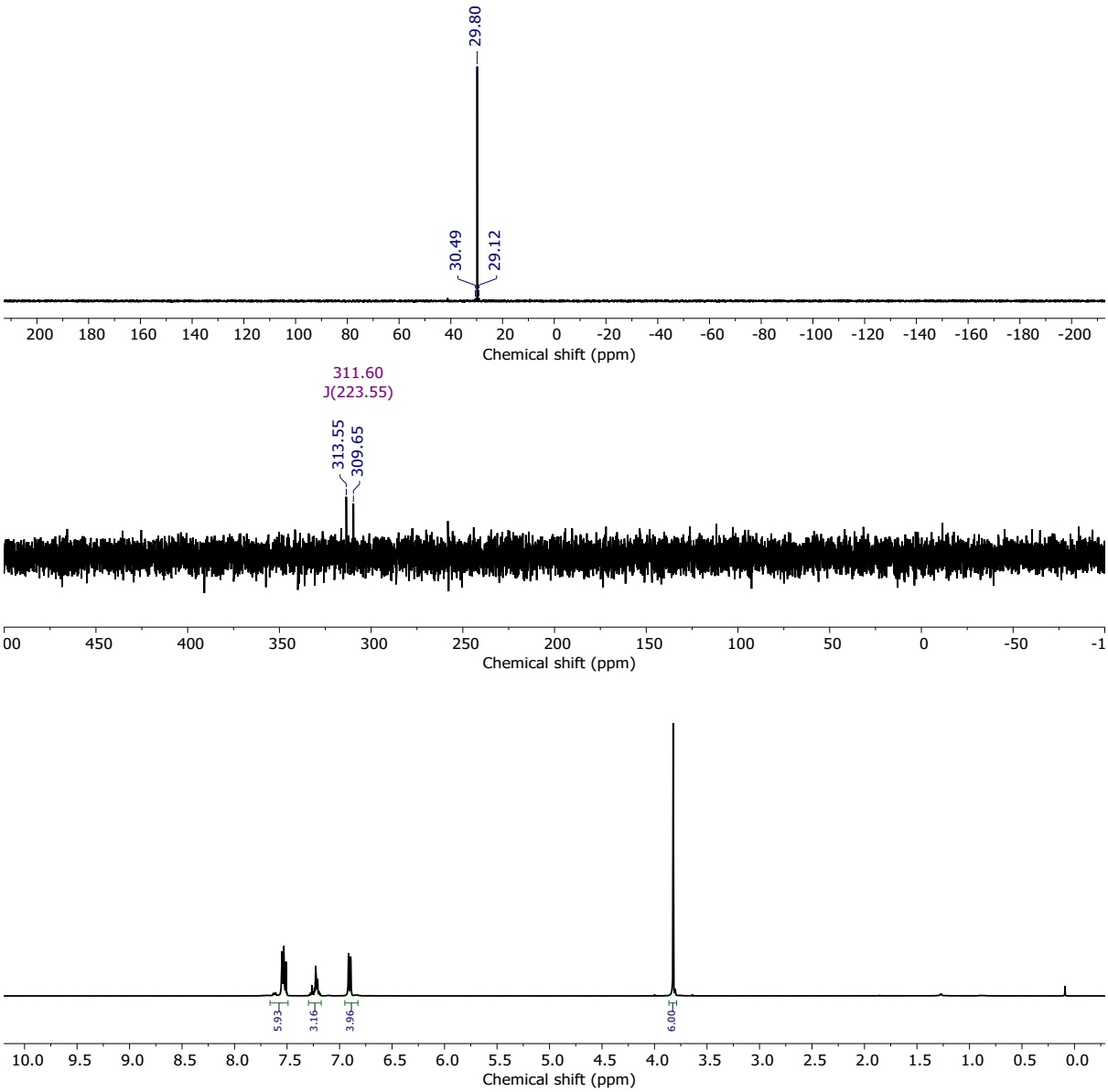
ESI 2.2. $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra of **2** in $CDCl_3$. Small quantities of grease are observed in the ^{1}H from. The doublet (J = 5.32 Hz) at 3.47 is an unknown impurity of *ca*. 4% integral (not observed in other spectra).



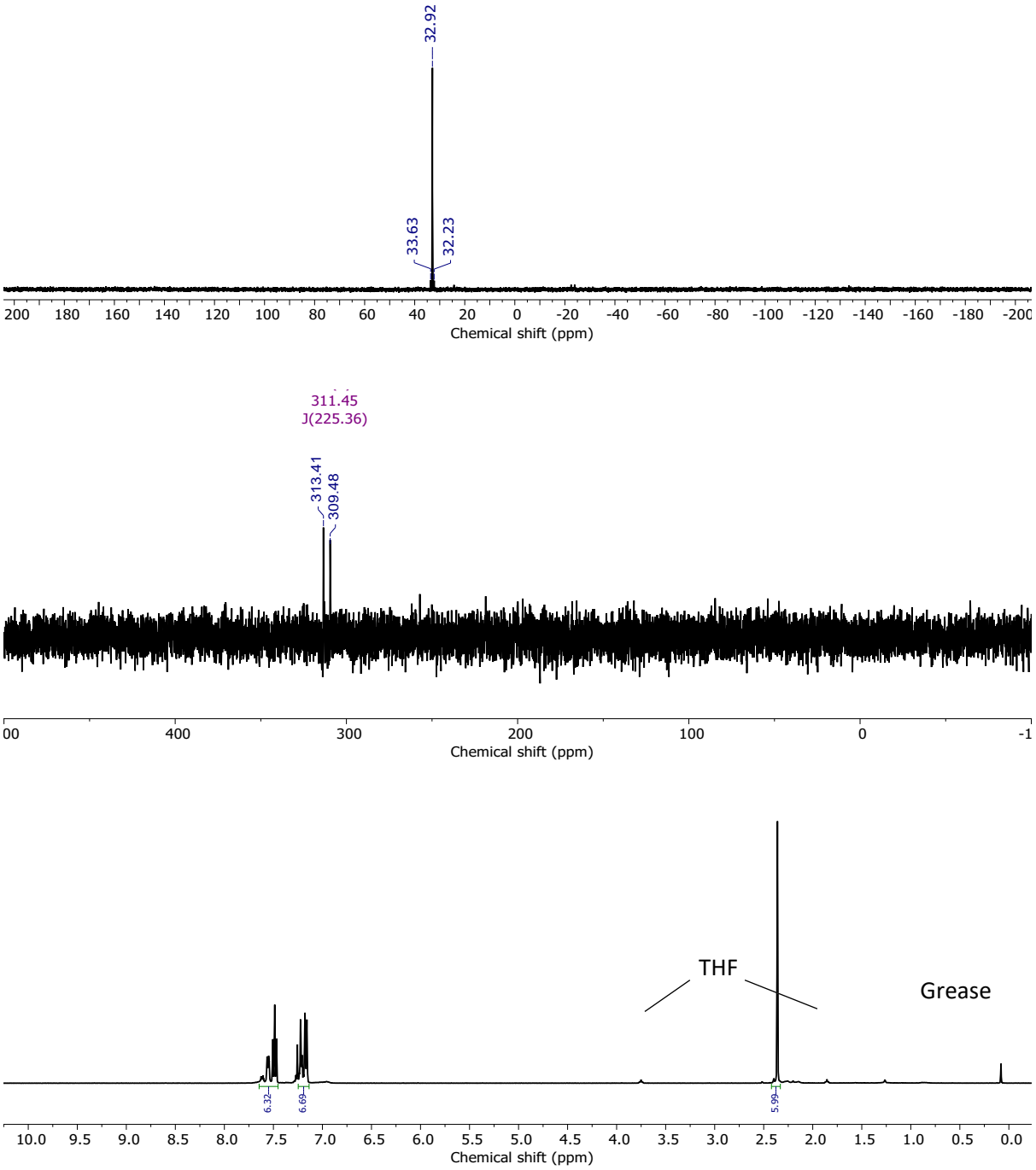
ESI 2.3. $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra of **3** (CD_2Cl_2). Significant quantities of residual solvent (tetrahydrofuran and diethyl ether) are labelled on the ^{1}H NMR spectrum, along with grease.



