The activation of Woollins’ reagent. Isolation of pyridine stabilised PhPSe$_2$\(+^{\dagger}$

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Woollins’ reagent (WR, (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 RPSe$_2$ system stabilised by an external molecule and has potential as a selenation reagent for reactions under mild conditions.

Species with the molecular formula RPE$_2$ (E = O, S, Se, 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 $\sigma^5\lambda^5$ 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 $\sigma^5\lambda^5$ 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.\(^7\)

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

Storing the resulting yellow solution at $\sim$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) \(\text{Å}\) are comparable to those reported for WR (2.102(3) \(\text{Å}\)).\(^\text{1e}\) Interestingly, the P1–N1 distance (1.886(7) \(\text{Å}\)) is significantly longer than usual P(V)–N single bonds reported before (e.g. 1.652(3) \(\text{Å}\) in PhP[NHCH$_2$Ph]$_2$Se, 1.665(2) \(\text{Å}\) for [iPrNH$_2$][iPr]PhPSe$_2$NiPr$_2^{\text{\dagger\dagger}}$ or 1.617(6)–1.688(3) \(\text{Å}\) in [(tBuH)N[Se]P$_2$[µ-µ-NtBu]$_2$]$^{\text{\dagger\dagger\dagger}}$ or 1.800(4) \(\text{Å}\) for Na[H$_2$NO,P]$_2^{\text{\dagger\dagger}}$). 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) \(\text{Å}\) for a 2,4-di-tert-butyl-6-(l-piperidino)phenyl stabilized PSe$_2$ system, which prompted us to investigate the bonding situation in 1a in more detail.\(^\text{9}\)
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. Ongoing 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 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/PCPM(py) level, the computed dissociation enthalpies and free energies at room temperature are ΔH = 13.0 kcal mol⁻¹ and ΔG = 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 ΔH = 18.0 kcal mol⁻¹ and ΔG = 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 σ³δ⁻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.¹⁶,¹³ 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.
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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Notes and references

7 Woollins’ reagent (WR) ([32 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. \(^{31}\)P NMR (202.5 MHz, C\(_6\)D\(_6\)): \(\delta = 101.6\), (d, J\(_{P-P}\) = 808.4 Hz) \(^{77}\)Se NMR (95.4 MHz, C\(_6\)D\(_6\)): \(\delta = 91.9\), (d, J\(_{P-Se}\) = 809.5 Hz) MS (EI): \(m/z = 79.0\) [C\(_5\)H\(_5\)N]\(^+\), 267.8 [C\(_6\)H\(_5\)PSe\(_2\)]\(^+\).
17 Crystals of 2a and 1a suitable for X-ray crystallography were isolated from the reaction mixture. A structural representation and in detail discussion can be found in the ES\(\text{†}\).
18 Detailed information on decomposition and behaviour of both solvent systems can be found in the ES\(\text{†}\) NMR data of 1b: \(^{31}\)P NMR (202.5 MHz, C\(_6\)D\(_6\)): \(\delta = 97.6\) ppm, (d, J\(_{P-P}\) = −808.8 Hz) \(^{77}\)Se NMR (95.4 MHz): \(\delta = 82.9\) ppm (d, J\(_{P-Se}\) = −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 ES\(\text{†}\).