

Electronic supporting information for

The activation of Woollins' Reagent. Isolation of pyridine stabilised PhPSe_2

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1. Materials and Methods

1.1. General Methods

NMR spectra were recorded using a *JEOL DELTA EX 270*, a *BRUKER Avance II 400*, or a *BRUKER Avance III 500* spectrometer ($^{31}\text{P}\{^1\text{H}\}$, $^{77}\text{Se}\{^1\text{H}\}$). $^{31}\text{P}\{^1\text{H}\}$ and ^{77}Se NMR spectra were measured using C_6D_6 (benzene d_6) filled glass capillaries. 85 % H_3PO_4 was used as external standard for $^{31}\text{P}\{^1\text{H}\}$ NMR, $(\text{CH}_3)_2\text{Se}$ for $^{77}\text{Se}\{^1\text{H}\}$ NMR. Chemical shifts (δ) are given in parts per million (ppm), relative to the solvent peaks. Coupling constants (J) are given in Hertz (Hz).

Mass spectrometry was performed on a *Finnigan MAT 95 XP*, an *Agilent 5975C Inert XL GC/MSD* or a *ThermoFisher LTQ Orbitrap XL* at the EPSRC UK National MS Facility in Swansea. The crystallographic data were collected with graphite-monochromated *Mo-K α* radiation ($\lambda = 0.71073 \text{ \AA}$) and corrected for Lorentz and polarization effects. The data for all of the compounds were collected and processed using *CrystalClear (Rigaku)*.¹

The crystal structures were solved by using direct methods² and expanded using Fourier techniques.³ The non-hydrogen atoms were refined anisotropically, hydrogen atoms were refined using the riding model. All calculations were performed using *CrystalStructure* crystallographic software package⁴ and *SHELXL-97*.⁵

1.2. General Synthetic Considerations

Unless otherwise stated, all the experiments were carried out under an atmosphere of dry nitrogen, using standard Schlenk techniques or in a Saffron glovebox equipped with argon. Before use, the glass apparatus were stored in a drying oven at 120 °C and flame dried *in vacuo* at 10^{-3} mbar. All chemical reagents and solvents of analytical grade were obtained from Sigma-Aldrich, Acros Organics, Alfa Aesar, ABCR or were taken from inventory of the laboratories and used without further purification. Dry solvents were collected from an MBraun solvent system. The products were stored in the glove box under an argon atmosphere or nitrogen flushed Schlenk flasks.

1.3. Computational Details

Geometries were fully optimised in the gas phase at the B3LYP level⁶ using Curtis and Binning's 962(d) basis⁷ on Se and 6-31+G(d) basis elsewhere. Wiberg Bond Indices were obtained in a natural bond orbital analysis⁸ at the same level. Geometries were reoptimised using the polarizable conductor calculation model (CPCM)⁹ with the parameters of pyridine, denoted CPCM(py), and with those of other, more polar solvents, namely dimethyl sulfoxide

(DMSO) and water. Harmonic vibrational frequencies were computed to characterise all stationary points as minima and to calculate enthalpies and free energies at the B3LYP/CPCM(py) level. Wiberg Bond Indices were obtained in a natural bond orbital analysis at the same level. The structure of **1a** was also reoptimised in the gas phase and the continua at the MP2 level using the same basis set.

Additional single-point energy calculations were performed on the B3LYP/CPCM(py) geometries, employing the same basis set on Se as before and 6-311+G(d) elsewhere, together with the CPCM(py) model. The resulting changes in relative energies were added as increments to the enthalpies and free energies calculated with the smaller basis. The final *DH* and *DG* values were further corrected for dispersion using Grimme's empirical three-body terms (denoted B3LYP-D3),¹⁰ and for basis-set superposition error according to the Counterpoise method.¹¹ All computations were performed using the Gaussian 09 suite of programs.¹²

Table S1: P–N distances for **1a** [6-31+G* basis, in Å], optimised at selected levels; in italics: experimental data from X-ray crystallography.

Environment^a \ Level	B3LYP	MP2
gas phase	2.152	2.049
CPCM(py)	1.974	1.934
CPCM(DMSO)	1.962	1.927
CPCM(water)	1.961	1.926
<i>X-Ray</i>	<i>1.886(7)</i>	

^aCPCM denotes a polarisable continuum model (py = pyridine).