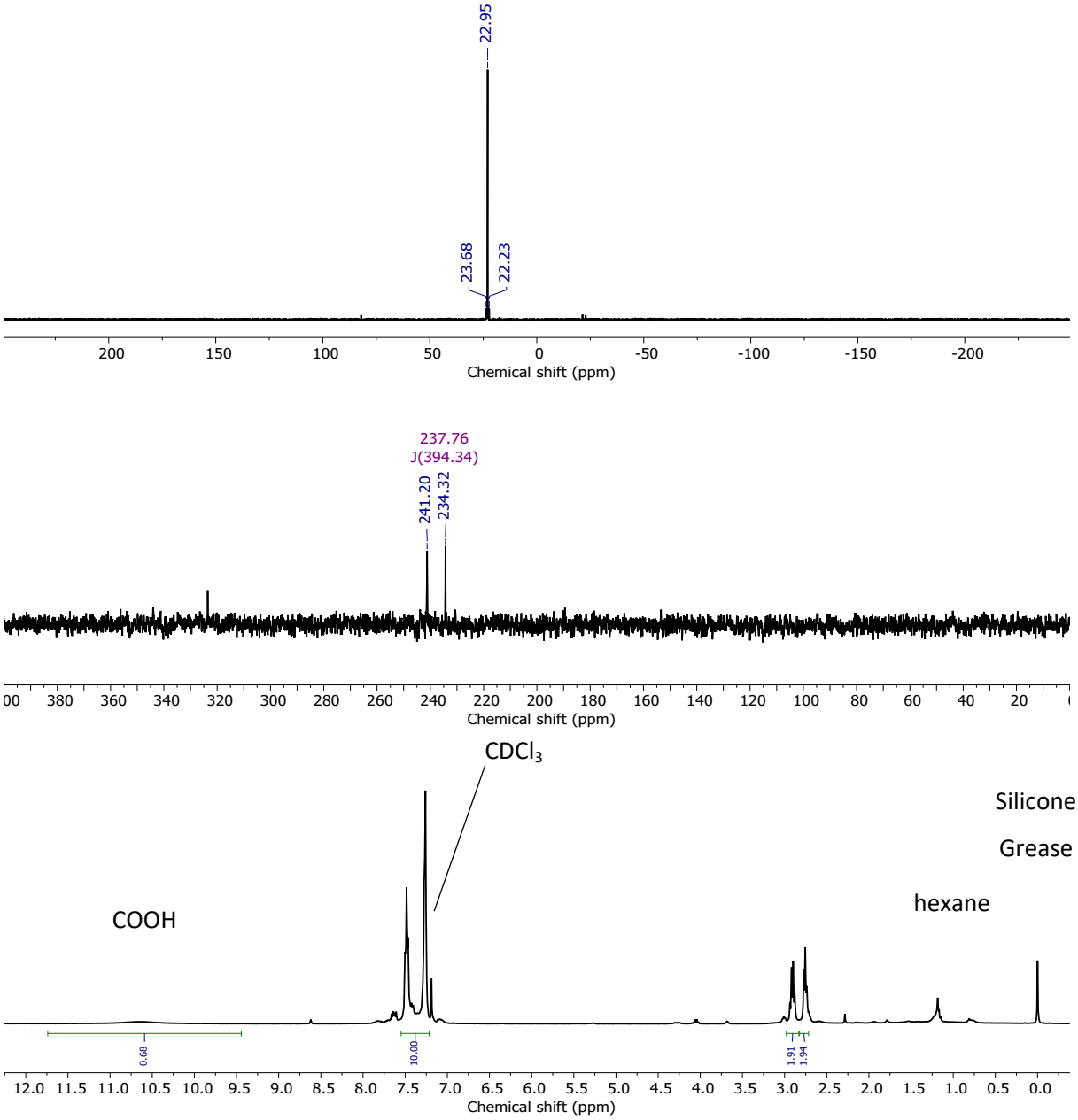
ESI 2.4. $^{31}P\{^{1}H\}$, $^{77}Se\{^{1}H\}$ and ^{1}H NMR spectra of **4** ($CDCl_3$). The small additional resonances in the ^{77}Se correspond to RSeR, RSeSeR, RSeSeSeR and other polyselenides. In the ^{1}H NMR spectrum, small aromatic resonances may correspond to P(V) species (see ^{31}P spectrum) and minor alkyl resonances (see ^{77}Se spectrum) corresponding to RSe_nR species are observed, which approximate to 10% of the total spectral integral, though due to overlap this figure is only an estimate.



ESI 2.5. $^{31}P\{^{1}H\}$, $^{77}Se\{^{1}H\}$ and ^{1}H NMR spectra of **5** ($CDCl_3$).



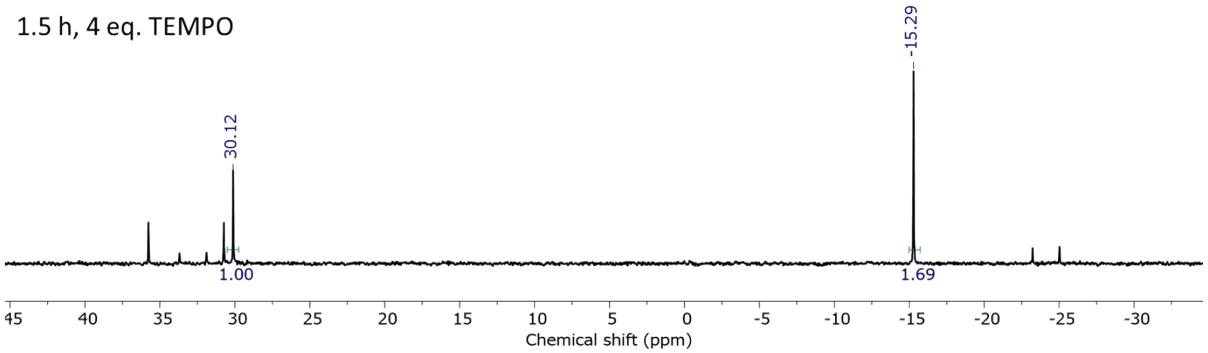
ESI 2.6. $^{31}P\{^{1}H\}$, $^{77}Se\{^{1}H\}$ and ^{1}H NMR spectra of **6** ($CDCl_3$). Trace quantities of residual solvent (tetrahydrofuran) and grease are labelled on the ^{1}H spectrum.



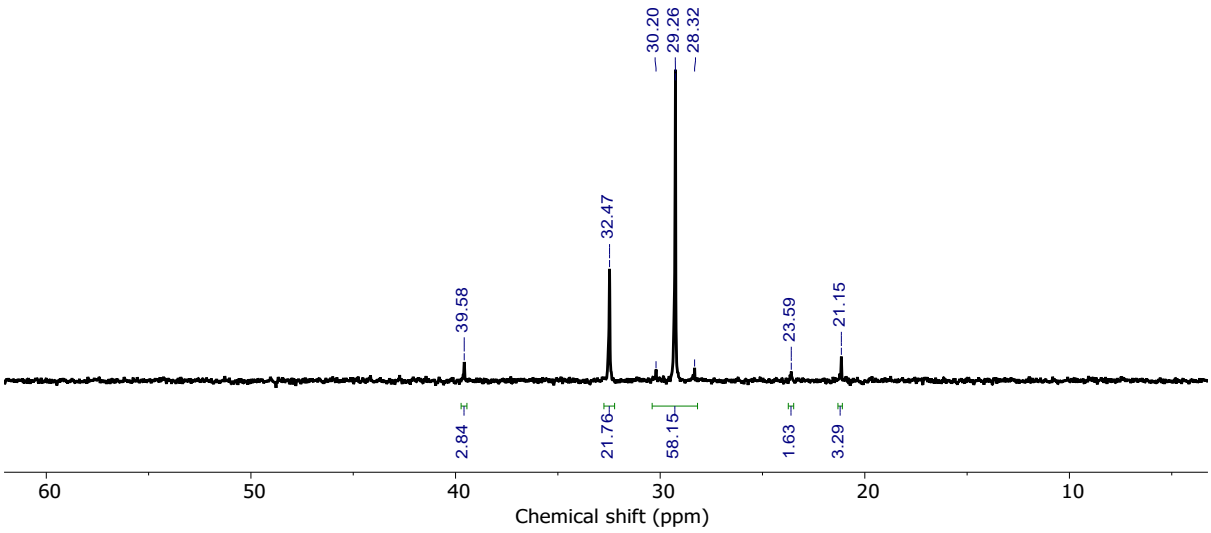
ESI 2.7. $^{31}P\{^{1}H\}$, $^{77}Se\{^{1}H\}$ and ^{1}H NMR spectra of **7** ($CDCl_3$). A range of minor unidentified impurities in the baseline of the ^{1}H NMR spectrum are visible, though the sum of all these integrations (excluding grease) accounts for <3% of the total. The most likely candidates to assign to the impurities are RSe_nR (particularly RSeR), which were formed in small quantities during diselenide synthesis.

ESI 3: $^{31}P\{^{1}H\}$ NMR spectra of test reactions.

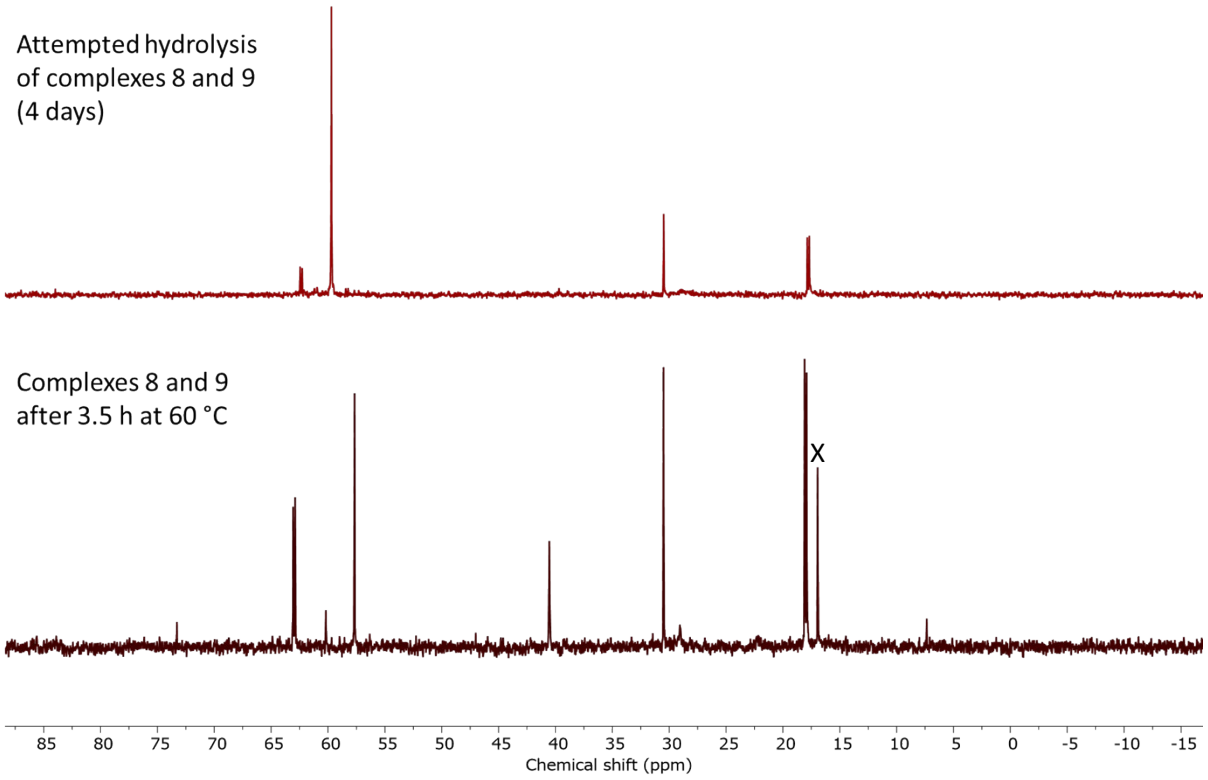
Note that each of these spectra correspond to NMR-scale reactions that were not stirred. The observed rates of reaction were slower than those reported in the syntheses of ESI 1.



