

The activation of Woollins' reagent. Isolation of pyridine stabilised PhPSe_2 [†]

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Woollins' reagent (WR, $(\text{PhPSe}_2)_2$) plays an essential role in the selenation of organic compounds. Reaction of WR with pyridine gives the P(V) species PhPSe_2 stabilised by pyridine coordination which is the first crystallographically characterised mononuclear RPS_2 system stabilised by an external molecule and has potential as a selenation reagent for reactions under mild conditions.

Species with the molecular formula RPE_2 ($\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$) exhibit a very unusual bonding situation: phosphorus is in the formal oxidation state of +V but only tricoordinated ($\sigma^3\lambda^5$). The coordination sphere of $\sigma^3\lambda^5$ phosphoranes is unsaturated, therefore a strong Lewis acidity is expected.¹ To prevent these species from dimerisation, two main routes are considered in synthesis: (A) stabilisation of the monomeric form with sterically demanding substituents and (B) provision of an intramolecular or intermolecular species, which is able to fill the electronic gap at the phosphorus atom.²

The monomeric form of Woollins' reagent (WR),³ a phenyldiselenoxophosphorane exhibiting a $\sigma^3\lambda^5$ phosphorus atom has been postulated.⁴ In comparison, the sulfur analogue of WR, Lawesson's reagent (LR) (Fig. 1),⁵ is known to be in equilibrium with its dithiophosphine ylide in solution. This ylide is said to be the reactive intermediate when it comes to thionation processes with LR.⁶

This supports the assumption that a similar equilibrium and thus a monomeric form can be found for WR as well.

Stirring WR in pyridine for 30 min indeed is a facile way to stabilise this $\sigma^3\lambda^5$ bonding situation, thus eliminating the need to use bulky substituents (Scheme 1). The resulting new phenyldiselenoxophosphorane **1a** is formed quantitatively.⁷

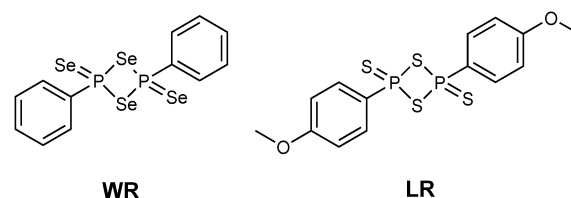
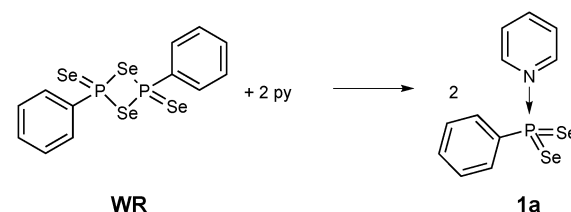


Fig. 1 Molecular structures of WR and LR.



Scheme 1 Reaction of Woollins' reagent WR with pyridine to form the pyridine adduct **1a**.

The ³¹P NMR spectrum of **1a** consists of a singlet at 101.6 ppm with satellites representing the ¹J_{PSe} coupling of −808.4 Hz, adequate for the representation of a P=Se double bond. Consistently, the ⁷⁷Se NMR signal appears as a doublet at 91.9 ppm.

Storing the resulting yellow solution at −40 °C for two days yielded yellow, prism shaped crystals of **1a**·py (Fig. 2).

The two P=Se double bonds in the range of 2.106(3) to 2.108(3) Å are comparable to those reported for WR (2.102(3) Å).^{3e} Interestingly, the P1–N1 distance (1.886(7) Å) is significantly longer than usual P^V–N single bonds reported before (e.g. 1.652(3) Å in $\text{PhP}(\text{NHCH}_2\text{Ph})_2\text{Se}$, 1.665(2) Å for $[\text{iPrNH}_2\text{iPr}][\text{PhPSe}_2\text{NHiPr}]$ ^{8a} or 1.617(6)–1.688(3) Å in $[(t\text{Bu}(\text{H})\text{N}(\text{Se})\text{P}_2(\mu\text{-N}t\text{Bu})_2)]$ ^{8b} or 1.800(4) Å for $\text{Na}[\text{H}_3\text{NO}_3\text{P}]$ ^{8c}). This suggests that the pyridine entity is bonded rather weakly to the phenyldiselenoxophosphorane and can be abstracted quite easily in order to release the reactive intermediate. In contrast a N→P^V donor–acceptor distance was reported to be 2.039(5) Å for a 2,4-di-*tert*-butyl-6-(1-piperidino)phenyl stabilized PSe₂ system, which prompted us to investigate the bonding situation in **1a** in more detail.⁹