1.4. Experimental details

Preparation of 1a

Woollins' Reagent (**WR**) (532 mg, 1.00 mmol) was stirred in dry pyridine (5 mL) for 30 minutes. The reaction mixture was filtered (Schlenk sinter, pore 3) to remove traces of the slight excess of elemental selenium within the Woollins' Reagent to yield a dark yellow solution.

Colourless, air sensitive crystals were obtained at $-40\text{ }^{\circ}\text{C}$ after two days. ^{31}P NMR (202.5 MHz): $\delta = 101.6$, (s, $^1J_{\text{PSe}} = -808.4$ Hz) ^{77}Se NMR (95.4 MHz): $\delta = 91.9$ (d, $^1J_{\text{SeP}} = -809.5$ Hz) MS (EI^+): $m/z = 79.0$ [$\text{C}_5\text{H}_5\text{N}$] $^+$, 267.8 [$\text{C}_6\text{H}_5\text{PSe}_2$] $^+$.

Preparation of 1b

Woollins' Reagent (**WR**) (532 mg, 1.00 mmol) was stirred in dry γ -picoline (5 mL) for 30 minutes. The reaction mixture was filtered to yield a dark yellow solution. ^{31}P NMR (202.5 MHz): $\delta = 97.6$, (s, $^1J_{\text{PSe}} = -808.8$ Hz) ^{77}Se NMR (95.4 MHz): $\delta = 82.9$ (d, $^1J_{\text{SeP}} = -809.2$ Hz).

Reaction of 1a with MeOH

1a was prepared *in situ* by stirring **WR** (532 mg, 1.00 mmol) in dry pyridine (8 mL). To this, MeOH (3 mL) was added *via* cannula transfer and the reaction mixture was heated at $50\text{ }^{\circ}\text{C}$ for 2 h. The colour of the reaction mixture changed from greenish-yellow to orange. ^{31}P NMR (109.4 MHz): $\delta = 83.6$ (s, $^1J_{\text{PSe}} = -967.4$ Hz).

Preparation of 2a

A solution of **1a** (5 mL) was exposed to air for 15 minutes. Afterwards, the flask was sealed and stored at $-40\text{ }^{\circ}\text{C}$ for 3 days, which resulted in the formation of yellow, air sensitive, platelet shaped crystals. ^{31}P NMR (202.5 MHz): $\delta = 9.85$ (s, $^1J_{\text{PSe}} = -659.3$, $^1J_{\text{PSeu}} = -354.8$ Hz) ^{77}Se NMR (95.4 MHz): $\delta = 765.1$ (d, $^1J_{\text{SeuP}} = -357.6\text{ Hz}$), 170.9 (d, $^1J_{\text{PSe}} = -662.8$ Hz) MS (EI^+): $m/z = 79.0$ [$\text{C}_5\text{H}_5\text{N}$] $^+$, 267.8 [$\text{C}_6\text{H}_5\text{PSe}_2$] $^+$, 425.7 [$\text{C}_6\text{H}_5\text{PSe}_4$] $^+$.

Preparation of 2b

A solution of **1b** (5 mL) was exposed to air for 5 minutes. The flask was sealed and stored at $5\text{ }^{\circ}\text{C}$. After three days, crystals of **2b** were isolated. ^{31}P NMR (202.5 MHz): $\delta = 9.3$ (s, $^1J_{\text{PSe}} = -659.3$, $^1J_{\text{PSeu}} = -354.8$ Hz) ^{77}Se NMR (95.4 MHz): $\delta = 659.7$ (d, $^1J_{\text{SeuP}} = -358.8\text{ Hz}$), 200.5 (d, $^1J_{\text{SeP}} = -660.4$ Hz) MS (EI^+): $m/z = 93.0$ [$\text{C}_6\text{H}_7\text{N}$] $^+$, 267.8 [$\text{C}_6\text{H}_5\text{PSe}_2$] $^+$, 611.6 [$\text{C}_{12}\text{H}_{10}\text{PSe}_5$] $^+$.