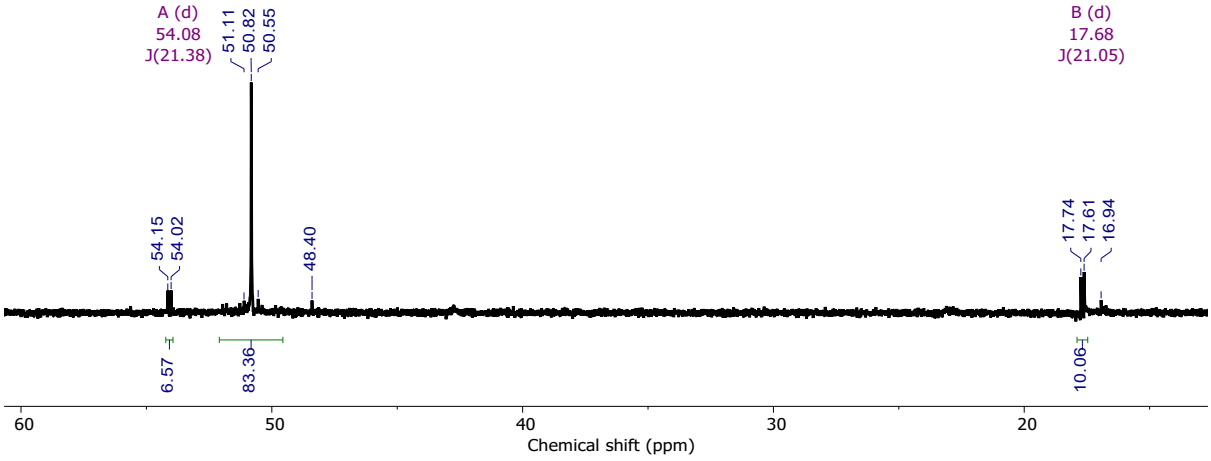
ESI 3.1. TEMPO inhibition of Ph_2P–SePh (**1**) formation (signal at δ 30.1) in tetrahydrofuran. After 1.5 h the ratio of PSe to PP is 1:1.7; accounting for double the phosphorus content in the PP resonance, this equates to a ratio of 54% conversion. In the absence of TEMPO this reaction proceeds to completion in <1 min at room temperature. The doublets at -24.1 and +32.8 ppm are attributed to $Ph_2P(O)$–PPh_2 and the signals at +30.8 and +35.8 are tentatively assigned to (TEMPO)$P(=O)Ph_2$ and (TEMP)$P(O)Ph_2$ [1-(diphenylphosphoryl)-2,2,6,6-tetramethylpiperidine] based on the similarity of their chemical shifts with the reported values.[1,4]



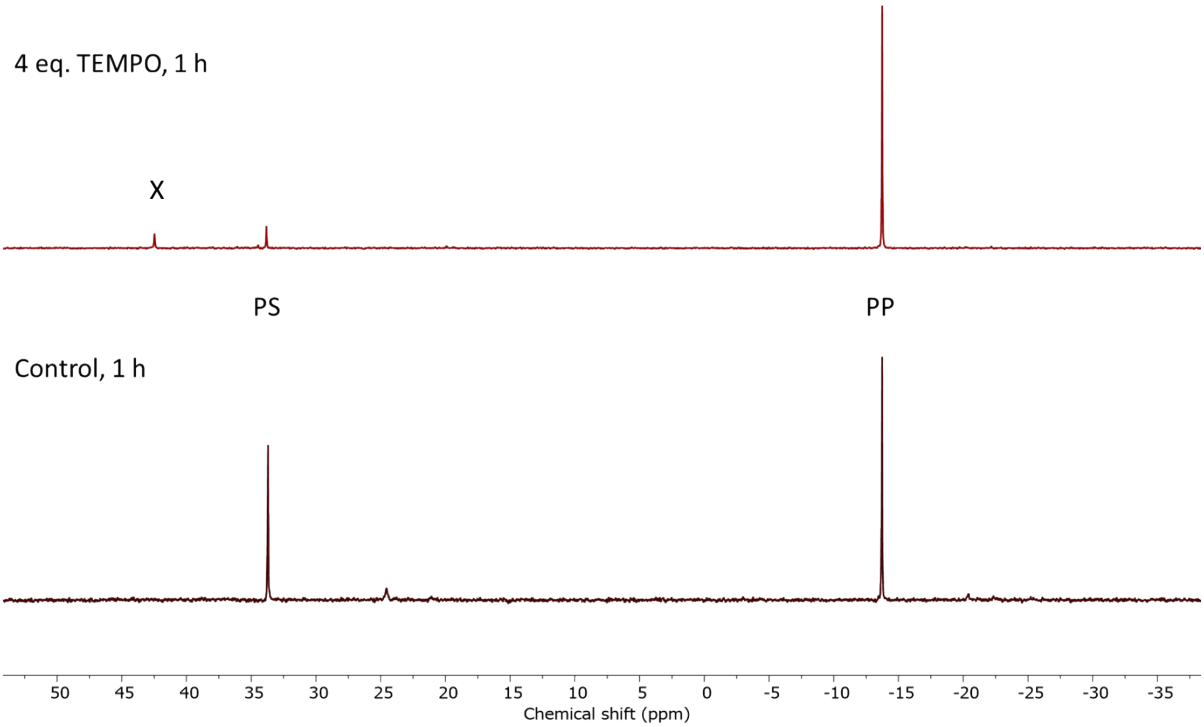
ESI 3.2. Attempted hydrolysis of **1**. After 2 days in 0.3 ml $CDCl_3$ and 0.2 ml DI H_2O (i.e. water-saturated $CDCl_3$), approximately 60% of the initial Ph_2P–SePh remains. The major hydrolysis product at +32.5 ppm corresponds to $Ph_2P(O)OH$.[5] The identity of the species responsible for the minor peak at +39.6 is unknown.



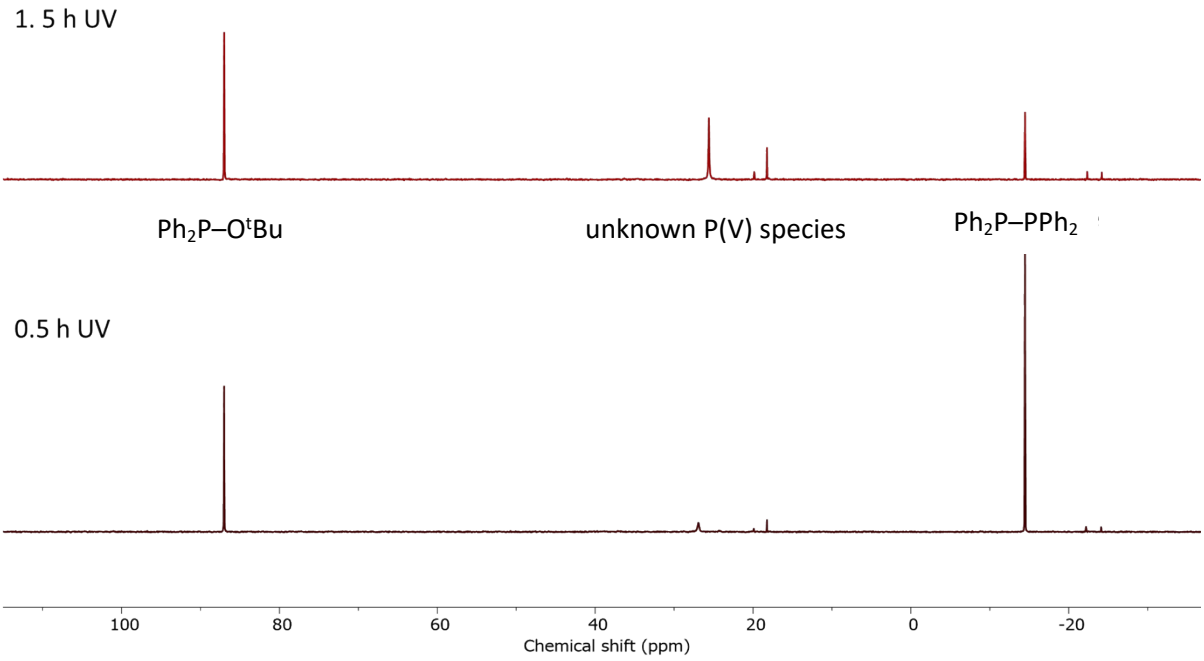
ESI 3.3. Top: molybdenum complexes of **1** (**8** and **9**) after attempted hydrolysis (4 days in water-saturated CD_2Cl_2), though negligible change is observed compared with Figure 2 in main article. Bottom: after heating to 60 °C for 3.5 h the pair of doublets assigned to complex **9** is the dominant species and the signal at *ca.* +16.9 (labelled X in Figure 2) has increased significantly in intensity.