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[†] Electronic supplementary information (ESI) available: Experimental and crystallographic as well as computational details in pdf form. CCDC 985890–985894. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc01073f



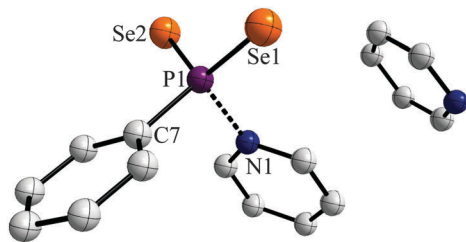


Fig. 2 X-ray structure of **1a**·py in the solid state; hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): P1–Se1 2.108(3), P1–N1 1.886(7), P1–Se2 2.106(3), P1–C7 1.830(7), Se1–P1–Se2 120.30(9), Se1–P1–C7 112.1(3), Se2–P1–C7 111.8(3).

In order to analyse the unusual bonding situation and predict the reactivity of the pyridine adduct **1a** compared to **WR** itself, density functional theory (DFT) and *ab initio* calculations were performed, calling special attention to the strength of the P–N interaction in **1a**. As a result the strength of this interaction depends strongly on the surrounding medium and, to a much lesser extent, on the method that is used.

Compared to the solid state structure, the popular B3LYP functional overestimates the P–N distance significantly by *ca.* 0.27 Å, when the optimisation is conducted in the gas phase (see Table S1 in the ESI†). The *ab initio* MP2 method furnishes a shorter P–N bond, but still 0.16 Å longer than in the solid. Adduct **1a** is characterised by a large dipole moment, 8.8 D at the B3LYP level. When the molecule is immersed in a polarisable continuum mimicking the solvent pyridine, the P–N bond contracts significantly (by *ca.* –0.18 Å and –0.12 Å at B3LYP and MP2, respectively, Table S1, ESI†) and the dipole moment increases (to 13.7 D at B3LYP). A further, minor bond-length decrease by *ca.* 0.01 Å is obtained with increasing polarity of the surrounding medium (as might be expected for a crystal consisting of highly polar molecules). This situation is reminiscent of other donor–acceptor complexes such as BH₃NH₃ and related species, where even larger gas-to-solid bond contractions can be found.¹⁰

The nature of the P–N bond was probed through the Wiberg Bond Index (WBI),¹¹ an indicator for the extent of covalent bonding, which approaches a value close to one for true single bonds. On-going from the gas phase into the continuum modelling pyridine, the P–N WBI increases from 0.31 to 0.44 (B3LYP), suggesting a strong covalent character in addition to the electrostatic interactions and charge-transfer that give rise to the high dipole moment.

According to natural population analysis (NPA),¹² the charge transfer from the pyridine to the PhPSe₂ moiety amounts to *ca.* 0.32e (the resulting electrostatic potential, which is free from ambiguities of population analyses, is shown in Fig. 3). In an unconstrained search for the localised natural bond orbitals (NBOs), the key bonding orbital between P and N is labelled as a lone pair on N, but with a rather low occupancy (1.62) and a large donor–acceptor interaction with a low-occupancy NBO on P (according to second-order perturbation analysis). When a P–N NBO is enforced using the CHOOSE option, it is strongly polarised towards N (77% contribution from the latter). Taken together, the P–N interaction shows the characteristics of a highly polar donor–acceptor bond with significant covalent character. In order to assess the strength of the P–N