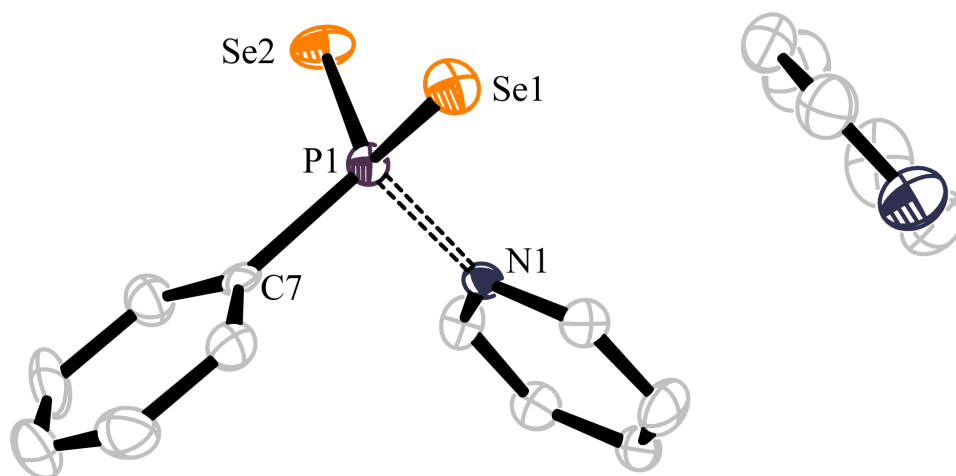
Preparation of 3a

A solution of **2a** was stored at room temperature for two weeks. The disproportion of **2a** was observable by the formation of elemental grey selenium and crystals of **3a**. ^{31}P NMR (202.5 MHz): $\delta = 59.7$ (s, $^1J_{\text{PSe}} = -738.7$ Hz) ^{77}Se NMR (95.4 MHz): $\delta = -117.6$ (d, $^1J_{\text{SeP}} = -738.3$ Hz) MS (EI^+): $m/z = 79.0$ [$\text{C}_5\text{H}_5\text{N}$] $^+$, 345.7 [$\text{C}_6\text{H}_5\text{PSe}_3$] $^+$.

Preparation of 3b

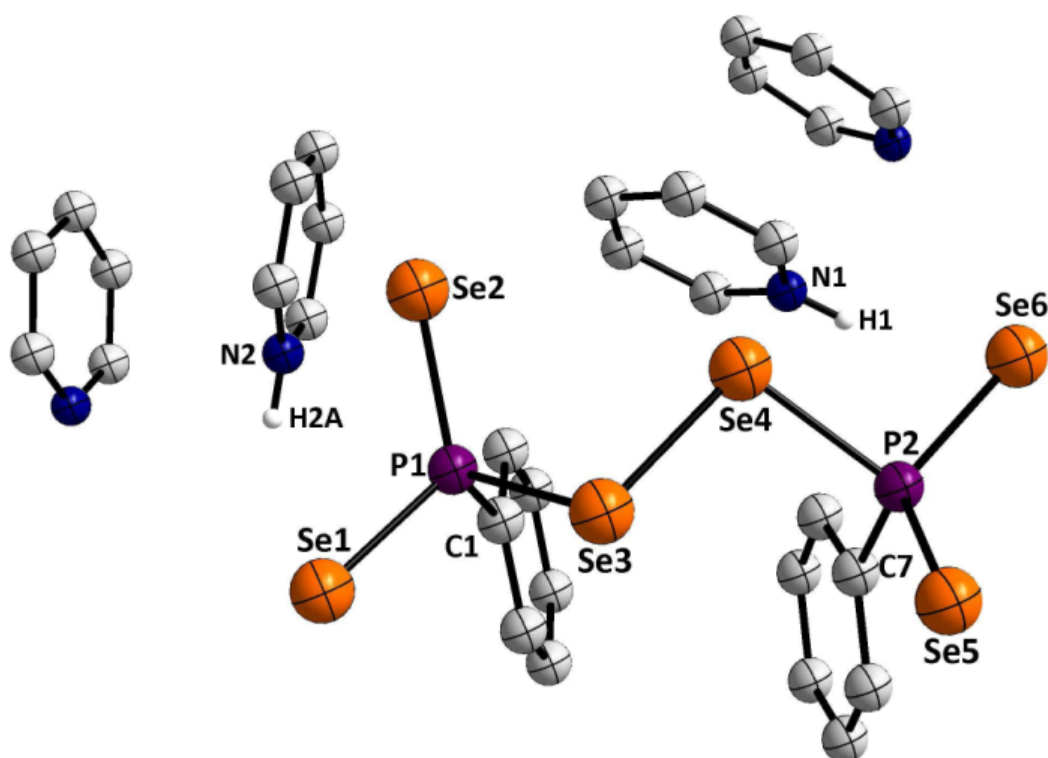
A solution of **2b** was stored at room temperature for 1 week. The disproportionation of **2b** was observable by the formation of elemental grey selenium and crystals of **3b**. ^{31}P NMR (202.5 MHz): $\delta = 15.6$ (s, $^1J_{\text{PSe}} = -556.9$ Hz).