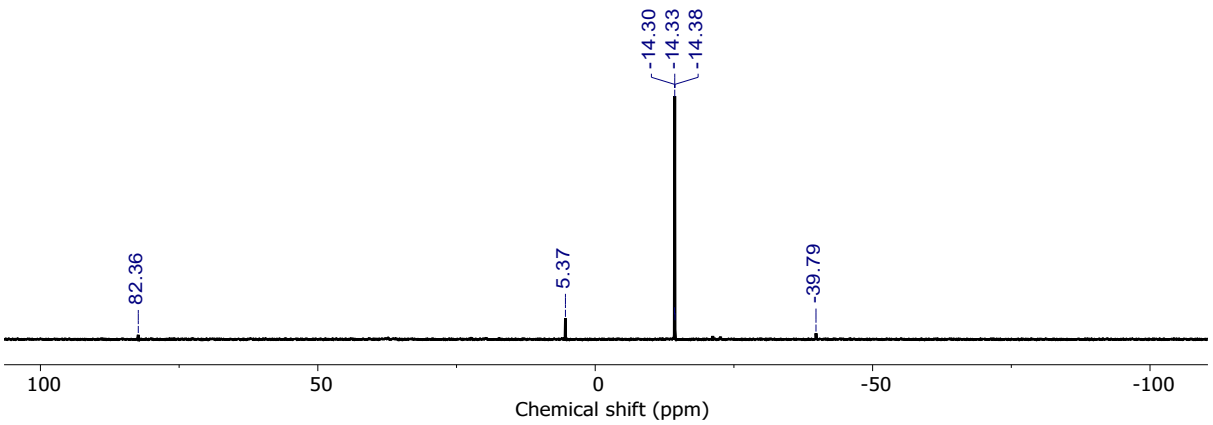
ESI 3.4. Molybdenum complex of **7** ($CDCl_3$).



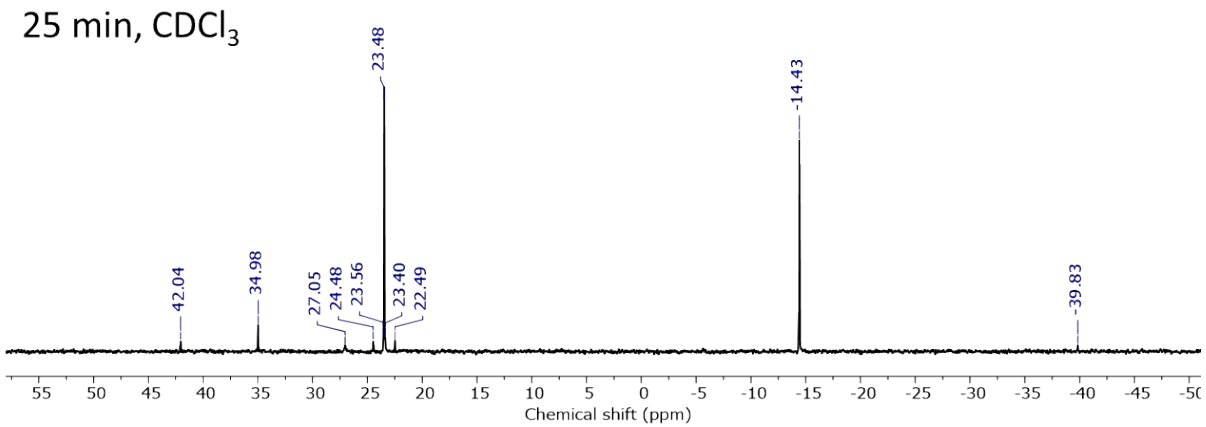
ESI 3.5. TEMPO inhibition of Ph_2P–SPh (**2**) formation ($CDCl_3$). After 1 h the control reaction exhibited 56% conversion to PS and in the inhibited reaction, only 16% conversion (for simplicity only the PP and PS species are considered in these calculations). The resonance X at +42.5 is downfield of the expected TEMPO-PPh_2 adduct and is unassigned.[1,4]



ESI 3.6. The reaction of tetraphenyldiphosphane with di(*tert*)butyl peroxide in C_6D_6.



ESI 3.7. The attempted reaction of tetraphenyldiphosphane with diphenyl ditelluride in C_6D_6 (after 24 h). A small resonance at -39.8 ppm corresponds to Ph_2PH.



ESI 3.8. The attempted reaction of tetraphenyldiphosphane and dibenzyl diselenide in $CDCl_3$. Within 25 min, a significant quantity of the desired species (Ph_2P–SeBn) appears to have formed (tentatively assigned as the resonance at +23.48 ppm); however, there are multiple unknown species and this reaction is seemingly much slower than all other PSe-forming reactions reported here.

ESI 4: Computational details.

ESI 4.1. Computational methods.

Geometry optimisation and single point energy calculations were performed in ORCA v. 4.2.1.[6] Unless otherwise specified calculations utilised the resolution of identity with the chain of spheres approximation for the exchange integrals (RIJCOSX) with the default auxiliary basis sets (*AutoAux* keyword).[7] Geometry optimisations were performed with the hybrid PBE0[8] functional, D3BJ dispersion correction[9,10] and the def2-SVP basis set.[11] Where applicable, vibrational frequencies were calculated at the same level of theory to assign stationary points as either minima or transition structures, as characterised by the presence of none or a single imaginary frequency respectively. Thermodynamic corrections were calculated at 298.15 K in a 1 M standard state using the quasi-rigid rotor harmonic oscillator (q-RRHO) approximation.[11] Single point energies were calculated using the hybrid B3LYP[1214] with the D3BJ dispersion corrected (B3LYP-D3BJ) in conjunction with the larger def2-TZVP basis set on all atoms with minimal augmentation (ma- prefix) for reactions involving radicals.[15] Transition state searches, conformational searches and combinatorial reaction energy calculations were performed with autodE v 1.1.[16]

ESI 4.2. Equilibria.

To establish an accurate computational method to predict the equilibria between X_2PPX_2 and X_2PY the smallest model system was considered, where X=H (**Table S1**). Comparing DFT energies to the coupled-cluster [DLPNO-CCSD(T)] reference values we find B3LYP to perform well, and that calculated free energy differences are very close to their potential energy analogues. For this reason, we select the B3LYP-D3BJ method and potential energies for optimal efficiency. The latter approximation also avoids any ambiguity in treating low-frequency phenyl rotation normal modes in the entropy calculation. An extended set of reaction energies presented in **Table 1** are shown in **Table S2**.

Table S1. Calculated reaction energies and enthalpies for $H_2PPH_2 + Y_2 \rightarrow 2\ H_2PY$ at different levels of theory. Geometries and thermal corrections calculated at the PBE0-D3BJ/def2-SVP level of theory. DFT single points evaluated using the def2-TZVP basis set while DLPNO-CCSD(T) use the def2-TZVPP basis and default auxiliary basis sets.

		ΔE(DFT) / kcal mol^{-1}			**DLPNO-CCSD(T)**		
Entry	**Y**	**PBE0-D3BJ**	**B3LYP-D3BJ**	**M06-2X**	**ΔE / kcal mol^{-1}**	**ΔH / kcal mol^{-1}**	**ΔG / kcal mol^{-1}**
1	OH	-67.2	-69.5	-73.5	-70.9	-70.6	-70.3
2	SH	-9.2	-9.3	-10.3	-9.9	-9.7	-9.2
3	SeH	-6.8	-6.7	-7.6	-7.1	-6.9	-7.5
4	NH_2	-26.0	-28.0	-30.3	-28.6	-29.4	-29.3

Table S2. Calculated reaction energies for Ph_2PPPh_2 + reactant → product, calculated at the B3LYP-D3BJ/def2-TZVP//PBE0-D3BJ/def2-SVP level of theory.

Entry	**Reactant**	**Product**	**ΔE / kcal mol^{-1}**
1	PhO–OPh	Ph_2P–OPh	-71.6
2	PhS–SPh	Ph_2P–SPh	-9.6
3	PhSe–SePh	Ph_2P–SePh	-4.0
4	PhTe–TePh	Ph_2P–TePh	4.3
5	PhNH–NHPh	Ph_2P–NMe_2	-24.6
6	Me_3Sn–$SnMe_3$	Ph_2P–$SnMe_3$	0.2
7	^{t}BuOO^{t}Bu	Ph_2P–O^{t}Bu	-69.4

ESI 4.3. Mechanistic considerations.

With a view to investigating the possibility of RSe· radicals initiating the P/Se metathesis reaction the kinetic feasibility of thermal initiation was calculated (PhSe–SePh → 2 PhSe·, **Table S3**). The standard free energy change suggests an inaccessible thermally activated pathway, with a similar endergonicity to the analogous $Ph_2P–PPh_2$ homolysis, which we found to be photoinitiated.[1]

Table S3. Calculated reaction energies for PhSeSePh → 2 PhSe·, calculated at the B3LYP-D3BJ/ma-def2-TZVP//PBE0-D3BJ/def2-SVP level of theory.

ΔE / kcal mol^{-1}	**ΔH / kcal mol^{-1}**	**ΔG / kcal mol^{-1}**
46.1	44.6	34.1

ESI 4.4. Cartesian coordinates

Optimised cartesian coordinates (Å), total potential energies (Ha).