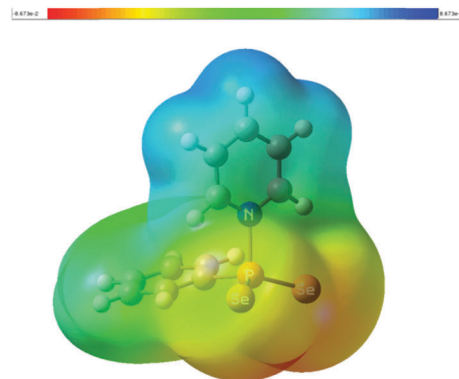
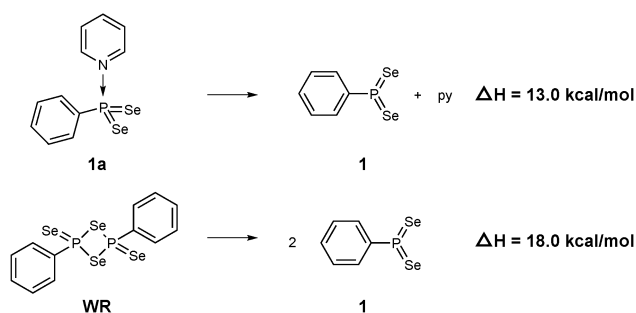


Fig. 3 Electrostatic potential of **1a** at the B3LYP/CPCM(py) level, plotted on a colour scale from $+8.65 \times 10^{-2}$ a.u. (blue) to -8.65×10^{-2} a.u. (red) and mapped onto an isodensity surface with $\rho = 4.10^{-4}$ a.u.



Scheme 2 Computed dissociation enthalpies of **1a** and **WR** into the active PhPSe₂ moiety **1** (B3LYP-D3-level).

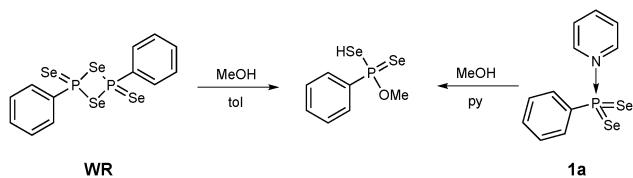
interaction in **1a**, we have computed the dissociation energy according to Scheme 2 using a more elaborate computational protocol (including dispersion, thermodynamic and BSSE corrections, see computational details in ESI†).

At the B3LYP-D3/CPCM(py) level, the computed dissociation enthalpies and free energies at room temperature are $\Delta H = 13.0$ kcal mol^{–1} and $\Delta G = 1.6$ kcal mol^{–1}. It should be noted that calculated entropy changes based on the ideal-gas assumption tend to overestimate entropy changes in solution when the number of particles change. This problem notwithstanding, the bond in **1a** is predicted to be rather weak, weaker actually than the multicentre bonds that hold **WR** together: the corresponding dissociation enthalpy and free energy are $\Delta H = 18.0$ kcal mol^{–1} and $\Delta G = 6.4$ kcal mol^{–1}, *i.e.* both higher by *ca.* 5 kcal mol^{–1}. Barring any additional kinetic barriers, **1a** should thus liberate the presumed reactive intermediate **1** more easily than **WR**.

As mentioned above, the coordination sphere of $\sigma^3\lambda^5$ phosphoranes is unsaturated and a strong Lewis acidity can therefore be expected. This assumption has been proved multiple times by the fact that dithiophosphoranes react willingly with nucleophiles such as, among others, methanol, acetylenes or dienes.^{1b,13} Furthermore dithiophosphorane species are known to undergo nucleophilic attack from the oxygen of carbonyl groups.^{6b}

In order to get a first insight into the reactivity of **1a** towards nucleophiles, the compound has been reacted with selected substrates that had been successfully reacted with **WR**.





Scheme 3 Reaction of **WR** and **1a** yield the same product (O-methyl Se-hydrogen phenylphosphonodiselenoate).