2 Crystal structures



ORTEP representation of **1a** · py in the solid state; hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): P1–Se1 2.108(3), P1–N1 1.886(7), P1–Se2 2.106(3), P1–C7 1.830(7), Se1–P1–Se2 120.30(9), Se1–P1–C7 112.1(3), Se2–P1–C7 111.8(3).

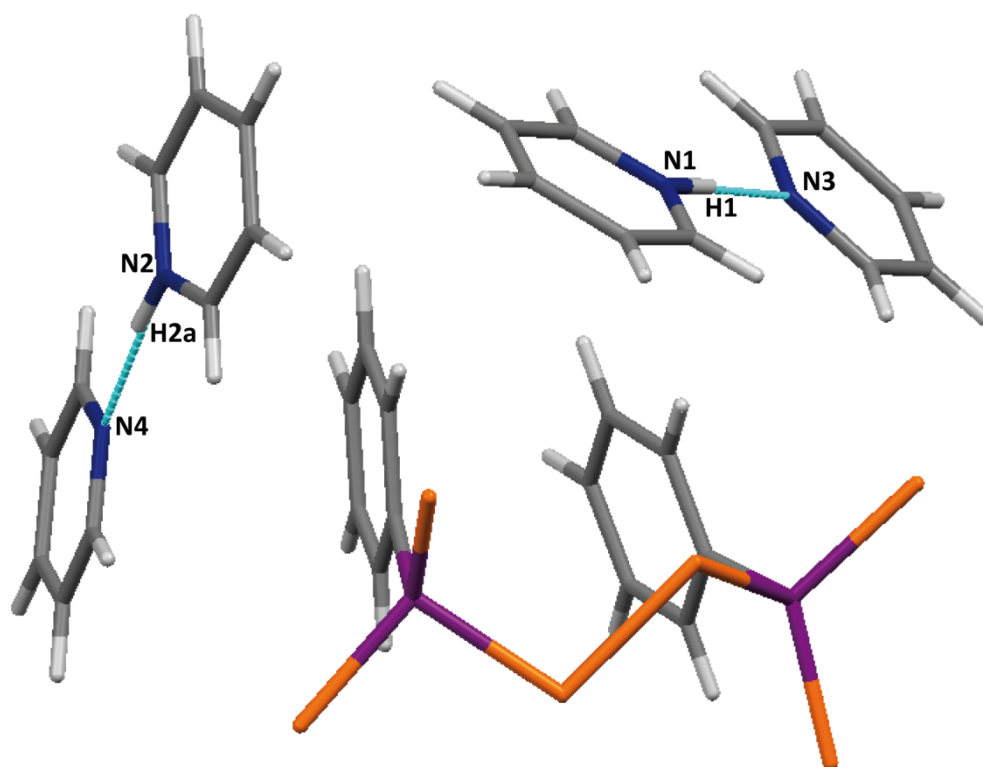
1a · py crystallises in the orthorhombic space group $Pna2_1$ with four formula units in the unit cell. The central phosphorus atom P1 adopts a distorted tetrahedral geometry and is bonded to two selenium atoms Se1 and Se2, a phenyl ring and a pyridine ring. The average P–Se bond distance of 2.107 Å indicates two double bonds (compared to other P=Se bonds found in the literature¹³) and is in accordance with the $^1J_{\text{PSe}}$ coupling constant mentioned above. The P=Se double bond in Woollins' Reagent is 2.102(3) and thus quite similar. The P1–C7 bond length is 1.830(7) Å and comparable with the reported P–C distance (1.822(10) Å) of Woollins' Reagent.¹⁴ The P1–N1 distance (1.886(7) Å) is significantly longer than usual P–N single bonds reported in the literature.¹⁵