BrC12H10P
E(PBE0-D3BJ/def2-SVP) = -3377.1404280
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -3378.6195159

C	-3.56437	0.70734	-1.02860
C	-2.25133	1.05904	-1.33617
C	-1.18678	0.43081	-0.69023
C	-1.43044	-0.55142	0.27728
C	-2.75546	-0.89201	0.58877
C	-3.81521	-0.27382	-0.06645
P	-0.11849	-1.35634	1.27713
C	1.38596	-0.57049	0.58415
C	2.02998	-0.95056	-0.59741
C	3.14675	-0.24704	-1.04131
C	3.62258	0.84771	-0.31873
C	2.98810	1.22908	0.86218
C	1.88076	0.51593	1.31804
Br	-0.08692	-3.40409	0.30241
H	-4.39434	1.20262	-1.53764
H	-2.04805	1.82846	-2.08548
H	-0.16173	0.71351	-0.93998
H	-2.95570	-1.65432	1.34760
H	-4.84109	-0.55640	0.18318
H	1.65278	-1.80413	-1.16478
H	3.64942	-0.55769	-1.96020
H	4.49600	1.39950	-0.67385
H	3.36423	2.07624	1.44047
H	1.39346	0.80777	2.25342

C12H11P
E(PBE0-D3BJ/def2-SVP) = -804.1570890
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -805.1360543

C	-3.61020	0.34581	0.77511
C	-3.04769	1.48250	0.19860
C	-1.96804	1.35954	-0.67618
C	-1.41825	0.10197	-0.95867
C	-1.99539	-1.03510	-0.37759
C	-3.08907	-0.91411	0.47692
P	0.05156	0.03711	-2.05989
C	1.41732	-0.09591	-0.82904
C	1.51737	0.83298	0.21527
C	2.60917	0.81042	1.08114
C	3.61867	-0.13875	0.91659
C	3.52504	-1.07064	-0.11706
C	2.43342	-1.04853	-0.98458
H	-4.46460	0.44140	1.44964
H	-3.46192	2.46832	0.42432
H	-1.54506	2.24777	-1.15484
H	-1.57729	-2.02192	-0.59398
H	-3.53624	-1.80654	0.92152
H	-0.01355	-1.35162	-2.38022
H	0.72684	1.57470	0.36521
H	2.67071	1.54012	1.89275
H	4.47681	-0.15126	1.59292
H	4.30622	-1.82345	-0.25370
H	2.37409	-1.78483	-1.79181

C12H10IP
E(PBE0-D3BJ/def2-SVP) = -1101.3072920
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -1102.2838149

C	-3.57509	-0.32264	0.94854
C	-2.28383	-0.26937	1.46830
C	-1.18426	-0.19012	0.61566
C	-1.36945	-0.15725	-0.77155
C	-2.67435	-0.20556	-1.28699
C	-3.76809	-0.29491	-0.43366
P	-0.00830	0.08124	-1.98126
C	1.43701	0.18253	-0.85101
C	1.85808	1.48897	-0.56470
C	2.87522	1.71658	0.36219
C	3.49880	0.63979	0.98957
C	3.10058	-0.66377	0.69081
C	2.07164	-0.89353	-0.22046

I 0.14809 -2.23096 -2.90878
H -4.43420 -0.38638 1.62016
H -2.12453 -0.29261 2.54961
H -0.17731 -0.14901 1.03517
H -2.83147 -0.17998 -2.36963
H -4.77748 -0.33878 -0.84997
H 1.37722 2.33313 -1.06890
H 3.19221 2.73746 0.58950
H 4.30437 0.81870 1.70596
H 3.59442 -1.50920 1.17511
H 1.75053 -1.91423 -0.44366

C12ClH10P
E(PBE0-D3BJ/def2-SVP) = -1263.4975340
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -1264.7366069

C 3.63972 0.88213 -0.42345
C 2.67291 1.22468 0.52702
C 1.56642 0.40483 0.72402
C 1.41920 -0.76942 -0.02835
C 2.39426 -1.11015 -0.97332
C 3.49991 -0.28207 -1.17574
P 0.01009 -1.92714 0.17641
C -1.40873 -0.75562 0.17659
C -2.45913 -0.86316 1.09596
C -3.58359 -0.04756 0.97782
C -3.67714 0.87442 -0.06443
C -2.63588 0.98387 -0.98678
C -1.50665 0.17616 -0.86837
Cl 0.15724 -2.31619 2.23246
H 4.50648 1.52996 -0.57588
H 2.78631 2.13824 1.11528
H 0.80890 0.66707 1.46761
H 2.28761 -2.03280 -1.55037
H 4.25674 -0.55520 -1.91523
H -2.38549 -1.57957 1.91804
H -4.39367 -0.13962 1.70641
H -4.56328 1.50618 -0.16289
H -2.70246 1.70618 -1.80447
H -0.68987 0.28447 -1.58847

C24H20P2
E(PBE0-D3BJ/def2-SVP) = -1607.1615840
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -1609.1099122

C 3.68344 -3.75691 0.38387
C 2.41552 -3.71946 0.95891
C 1.52676 -2.69477 0.63256
C 1.89184 -1.69235 -0.27514
C 3.16733 -1.74836 -0.85916
C 4.05729 -2.76502 -0.52524
P 0.73542 -0.38134 -0.85306
C 1.61005 1.14960 -0.32784
C 2.44322 1.21461 0.79700
C 2.97797 2.43390 1.20624
C 2.68284 3.60161 0.50069
C 1.86179 3.54354 -0.62446
C 1.33256 2.32322 -1.04018
P -0.74970 -0.35795 0.83476
C -2.05227 -1.45326 0.13913
C -3.37222 -1.29533 0.58940
C -4.38510 -2.12742 0.12233
C -4.09499 -3.14590 -0.78844
C -2.78351 -3.32861 -1.22161
C -1.76961 -2.48828 -0.76197
C -1.43427 1.30744 0.45545
C -2.25897 1.57066 -0.64762
C -2.68217 2.87025 -0.91510
C -2.28195 3.92217 -0.08975
C -1.46181 3.66894 1.00894
C -1.04502 2.36729 1.28399
H 4.38368 -4.55382 0.64479
H 2.11091 -4.48756 1.67417
H 0.54467 -2.67496 1.11108
H 3.46970 -0.97693 -1.57402
H 5.04952 -2.78486 -0.98209
H 2.66521 0.30437 1.35869
H 3.62117 2.47658 2.08887
H 3.09740 4.55636 0.83404
H 1.62115 4.45294 -1.17994
H 0.67427 2.27875 -1.91227
H -3.61235 -0.49510 1.29572
H -5.40864 -1.97478 0.47395
H -4.89047 -3.79587 -1.15947

H -2.54150 -4.12092 -1.93439
H -0.75293 -2.63628 -1.13540
H -2.56817 0.75135 -1.30037
H -3.32573 3.06704 -1.77630
H -2.61695 4.93955 -0.30790
H -1.14339 4.48711 1.65872
H -0.39188 2.16873 2.13841

C4H12P2
E(PBE0-D3BJ/def2-SVP) = -841.6017890
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -842.2867335

C -1.77567 1.36148 0.45389
P -0.72309 -0.11518 0.84267
C -1.77775 -1.44471 0.09655
P 0.72232 0.11277 -0.84009
C 1.77452 1.44503 -0.09545
C 1.77871 -1.36140 -0.45422
H -2.70260 1.30865 1.04453
H -2.03742 1.42926 -0.61423
H -1.24436 2.27753 0.75338
H -2.71296 -1.52087 0.67196
H -1.25903 -2.41199 0.17648
H -2.02495 -1.25389 -0.96044
H 2.02306 1.25676 0.96169
H 1.25485 2.41151 -0.17769
H 2.70947 1.52050 -0.67143
H 1.24760 -2.27790 -0.75301
H 2.70395 -1.30740 -1.04742
H 2.04327 -1.43024 0.61312

Cl2
E(PBE0-D3BJ/def2-SVP) = -919.7633540
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -920.2929551

Cl 1.01247 0.00000 0.00000
Cl -1.01247 0.00000 0.00000

C2FH6P
E(PBE0-D3BJ/def2-SVP) = -520.4826540
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -521.0215296

C 1.41830 0.06417 0.13992
P -0.07982 0.70434 0.98748
C -1.37158 0.05384 -0.14000
F -0.21042 -0.44074 2.15468
H 1.53023 0.59040 -0.82155
H 1.35724 -1.01986 -0.04502
H 2.30853 0.28027 0.74901
H -2.34835 0.15498 0.35695
H -1.20650 -1.00350 -0.40146
H -1.39565 0.65802 -1.05972

Br2
E(PBE0-D3BJ/def2-SVP) = -5147.0781980
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -5148.0831228

Br 1.14799 0.00000 0.00000
Br -1.14799 0.00000 0.00000

C2H7P
E(PBE0-D3BJ/def2-SVP) = -421.3829750
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -421.7292782

C 1.43332 -0.05142 0.08319
P -0.11219 0.60012 0.87287
C -1.36857 0.16111 -0.41495
H 1.68714 0.58359 -0.77849
H 2.26235 0.02416 0.80306
H 1.35076 -1.09366 -0.26273
H -0.35274 -0.51040 1.74135
H -1.22451 0.81387 -1.28874
H -2.37241 0.36434 -0.01138
H -1.32072 -0.88704 -0.74889

F2
E(PBE0-D3BJ/def2-SVP) = -199.1560020
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -199.5311866

F 0.68797 0.00000 0.00000

F -0.68797 0.00000 0.00000

C12FH10P
E(PBE0-D3BJ/def2-SVP) = -903.2559020
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -904.4251256

C 3.44846 -0.29047 1.10892
C 2.81699 -1.36754 0.48673
C 1.81179 -1.13963 -0.45091
C 1.41157 0.16816 -0.74968
C 2.05680 1.24582 -0.13711
C 3.07321 1.01323 0.78826
P 0.06255 0.42852 -1.96600
C -1.36837 0.15740 -0.84831
C -2.06015 1.22582 -0.27108
C -3.12034 0.97884 0.60013
C -3.49512 -0.32993 0.90017
C -2.82336 -1.39783 0.30521
C -1.77376 -1.15559 -0.57878
F 0.06442 2.06593 -1.95868
H 4.24255 -0.47129 1.83727
H 3.11987 -2.38908 0.73015
H 1.33387 -1.98736 -0.95220
H 1.75504 2.26392 -0.39078
H 3.57506 1.85821 1.26510
H -1.76013 2.24842 -0.50840
H -3.65703 1.81632 1.05156
H -4.32230 -0.52176 1.58784
H -3.12838 -2.42344 0.52844
H -1.26324 -1.99669 -1.05855