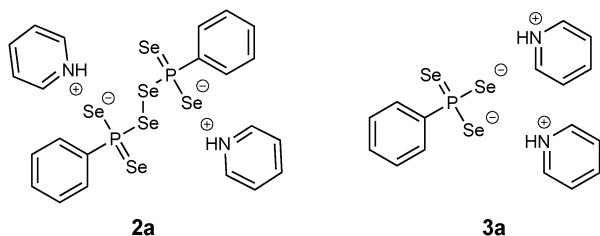


Fig. 4 Molecular structures of **2a** and **3a**.

Thus, the reaction of methanol with **1a** in pyridine at 50 °C yielded O-methyl Se-hydrogen phenylphosphonodiselenoate as found for the reaction of **WR** with methanol (Scheme 3).¹⁴ Observed were short reaction times, mild conditions and as an advantage the solubility of **1a** in pyridine, whereas a suspension has to be used for **WR**.

In contrast, the reaction of **1a** with diphenylacetylene,^{13c} benzamide¹⁵ or DMF¹⁶ led to a different product distribution in the ³¹P and ⁷⁷Se NMR when compared to **WR**. This indicates a rather different reactivity of **1a** in comparison to **WR** that provides new possibilities in future investigations.

In terms of air sensitivity **1a** seems to be less stable compared to **WR**. Upon exposure to air for about 15 min **1a** decomposed to form the dianionic hexaselenodiphosphonate **2a** (Fig. 4).¹⁷ The pathway of the formation is most likely a result of a hydrolysis process followed by subsequent oxidation. Although traces of water and oxygen probably lead to the formation of the dianionic species **2a**, the compound itself is air sensitive and prone to disproportionation. Thus, after two weeks, the formation of the dipyrindiniumphenyltriselenophosphonate **3a** (Fig. 4) could be observed by storing a solution of **2a** at room temperature.¹⁷ This compound is likely to be formed *via* disproportionation of **2a** to **3a** and elemental selenium, which precipitates from the solution.

However, pyridine is not unique in being able to stabilise the monomeric **WR**: Using γ -picoline (4-methylpyridine) instead results in similar ³¹P and ⁷⁷Se NMR spectra as well as similar decomposition products **2b** and **3b**.¹⁸ This suggests that γ -picoline also forms the stabilised $\sigma^3\lambda^5$ adduct, analogous with that of pyridine, and opens the possibility to fine tune the reactivity and stability of these new species.

To conclude, the new phenyldiselenoxophosphorane **1a** was synthesised and characterised. DFT and *ab initio* calculations indicate a weakly covalent, but highly polar donor–acceptor bond for the P–N interaction. Furthermore, quantum chemical calculations showed that the reaction of **WR** with pyridine indeed results in an activation of **WR** forming a $\sigma^3\lambda^5$ stabilised species.

The release of the reactive intermediate **1a** and therefore the corresponding dissociation enthalpy is *ca.* 5 kcal mol^{−1} lower for **1a** compared to **WR**.

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- Woollins' reagent (**WR**) (532 mg, 1.00 mmol) was stirred in dry pyridine (5 mL) for 30 min. 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 of **1a** in quantitative yield. Colourless, air sensitive crystals were obtained at −40 °C after two days. ³¹P NMR (202.5 MHz, C₆D₆): δ = 101.6, (s, J_{PSe} = −808.4 Hz) ⁷⁷Se NMR (95.4 MHz, C₆D₆): δ = 91.9 (d, J_{SeP} = −809.5 Hz) MS (EI⁺): m/z = 79.0 [C₅H₅N]⁺, 267.8 [C₆H₅PSe₂]⁺.
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- Crystals of **2a** and **3a** suitable for X-ray crystallography were isolated from the reaction mixture. A structural representation and in detail discussion can be found in the ESI[†].
- Detailed information on decomposition and behaviour of both solvent systems can be found in the ESI[†] NMR data of **1b**: ³¹P NMR (202.5 MHz, C₆D₆): δ = 97.6 ppm, (s, J_{PSe} = −808.8 Hz) ⁷⁷Se NMR (95.4 MHz): δ = 82.9 ppm (d, J_{SeP} = −809.2 Hz). Crystals of **2b** and **3b** suitable for X-ray crystallography were isolated from the reaction mixture. A structural representation and in detail discussion can be found in the ESI[†].