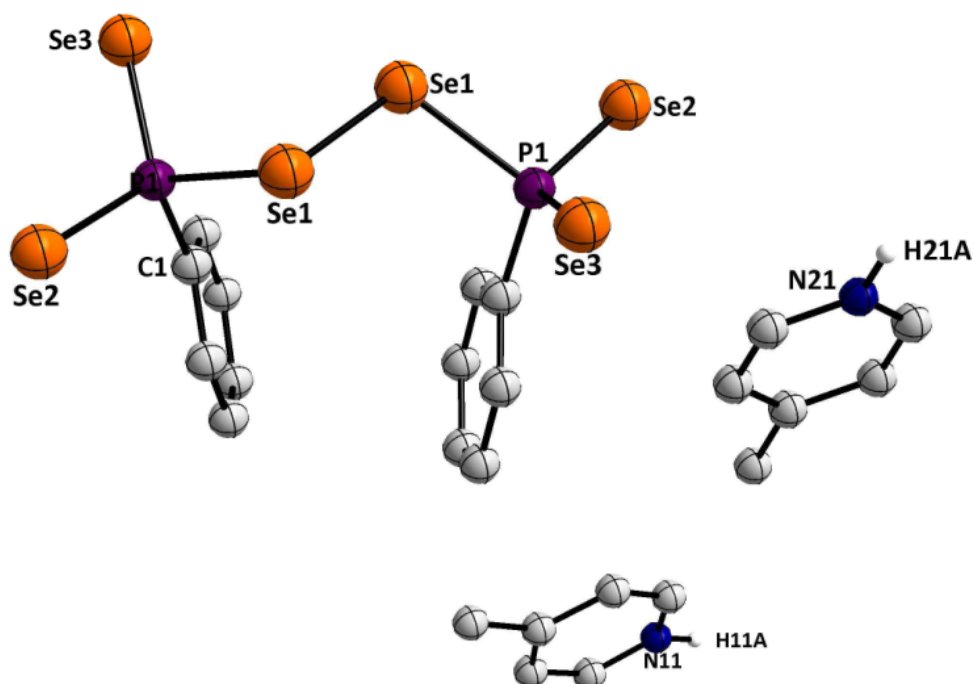
X-ray structure of **2a** · 2 py in the solid state; hydrogen atoms bond to carbon atoms are omitted for clarity. Selected bond distances (Å) and angles (°): P1–Se1 2.1422(18) P2–Se4 2.2644(19) P1–Se2 2.1286(18) P2–Se5 2.1176(18) P1–Se3 2.261(2) P2–Se6 2.1442(18) P1–C1 1.829(8) P2–C7 1.835(8) Se3–Se4 2.3551(11) Se1–P1–Se2 120.13(9) Se4–P2–Se5 112.09(8) Se1–P1–Se3 97.82(7) Se4–P2–Se6 98.31(7) Se2–P1–Se3 110.95(8) Se5–P2–Se6 119.55(8) P1–Se3–Se4–P2 –131.00(7).

2a · 2 py crystallises in the triclinic space group *P*1 with two formula units in the unit cell. The phosphorus atoms are coordinated by three selenium atoms and a phenyl ring in a distorted tetrahedral arrangement. The phosphorus atom P1 is coordinated by the two exocyclic selenium atoms Se1 and Se2, the bridging selenium atom Se3 and a phenyl ring with an angular sum of 328.9(24)°, differing slightly from the ideal tetrahedral angle of 324°. The second phosphorus atom, P2, also shows a slight deviation from tetrahedral ideality as shown by the angular sum of 330.0(23)° around P2. The Se3–Se4 distance within the diselenide bridge is 2.3551(11) Å and thus typical for Se–Se single bonds¹⁶ and comparable to the Se–Se distance within other known P–Se–Se–P moieties.¹⁷ The two P–Se single bonds P1–Se3 (2.261(2) Å) and P2–Se4 (2.2644(19) Å) of the P–Se–Se–P bridge are slightly longer

than the P–Se distances of the four P–Se bonds that host negative charge. These bond distances range from 2.1176(18) Å to 2.1442(18) Å. These are almost equal and are shorter than common P–Se single bonds, but longer than P=Se double bonds.¹⁸ This is in accordance with the $^1J_{\text{PSe}}$ coupling constants mentioned above and shows there is a delocalisation of the negative charge across both P=Se bonds.