C2H6IP
E(PBE0-D3BJ/def2-SVP) = -718.5340650
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -718.8777893

C 1.39291 -0.09078 -0.32590
P -0.25399 0.55514 -0.85853
C -1.34427 -0.45148 0.23369
I -0.26117 2.70250 0.38853
H 1.49635 -1.10787 -0.74018
H 2.18814 0.53365 -0.75640
H 1.50945 -0.12957 0.76740
H -1.33988 -1.47946 -0.16608
H -1.01544 -0.46640 1.28346
H -2.37202 -0.06584 0.17411

C2ClH6P
E(PBE0-D3BJ/def2-SVP) = -880.7237890
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -881.3316345

C 1.39630 -0.25772 0.06049
P -0.02460 0.79591 0.57210
C -1.41949 -0.18954 -0.11254
Cl 0.10330 2.24029 -0.94154
H 2.32943 0.29756 0.23589
H 1.40964 -1.15962 0.69278
H 1.34300 -0.55534 -0.99801
H -1.54747 -1.08834 0.51146
H -2.34023 0.40798 -0.04860
H -1.24999 -0.49180 -1.15739

H2
E(PBE0-D3BJ/def2-SVP) = -1.1640140
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -1.1729802

H 0.38046 0.00000 0.00000
H -0.38046 0.00000 0.00000

BrC2H6P
E(PBE0-D3BJ/def2-SVP) = -2994.3679190
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -2995.2141197

C -1.25578 0.61641 -0.56089
P 0.02829 -0.57135 -1.13850
C 1.40645 -0.12635 -0.00130
Br -0.74472 -2.41768 -0.09330
H -2.21786 0.35060 -1.02172
H -0.97074 1.62085 -0.91523
H -1.36524 0.62617 0.53377
H 1.80828 0.84430 -0.33679
H 1.09049 -0.05225 1.05011

H 2.20803 -0.87329 -0.09344

I2
E(PBE0-D3BJ/def2-SVP) = -595.3219880
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -595.4403928

I 1.83807 0.00000 0.00000
I -1.83807 0.00000 0.00000

C12H10Se2
E(PBE0-D3BJ/def2-SVP) = -5264.4157000
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -5266.1421828

C -1.93146 -1.05585 -0.03952
Se -0.43799 -2.20045 0.34320
Se 0.62050 -1.12599 2.09835
C 2.01302 -0.22923 1.12613
C 3.33699 -0.49382 1.48457
C 4.37878 0.13763 0.80554
C 4.10064 1.02315 -0.23448
C 2.77618 1.28317 -0.59222
C 1.73039 0.66488 0.08838
C -2.86814 -1.57954 -0.93793
C -3.98592 -0.83115 -1.29605
C -4.18214 0.44027 -0.75713
C -3.25198 0.95304 0.14559
C -2.12561 0.21330 0.50586
H 3.55291 -1.20727 2.28326
H 5.41201 -0.08297 1.08579
H 4.91585 1.50536 -0.77823
H 2.55257 1.96883 -1.41344
H 0.69581 0.86077 -0.20449
H -2.72884 -2.58063 -1.35523
H -4.71324 -1.25162 -1.99483
H -5.05829 1.02766 -1.03945
H -3.40144 1.94498 0.57903
H -1.40072 0.61550 1.21911

C8H18O2
E(PBE0-D3BJ/def2-SVP) = -465.1981620
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -465.9910402

C 2.06302 0.67244 -1.53886
C 1.73473 0.11741 -0.15603
O 0.49067 0.65381 0.29318
O -0.52209 0.23894 -0.62421
C -1.74084 0.05882 0.09424
C -2.68026 -0.41792 -1.00554
C -2.18820 1.39005 0.68936
C -1.58675 -1.00348 1.17714
C 2.70219 0.62818 0.90058
C 1.69535 -1.40510 -0.16882
H 1.32853 0.32135 -2.27585
H 3.06376 0.34853 -1.86100
H 2.03283 1.77195 -1.52170
H -3.66790 -0.65859 -0.58715
H -2.80176 0.35272 -1.78026
H -2.27084 -1.32289 -1.47869
H -3.17023 1.29332 1.17647
H -2.25854 2.15230 -0.10003
H -1.46182 1.73444 1.43793
H -0.83054 -0.69548 1.91103
H -1.27432 -1.96194 0.73681
H -2.54122 -1.15604 1.70303
H 2.71300 1.72737 0.91861
H 2.40105 0.26555 1.89506
H 3.71806 0.26435 0.68929
H 0.89083 -1.75559 -0.82787
H 1.51473 -1.79958 0.84177
H 2.64655 -1.81528 -0.53898

C24H20P2
E(PBE0-D3BJ/def2-SVP) = -1607.1606010
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -1609.1089335

P 0.93067 -0.72959 -0.14580
C 1.60533 0.54161 -1.28096
C 2.23738 1.72431 -0.86918
C 2.65965 2.65759 -1.81285
C 2.45350 2.42403 -3.17423
C 1.82748 1.25051 -3.59140
C 1.40894 0.31423 -2.64849

C	2.02827	-0.60082	1.31962
C	3.41941	-0.64525	1.14229
C	4.27490	-0.64390	2.24020
C	3.75737	-0.61830	3.53551
C	2.37725	-0.59291	3.72260
C	1.51912	-0.58336	2.62499
P	-0.82348	0.44736	0.61809
C	-1.69242	0.71763	-0.98017
C	-2.71132	-0.10911	-1.46949
C	-3.36195	0.20569	-2.66199
C	-2.99659	1.34166	-3.38306
C	-1.97624	2.16515	-2.90731
C	-1.33830	1.86376	-1.70802
C	-1.80097	-0.92955	1.36221
C	-2.74766	-0.57985	2.33684
C	-3.51475	-1.55733	2.96782
C	-3.33624	-2.90139	2.64019
C	-2.39618	-3.26088	1.67413
C	-1.63773	-2.28288	1.03504
H	2.39993	1.91348	0.19544
H	3.15381	3.57443	-1.48168
H	2.79033	3.15722	-3.91037
H	1.66192	1.05632	-4.65435
H	0.91108	-0.60353	-2.97238
H	3.83926	-0.66893	0.13251
H	5.35623	-0.66548	2.07981
H	4.42926	-0.61869	4.39659
H	1.95660	-0.57353	4.73117
H	0.43999	-0.55664	2.79833
H	-3.00390	-1.00161	-0.91166
H	-4.15881	-0.44543	-3.03032
H	-3.50850	1.58865	-4.31618
H	-1.67621	3.05336	-3.46814
H	-0.54716	2.51973	-1.33509
H	-2.87905	0.47193	2.60867
H	-4.24745	-1.26717	3.72512
H	-3.92775	-3.66981	3.14274
H	-2.24876	-4.31122	1.40879
H	-0.90645	-2.57156	0.27460

C12H12N2
E(PBE0-D3BJ/def2-SVP) = -572.9275820
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -573.8806339

C	1.54256	0.47746	-0.72489
N	0.45317	0.33595	-1.58538
N	-0.36976	-0.74796	-1.44504
C	-1.47782	-0.67670	-0.60359
C	-1.55442	0.27820	0.42241
C	-2.67254	0.31881	1.25345
C	-3.72318	-0.58182	1.08792
C	-3.64199	-1.53689	0.07186
C	-2.53521	-1.58670	-0.76826
C	2.04992	1.75680	-0.45346
C	3.13960	1.91248	0.39895
C	3.74317	0.80353	0.99051
C	3.24393	-0.46843	0.70874
C	2.15467	-0.63855	-0.14082
H	-0.02727	1.20869	-1.79729
H	-0.49542	-1.28421	-2.29585
H	-0.72810	0.97219	0.58618
H	-2.71521	1.06805	2.04857
H	-4.59870	-0.53584	1.73885
H	-4.45832	-2.24778	-0.08153
H	-2.48766	-2.33071	-1.56932
H	1.57807	2.63152	-0.91146
H	3.51951	2.91518	0.61222
H	4.59668	0.93158	1.65943
H	3.71194	-1.34656	1.16040
H	1.75259	-1.62829	-0.36278

C18H16NP
E(PBE0-D3BJ/def2-SVP) = -1090.0576030
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -1091.5143662

P	-0.09958	0.45091	0.78948
C	-1.19192	1.77178	0.14678
C	-2.29148	2.16737	0.92496
C	-3.12513	3.20032	0.50302
C	-2.85527	3.87474	-0.68814
C	-1.74569	3.51071	-1.44887
C	-0.92018	2.46516	-1.03745
C	-1.11503	-1.07560	0.56132
C	-2.51168	-1.11252	0.50189

C -3.18468 -2.33281 0.44031
C -2.47521 -3.53109 0.42926
C -1.08101 -3.50462 0.47472
C -0.40731 -2.28877 0.54609
N 1.02272 0.24176 -0.50556
C 2.36037 -0.10483 -0.29455
C 3.06971 0.35903 0.82416
C 4.38943 -0.03016 1.02793
C 5.03595 -0.87519 0.12542
C 4.34288 -1.31918 -0.99949
C 3.01873 -0.94353 -1.20801
H -2.49525 1.67073 1.87870
H -3.98062 3.49126 1.11738
H -3.50355 4.69069 -1.01619
H -1.51637 4.04519 -2.37383
H -0.04553 2.19091 -1.63117
H -3.08502 -0.18364 0.49516
H -4.27689 -2.34425 0.39417
H -3.00819 -4.48375 0.38260
H -0.51208 -4.43750 0.46241
H 0.68613 -2.28089 0.59349
H 0.63974 -0.14547 -1.36394
H 2.56821 1.01296 1.54030
H 4.92120 0.33900 1.90827
H 6.06649 -1.19005 0.30124
H 4.82999 -1.97865 -1.72248
H 2.47601 -1.31994 -2.07938

C12H10Te2
E(PBE0-D3BJ/def2-SVP) = -998.5177790
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -999.2907556

C -2.31198 -0.94033 -0.25864
Te -0.66987 -2.30143 -0.18558
Te 0.61030 -1.29341 1.97233
C 2.28684 -0.39759 1.00135
C 3.56359 -0.77689 1.42559
C 4.69134 -0.18936 0.85111
C 4.54945 0.76590 -0.15418
C 3.27439 1.13735 -0.58290
C 2.14495 0.56252 -0.00384
C -2.12813 0.44472 -0.25538
C -3.23103 1.29307 -0.30919
C -4.52122 0.76667 -0.38064
C -4.70444 -0.61425 -0.39481
C -3.60398 -1.46886 -0.32868
H 3.68221 -1.54258 2.19641
H 5.68441 -0.49701 1.18874
H 5.43099 1.22086 -0.61153
H 3.15397 1.88272 -1.37324
H 1.15223 0.85751 -0.35069
H -1.12327 0.86757 -0.18908
H -3.07791 2.37559 -0.29761
H -5.38413 1.43492 -0.42182
H -5.71123 -1.03675 -0.44373
H -3.75766 -2.55106 -0.31328

C18H15OP
E(PBE0-D3BJ/def2-SVP) = -1109.8906710
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -1111.3926710

P 0.28992 0.51623 -1.06212
C -0.74228 -0.97791 -0.75289
C -1.26501 -1.65137 -1.86115
C -2.12586 -2.73518 -1.68397
C -2.44904 -3.16322 -0.39783
C -1.90284 -2.51440 0.71121
C -1.05244 -1.42574 0.53678
C -0.95530 1.79659 -0.65491
C -1.27533 2.16917 0.65589
C -2.26403 3.12319 0.88606
C -2.93932 3.71003 -0.18546
C -2.61824 3.34681 -1.49198
C -1.62289 2.39821 -1.72606
O 1.12388 0.61025 0.40297
C 2.30117 -0.03005 0.62620
C 3.05330 0.40550 1.72162
C 4.25251 -0.22655 2.03037
C 4.71394 -1.29106 1.25346
C 3.96437 -1.71369 0.15803
C 2.75586 -1.09301 -0.15928
H -0.99542 -1.32122 -2.86968
H -2.54037 -3.25340 -2.55173
H -3.11822 -4.01519 -0.25438

H -2.15002 -2.86231 1.71765
H -0.62421 -0.91215 1.40093
H -0.73683 1.71222 1.48861
H -2.51532 3.41634 1.90881
H -3.71448 4.45693 0.00316
H -3.13855 3.81119 -2.33251
H -1.35634 2.12144 -2.75124
H 2.67611 1.24171 2.31294
H 4.83700 0.12130 2.88557
H 5.65433 -1.78627 1.50369
H 4.31682 -2.54339 -0.45974
H 2.16294 -1.44100 -1.00891

C15H19PSn
E(PBE0-D3BJ/def2-SVP) = -1137.3973240
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -1138.5705116

C 3.32975 -3.59369 0.23812
Sn 1.96784 -2.30297 1.30928
C 3.10574 -0.83276 2.39579
C 0.71549 -3.45227 2.63295
P 0.53236 -0.93977 -0.27839
C -0.38051 -0.08377 1.07662
C 0.02874 1.22354 1.38040
C -0.53689 1.92039 2.44782
C -1.54454 1.33485 3.21239
C -1.97393 0.04234 2.90878
C -1.39102 -0.66419 1.85905
C -0.64304 -2.20658 -0.90431
C -0.15845 -3.43071 -1.39214
C -1.00353 -4.34035 -2.02275
C -2.35614 -4.04513 -2.18405
C -2.85006 -2.82856 -1.71439
C -2.00456 -1.91684 -1.08582
H 2.79436 -4.37753 -0.31462
H 3.92741 -3.00154 -0.46962
H 4.00945 -4.07712 0.95632
H 3.70316 -0.22894 1.69645
H 3.78344 -1.32324 3.10951
H 2.42601 -0.16528 2.94540
H 0.13053 -2.77076 3.26619
H 0.02927 -4.07988 2.04711
H 1.33717 -4.09460 3.27437
H 0.80176 1.69685 0.76757
H -0.18911 2.93020 2.68020
H -1.99917 1.88638 4.03861
H -2.76150 -0.42634 3.50425
H -1.72552 -1.68103 1.64268
H 0.90075 -3.67991 -1.28664
H -0.59812 -5.28656 -2.39023
H -3.02143 -4.75986 -2.67352
H -3.90466 -2.57529 -1.85124
H -2.40810 -0.96234 -0.73896

C12H10S2
E(PBE0-D3BJ/def2-SVP) = -1258.3098510
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -1259.5473989

C 1.99314 -0.39552 -0.78509
S 0.81593 -1.34423 -1.72568
S -0.42600 -2.13920 -0.29431
C -1.82430 -1.03990 -0.19795
C -2.79717 -1.39469 0.74656
C -3.94452 -0.61883 0.88371
C -4.13190 0.51040 0.08497
C -3.15656 0.86242 -0.84675
C -2.00278 0.09273 -0.99347
C 3.34280 -0.57937 -1.10032
C 4.31552 0.16612 -0.43746
C 3.94654 1.08037 0.54829
C 2.59786 1.25454 0.86622
C 1.61753 0.52691 0.19705
H -2.65554 -2.28197 1.36959
H -4.70015 -0.90588 1.61918
H -5.03471 1.11524 0.19087
H -3.29181 1.74828 -1.47193
H -1.23669 0.36368 -1.72434
H 3.62689 -1.31868 -1.85293
H 5.36893 0.01369 -0.68645
H 4.71059 1.65363 1.07741
H 2.30361 1.96645 1.64150
H 0.56268 0.66389 0.44773

C12H10O2
E(PBE0-D3BJ/def2-SVP) = -612.5198190
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -613.5623367

C	-1.53509	-0.61525	0.45457
O	-0.50366	-1.16602	1.17290
O	0.35690	-0.16788	1.66406
C	1.46299	-0.03265	0.86355
C	1.81023	-0.93446	-0.14047
C	2.97308	-0.70637	-0.87672
C	3.78019	0.39859	-0.61521
C	3.41448	1.29056	0.39505
C	2.25641	1.08417	1.13829
C	-2.19441	-1.49724	-0.40258
C	-3.28212	-1.04293	-1.14147
C	-3.70407	0.28303	-1.03715
C	-3.03055	1.14885	-0.17794
C	-1.94284	0.71136	0.57659
H	1.17576	-1.79691	-0.33883
H	3.25001	-1.41453	-1.66155
H	4.68889	0.56767	-1.19590
H	4.03635	2.16348	0.60656
H	1.95062	1.77753	1.92436
H	-1.83847	-2.52657	-0.48126
H	-3.79831	-1.73437	-1.81116
H	-4.55377	0.63936	-1.62297
H	-3.36058	2.18609	-0.08113
H	-1.41204	1.38430	1.24861

C18H15PTe
E(PBE0-D3BJ/def2-SVP) = -1302.8344170
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -1304.1964249

P	-0.27345	0.45733	-0.67608
C	-1.16690	-1.07012	-0.15713
C	-2.24919	-1.45088	-0.96743
C	-2.98144	-2.59862	-0.67565
C	-2.62871	-3.39505	0.41532
C	-1.54106	-3.03715	1.20872
C	-0.81457	-1.88068	0.92533
C	-1.45532	1.76367	-0.13467
C	-2.53629	1.53430	0.72484
C	-3.35467	2.59169	1.12033
C	-3.10155	3.88512	0.66582
C	-2.03442	4.11827	-0.20411
C	-1.22108	3.06391	-0.60642
Te	1.37690	0.90589	1.13221
C	3.02952	-0.01270	0.15942
C	2.86591	-1.00967	-0.80614
C	3.98420	-1.58630	-1.40769
C	5.26827	-1.18706	-1.03935
C	5.43012	-0.19804	-0.06878
C	4.31679	0.39456	0.52475
H	-2.52921	-0.83479	-1.82789
H	-3.82800	-2.87750	-1.30776
H	-3.20065	-4.29712	0.64442
H	-1.25266	-3.65966	2.05921
H	0.03085	-1.59411	1.55697
H	-2.73458	0.52553	1.09411
H	-4.19032	2.40006	1.79802
H	-3.73911	4.71183	0.98716
H	-1.82968	5.12596	-0.57427
H	-0.38004	3.24944	-1.28068
H	1.86807	-1.34566	-1.10001
H	3.84327	-2.36024	-2.16673
H	6.13953	-1.64691	-1.51096
H	6.42982	0.13002	0.22812
H	4.45948	1.18467	1.26714

C16H19OP
E(PBE0-D3BJ/def2-SVP) = -1036.2283330
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -1037.6053102

C	2.72121	-1.39176	0.00680
C	2.47084	-0.03949	0.66594
O	1.08012	0.31250	0.57717
P	0.30056	0.36338	-0.90020
C	-0.98417	1.57940	-0.41948
C	-2.26346	1.51769	-0.98625
C	-3.21672	2.48514	-0.67870
C	-2.90407	3.52683	0.19582
C	-1.63037	3.59691	0.75887
C	-0.67382	2.63131	0.45050
C	-0.68623	-1.18483	-0.81829