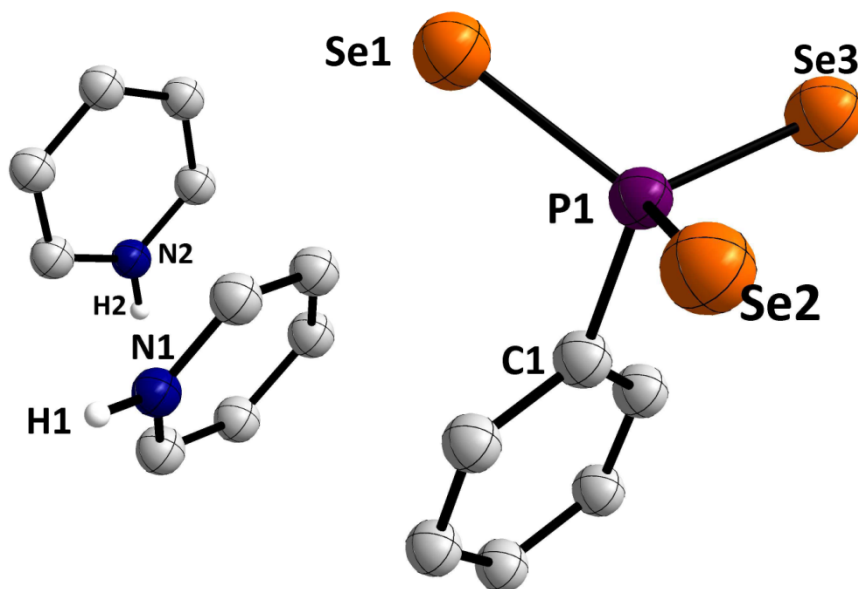


The $[\text{PhP}(\text{Se})_2\text{Se}-\text{Se}(\text{Se})_2\text{PPh}]^{2-}$ anions are located along the c axis of the unit cell. Within the crystal the two pyridinium cations are connected to the two solvating pyridine molecules *via* hydrogen bonding $\text{N1}-\text{H1}\cdots\text{N3}$ and $\text{N2}-\text{H2a}\cdots\text{N4}$ interactions. The distance between the hydrogen atoms and the acceptor nitrogen atoms are 2.715 Å ($\text{N1}-\text{H1}\cdots\text{N3}$) and 2.727 Å ($\text{N2}-\text{H2a}\cdots\text{N4}$) which is below the sum of the van der Waals radii of hydrogen and nitrogen (2.75 Å) indicating hydrogen bonding.¹⁹ The $\text{N1}-\text{H1}\cdots\text{N3}$ angle is 174.54° , the $\text{N2}-\text{H2a}\cdots\text{N4}$ angle is 172.53° . The torsions angles of 13.88° ($\text{C17}-\text{N1}-\text{N3}-\text{C23}$) and 8.45° ($\text{C22}-\text{N2}-\text{N4}-\text{C28}$) clearly indicate that the pyridinium and the pyridine entities are coplanar.



X-ray structure of **2b** in the solid state; hydrogen atoms bond to carbon atoms are omitted for clarity. Selected bond distances (Å) and angles (°): P1–Se1 2.265(1) P1–C1 1.829(5) P1–Se2 2.145(1) Se1–Se1 2.353(1) P1–Se3 2.126(2) Se1–P1–Se2 98.75(5) Se2–P1–Se3 119.95(6) Se1–P1–Se3 110.86(5).

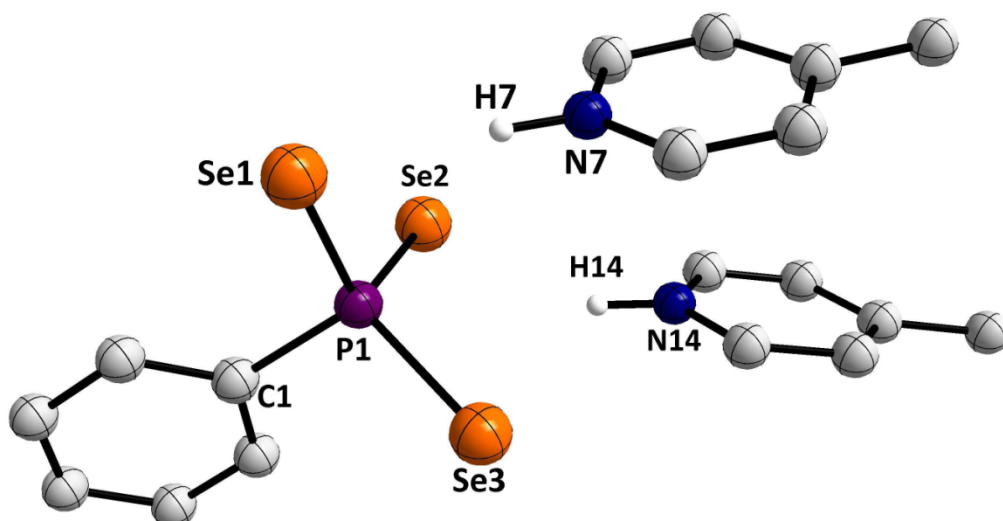
2b crystallises in the monoclinic space group $C2/c$ with four formula units in the unit cell. Similarly to **2a** · 2 py, the phosphorus atoms have a distorted tetrahedral geometry, and are bonded to three selenium atoms and a phenyl ring. The angular sum around P1 of $329.58(16)^\circ$ again shows a slight deviation from an ideal tetrahedral geometry of 324° . The Se1–Se1 distance of the diselenide bridge is 2.353(1) Å. This is almost equal to the Se–Se bridge distance of 2.3551(11) Å in **2a** · 2 py. The P1–Se1 distance of 2.265(1) Å is slightly longer than the P–Se distances to the other Se atoms, which exhibit slight double bond character. These bond distances of 2.145(1) Å (P1–Se2) and 2.126(2) Å (P1–Se3) are almost equal to each other, but shorter than common P–Se single bonds yet longer than P=Se double bonds.¹⁸ This is in accordance with the $^1J_{\text{PSe}}$ coupling constants mentioned above. The P1–Se1–Se1–P1 torsion angle is $-129.04(5)^\circ$. As expected, there is very little intramolecular structural differences between **2a** · 2 py and **2b**. It is worth noting that no γ -picoline was incorporated into the solid state structure.