C -0.90146 -1.91106 -1.99296
C -1.63734 -3.09707 -1.96298
C -2.13775 -3.57258 -0.75363
C -1.91156 -2.85914 0.42645
C -1.19567 -1.66638 0.39427
C 2.73825 -0.13032 2.15970
C 3.30218 1.06237 0.01989
H 2.51641 -1.35128 -1.07512
H 2.07294 -2.16093 0.45101
H 3.77027 -1.69608 0.14203
H -2.52642 0.69202 -1.65383
H -4.21505 2.41528 -1.11738
H -3.65679 4.27907 0.44346
H -1.37657 4.40578 1.44882
H 0.31806 2.67707 0.90392
H -0.47964 -1.54698 -2.93484
H -1.81186 -3.65857 -2.88416
H -2.69896 -4.50956 -0.72512
H -2.30118 -3.24129 1.37352
H -1.00991 -1.09842 1.30957
H 3.78494 -0.40987 2.35380
H 2.52992 0.83418 2.64515
H 2.08549 -0.89025 2.61098
H 3.05339 1.15677 -1.04890
H 4.37948 0.85352 0.10579
H 3.09454 2.02665 0.50860

C18H15PS
E(PBE0-D3BJ/def2-SVP) = -1432.7429630
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -1434.3354009

P -0.07147 -0.53275 0.69914
C -0.76351 1.16734 0.55422
C -0.45374 2.04568 -0.48762
C -0.97662 3.33903 -0.49624
C -1.81528 3.76367 0.53235
C -2.12643 2.89358 1.57875
C -1.59426 1.60761 1.59680
C -1.55801 -1.54836 0.32160
C -2.74253 -1.02210 -0.20711
C -3.84032 -1.85113 -0.43014
C -3.76282 -3.21222 -0.13830
C -2.58182 -3.74560 0.37885
C -1.48799 -2.91769 0.61399
S 0.89460 -0.82814 -1.18186
C 2.57662 -0.40786 -0.80177
C 2.93000 0.56203 0.14323
C 4.27189 0.86657 0.36160
C 5.26907 0.22607 -0.37132
C 4.91594 -0.73062 -1.32422
C 3.57827 -1.05529 -1.53574
H 0.19022 1.70083 -1.30159
H -0.72774 4.01698 -1.31623
H -2.23073 4.77380 0.52144
H -2.78282 3.22239 2.38827
H -1.84268 0.93008 2.41974
H -2.80575 0.04171 -0.44694
H -4.75878 -1.42806 -0.84477
H -4.62443 -3.86022 -0.31551
H -2.51551 -4.81015 0.61633
H -0.56720 -3.33541 1.03119
H 2.15799 1.08799 0.70833
H 4.53769 1.62143 1.10567
H 6.31843 0.47771 -0.19997
H 5.68834 -1.24069 -1.90419
H 3.30147 -1.81841 -2.26794

C18H15PSe
E(PBE0-D3BJ/def2-SVP) = -3435.7907150
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -3437.6287160

P -0.17622 0.32921 0.65078
C -1.22973 -1.14550 0.31731
C -2.28920 -1.37170 1.21183
C -3.07983 -2.51240 1.09924
C -2.81272 -3.45426 0.10340
C -1.76057 -3.24020 -0.78509
C -0.97192 -2.09319 -0.67915
C -1.30237 1.70751 0.19280
C -0.94342 2.98362 0.64883
C -1.68800 4.10016 0.28134
C -2.80607 3.95152 -0.54090
C -3.18090 2.68269 -0.98124
C -2.43534 1.56286 -0.61564

Se	1.14200	0.51282	-1.19012
C	2.79692	-0.09815	-0.45407
C	2.87359	-1.09869	0.51858
C	4.11814	-1.51910	0.98404
C	5.28913	-0.96329	0.46993
C	5.21083	0.02902	-0.50724
C	3.97011	0.46953	-0.96294
H	-2.50265	-0.64289	2.00011
H	-3.90475	-2.67312	1.79771
H	-3.42581	-4.35471	0.02217
H	-1.54489	-3.97128	-1.56842
H	-0.14894	-1.92347	-1.37891
H	-0.05809	3.09922	1.28045
H	-1.38921	5.08843	0.63963
H	-3.38910	4.82584	-0.83925
H	-4.05771	2.56124	-1.62188
H	-2.72809	0.57197	-0.97048
H	1.96368	-1.55424	0.91621
H	4.17220	-2.29693	1.74989
H	6.25976	-1.30586	0.83613
H	6.11985	0.47858	-0.91433
H	3.90951	1.26484	-1.71072

C6H18Sn2
E(PBE0-D3BJ/def2-SVP) = -667.6353390
E(B3LYP-D3BJ//def2-TZVP/PBE0-D3BJ/def2-SVP) = -668.0324649

C	0.57099	-0.47789	0.14295
Sn	-0.02963	-0.21565	2.20913
C	-1.22462	1.58896	2.31794
C	1.78751	0.16287	3.32574
Sn	-1.44467	-2.41514	3.18364
C	-2.05186	-2.14416	5.24687
C	-0.25727	-4.22500	3.07852
C	-3.25911	-2.78993	2.06118
H	0.98649	0.46836	-0.23623
H	1.34283	-1.25586	0.05937
H	-0.28582	-0.76371	-0.48354
H	-0.62919	2.44674	1.97055
H	-1.54870	1.77785	3.35186
H	-2.11831	1.50095	1.68440
H	2.29875	1.03066	2.88239
H	1.56785	0.38503	4.38015
H	2.46176	-0.70448	3.27631
H	-1.19680	-1.85939	5.87613
H	-2.82083	-1.36252	5.32320
H	-2.47353	-3.08694	5.62791
H	0.63598	-4.14233	3.71330
H	-0.85834	-5.07942	3.42451
H	0.06691	-4.41513	2.04485
H	-3.93266	-1.92189	2.10800
H	-3.03513	-3.01167	1.00754
H	-3.77350	-3.65747	2.50142

ESI 5: Crystallography

Crystallography

X-ray diffraction experiments on **1** were carried out at 100(2) K on a Bruker APEX II diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Intensities were integrated in SAINT[17] and absorption corrections based on equivalent reflections were applied using SADABS.[18] The structures was solved using Superflip[19,20] and refined by full matrix least squares against F^2 in ShelXL[21,22] using Olex2.[23] All of the non-hydrogen atoms were refined anisotropically. While all of the hydrogen atoms were located geometrically and refined using a riding model. Crystal structure and refinement data are given in Table 1. Crystallographic data for compound **1** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 2162103. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax(+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

Table S4. Crystal data and structure refinement for 1.

Identification code	**1**
Empirical formula	$C_{18}H_{15}PSe$
Formula weight	341.23
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.6381(7)
b/Å	5.8673(3)
c/Å	16.6147(7)
α/°	90
β/°	107.392(3)
γ/°	90
Volume/Å^3	1547.78(12)
Z	4
ρ_{calc}g/cm^3	1.464
μ/mm^{-1}	2.516
F(000)	688.0
Crystal size/mm^3	0.416 × 0.18 × 0.112
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.01 to 60.026
Index ranges	$-23 \le h \le 23$, $-8 \le k \le 6$, $-23 \le l \le 22$
Reflections collected	25128
Independent reflections	4519 [R_{int} = 0.0579, R_{sigma} = 0.0430]
Data/restraints/parameters	4519/0/181
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0308, wR_2 = 0.0624
Final R indexes [all data]	R_1 = 0.0463, wR_2 = 0.0665
Largest diff. peak/hole / e Å^{-3}	0.58/-0.38

ESI 6: References

1 C. Branfoot, T. A. Young, D. F. Wass and P. G. Pringle, *Dalton Trans.*, 2021, **50**, 7094–7104.

2 J. Ścianowski, *Tetrahedron Lett.*, 2005, **46**, 3331–3334.

3 V. Nascimento, N. L. Ferreira, R. F. S. Canto, K. L. Schott, E. P. Waczuk, L. Sancineto, C. Santi, J. B. T. Rocha and A. L. Braga, *Eur. J. Med. Chem.*, 2014, **87**, 131–139.

4 T. Heurich, Z.-W. Qu, S. Nožinović, G. Schnakenburg, H. Matsuoka, S. Grimme, O. Schiemann and R. Streubel, *Chem. Eur. J.*, 2016, **22**, 10102–10110.

5 J. Ash, H. Huang, P. Cordero and J. Y. Kang, *Org. Biomol. Chem.*, 2021, **19**, 6007–6014.

6 F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2018, **8**, 4–9.

7 A. Hellweg, C. Hättig, S. Höfener and W. Klopper, *Theor. Chem. Acc.*, 2007, **117**, 587–597.

8 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6170.

9 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.

10 Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.

11 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.

12 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100.

13 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372–1377.

14 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.

15 S. Grimme, *Chem. Eur. J.*, 2012, **18**, 9955–9964.

16 T. A. Young, J. J. Silcock, A. J. Sterling and F. Duarte, *Angew. Chem. Int. Ed.*, 2021, **60**, 4266–4274.

17 Bruker, *SAINT+ v8.38A Integration engine, Data Reduction Software*, 2015.

18 Bruker, *SADABS 2014/5, Bruker AXS area detector and absorption correction*, 2014.

19 I. Orlov, L. Palatinus and G. Chapuis, *J. Appl. Crystallogr.*, 2008, **41**, 1182–1186.

20 L. Palatinus, S. J. Prathapa and S. van Smaalen, *J. Appl. Crystallogr.*, 2012, **45**, 575–580

21 G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112–122.

22 G. M. Sheldrick, *Acta Crystallogr. Sect. C*, 2015, **71**, 3–8.

23 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.