X-ray structure of **3a** in the solid state; hydrogen atoms bond to carbon atoms are omitted for clarity. Selected bond distances (Å) and angles (°): P1–Se1 2.1954(10) P1–Se3 2.1823(10) P1–Se2 2.1692(10) P1–C1 1.848(3) Se1–P1–Se2 110.72(4) Se2–P1–Se3 113.17(5) Se1–P1–Se3 112.07(5).

3a crystallises in the monoclinic space group $P2_1/c$ with four formula units in the unit cell. The central phosphorus atom adopts a tetrahedral arrangement with three selenium atoms and one phenyl ring. The Se–P–Se bond angles are 110.72(4)° (Se1–P1–Se2), 112.07(5)° (Se1–P1–Se3) and 113.17(5)° (Se2–P1–Se3). This results in a sum of 335.96(14)°, which is close to the ideal tetrahedral angle of 324°, but does show some distortion, likely due to the size of the selenium atoms.

The P1–Se1 (2.1954(10) Å), P1–Se2 (2.1692(10) Å) and P1–Se3 (2.1823(10) Å) bond lengths are in between the length of P–Se single and P=Se double bonds,¹⁸ which is in good accordance with the NMR data mentioned above.



X-ray structure of **3b** in the solid state; hydrogen atoms bond to carbon atoms are omitted for clarity. Selected bond distances (Å) and angles (°): P1–Se1 2.188(1) P1–C1 1.837(4) P1–Se2 2.183(1) P1–Se3 2.167(1) Se1–P1–Se2 112.63(5) Se2–P1–Se3 111.73(5) Se1–P1–Se3 112.01(5).

3b crystallises in the monoclinic space group $P2_1/n$ with four formula units in the unit cell. As with the other phenyltriselenophosphonate **3a**, the phosphorus atom adopts a distorted tetrahedral geometry with three selenium atoms and one phenyl ring. The angular sum of $336.37(15)^\circ$ at the phosphorus centre again deviates from an ideal tetrahedral geometry similar to that of **3a**.

The P–Se bond lengths are 2.188(1) Å (P1–Se1), 2.183(1) Å (P1–Se2) and 2.167(1) Å (P1–Se3) and can therefore be considered to have both single and double bond character, since they are not as long as typical P–Se bonds but are equally not as short as typical P=Se bonds.¹⁸ As one would expect, there is very little structural difference between **3a** and **3b** with the exception of the orientation of the pyridinium and picolinium cations.

Table S2: Details of X-ray crystal structure analyses .

Compound number	1a · py	2a · 2 py
Empirical formula	C ₁₆ H ₁₅ N ₂ PSe ₂	C ₃₂ H ₃₂ N ₄ P ₂ Se ₆
Formula weight	424.20	1008.34
Crystal size [mm³]	0.200 × 0.130 × 0.030	0.150 x 0.120 x 0.030
Crystal system	orthorhombic	triclinic
Space group	Pna21	P ⁻ 1
a [Å]	13.948(3)	9.422(3)
b [Å]	10.4836(18)	9.570(3)
c [Å]	11.642(2)	21.600(6)
α [°]	90.0000	94.891(8)
β [°]	90.0000	94.73(1)
γ [°]	90.0000	106.893(9)
Volume [Å³]	1702.3(5)	1845.2(9)
Z	4	2
ρ_{calc} [mg/mm³]	1.655	1.815
F(000)	832.0	972.00
μ [mm⁻¹]	4.433	6.065
2Θ range [°]	5.99 - 50.658	3.13 - 25.41
Index ranges	-16 ≤ h ≤ 16, -12 ≤ k ≤ 12, -13 ≤ l ≤ 8	-11 ≤ h ≤ 11, -10 ≤ k ≤ 11, -25 ≤ l ≤ 25
Reflections collected	10588	13313
Independent reflections	2544 [R(int) = 0.0655]	6183 [R(int) = 0.0387]
Data/restraints/parameters	2544/1/190	6183/0/397
Goodness-of-fit on F²	1.055	1.076
Final R indexes [I ≥ 2σ (I)]	R1 = 0.0392, wR2 = N/A	R1 = 0.0446, wR2 = N/A
Final R indexes [all data]	R1 = N/A, wR2 = 0.0803	R1 = 0.0678, wR2 = 0.1118
Largest diff. peak/hole / e Å⁻³	0.51/-0.78	2.34/-0.86

Compound number	2b	3a
Empirical formula	C ₃₆ H ₄₀ N ₄ P ₂ Se	C ₁₆ H ₁₇ N ₂ PSe ₃
Formula weight	1064.45	505.18
Crystal size [mm ³]	0.140 × 0.090 × 0.020	0.060 × 0.050 × 0.020
Crystal system	monoclinic	monoclinic
Space group	C2/c	P21/c
a [Å]	10.406(5)	11.284(2)
b [Å]	15.548(7)	11.263(2)
c [Å]	26.232(10)	14.482(3)
α [°]	90.0000	90.0000
β [°]	99.693(11)	92.710(7)
γ [°]	90.0000	90.0000
Volume [Å ³]	4184(3)	1838.3(6)
Z	4	4
ρ _{calc} [mg/mm ³]	1.690	1.825
F(000)	2072.00	976.00
μ [mm ⁻¹]	5.355	6.088
2Θ range [°]	2.38 - 25.35	3.27 - 25.35
Index ranges	-12 ≤ h ≤ 8, -18 ≤ k ≤ 18, -28 ≤ l ≤ 31	-9 ≤ h ≤ 13, -13 ≤ k ≤ 13, -17 ≤ l ≤ 15
Reflections collected	13217	11498
Independent reflections	3777[R(int) = 0.0469]	3217[R(int) = 0.0351]
Data/restraints/parameters	3777/0/219	3215/0/199
Goodness-of-fit on F ²	1.065	1.078
Final R indexes [I ≥ 2σ (I)]	R1 = 0.0421, wR2 = N/A	R1 = 0.0294, wR2 = N/A
Final R indexes [all data]	R1 = N/A, wR2 = 0.0979	R1 = 0.0390, wR2 = 0.0520
Largest diff. peak/hole / e Å ⁻³	0.66/-0.54	0.39/-0.43

Compound number	3b
Empirical formula	C ₁₈ H ₂₁ N ₂ PS ₃
Formula weight	533.23
Crystal size [mm³]	0.100 × 0.100 × 0.020
Crystal system	monoclinic
Space group	P2 ₁ /n
a [Å]	8.7259(11)
b [Å]	14.3639(18)
c [Å]	16.1845(19)
α [°]	90.0000
β [°]	94.997(7)
γ [°]	90.0000
Volume [Å³]	2020.8(5)
Z	4
ρ_{calc} [mg/mm³]	1.753
F(000)	1040.00
μ [mm⁻¹]	5.543
2Θ range [°]	3.101 - 25.347
Index ranges	-10 ≤ h ≤ 9, -13 ≤ k ≤ 16, -19 ≤ l ≤ 15
Reflections collected	11983
Independent reflections	3598 [R(int) = 0.0433]
Data/restraints/parameters	3598/2/225
Goodness-of-fit on F²	1.071
Final R indexes [I ≥ 2σ (I)]	R1 = 0.0379, wR2 = N/A
Final R indexes [all data]	R1 = N/A, wR2 = 0.0743
Largest diff. peak/hole / e Å⁻³	0.54/-0.47

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