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The activation of Woollins’ Reagent. Isolation of pyridine stabilised PhPSe₂

Laura Ascherl, Andreas Nordheider, Kasun S. Athukorala Arachchige, David B. Cordes, Konstantin Karaghiosoff, Michael Bühl, Alexandra M. Z. Slawin and J. Derek Woollins*

Woollins’ Reagent (WR, (PhPSe₂)₂) plays an essential role in the selenation of organic compounds. Reaction of WR with pyridine gives the P(V) species PhPSe₂ stabilized by pyridine coordination which is the first crystallographically characterised mononuclear RPSe₂ system stabilised by a pyridin molecule and has potential as a selenation reagent for reactions under mild conditions.

Species with the molecular formula RPE₂ (E = O, S, Se, Te) exhibit a very unusual bonding situation: Phosphorus is in the formal oxidation state of +V but only tricoordinate (σ³λ⁵). The coordination sphere of σ³λ⁵ phosphoranes is unsaturated, therefore a strong Lewis acidity is expected. 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.

The monomeric form of Woollins’ reagent (WR), a phenyldiselenoxophosphorane exhibiting a σ³λ⁵ phosphorus atom has been postulated. In comparison, the sulfur analogue of WR, Lawesson’s Reagent (LR), 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.

The ³¹P NMR spectrum of 1a consists of a singlet at 101.6 ppm with satellites representing the ¹JₚSe 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). Interestingly, the P1–N1 distance (1.886(7) Å) is significantly longer than usual P⁵–N single bonds reported before (e.g. 1.652(3) Å in PhP(NHCH₂Ph)₂Se, 1.665(2) Å for [PrNH₂Pr][PhPSe₂NHPr]²⁺ or 1.617(6)–1.688(3) Å in [(tBu (H)N(Se)P)₂(μ-NtBu)]³⁻ or 1.800(4) Å for Na[H₂NO₃P]⁶⁻). This suggests that the pyridine entity is bonded rather weakly to
the phenylselenoxo-phosphorane and can be abstracted quite easily in order to release the reactive intermediate. In contrast a N→P 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.³

In order to analyze 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. 0.07 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) 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),¹¹ 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 and ΔG = 1.6 kcal/mol. 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 and ΔG = 6.4 kcal/mol, i.e. both higher by ca. 5 kcal/mol. 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 σ₅²⁺,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.¹⁰,¹³ It has also been shown that dithiophosphorane species are known to undergo nucleophilic attack from the oxygen of carbonyl groups.⁶ 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.

Thus, the reaction of methanol with 1a in pyridine at 50 °C yielded O-Methyl Se-hydrogen phenylphosphonodiselenoate as observed for the reaction of WR with methanol (Scheme 3).¹⁴

Observed were low reaction times, mild conditions and as an advantage the solubility of 1a in pyridine, whereas a suspension has to be used for WR.

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Figure 3. Electrostatic potential of 1a at the B3LYP/PCPM(py) level, plotted on a colour scale from +8.65×10⁻² a.u. (blue) to −8.65×10⁻² a.u. (red) and mapped onto an isodensity surface with ρ = 4.10⁻⁴ a.u.

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

Scheme 3. Reaction of WR and 1a yield the same product (O-Methyl Se-hydrogen phenylphosphonodiselenoate).
In contrast, the reaction of 1a with diphenylacetylene,13e benzamide15 or DME16 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 hexa selenium phosphonate 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 dipyridiniumphenyltriselenophosphonate 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.

![Figure 4. Molecular structures of 2a and 3a.](image)

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 σ2Pω 1a aduct, analogous with that of pyridine, and opens the possibility to fine tune the reactivity and stability of these new species.

Conclusions

The new phenyl diselenoxophosphorane 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 σ2Pω stabilised species. The release of the reactive intermediate 1a and therefore the corresponding dissociation enthalpy is ca. 5 kcal/mol lower for 1a compared to WR.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental and crystallographic as well as computational details in pdf form. See DOI: 10.1039/e000000x/

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Detailed information on decomposition and behaviour of both solvent systems can be found in the ESI. NMR data of 1b: $^{31}$P NMR (202.5 MHz, C$_6$D$_6$): $\delta = 97.6$ ppm, (s, $^1J_{PSe} = -808.8$ Hz) $^{77}$Se NMR (95.4 MHz): $\delta = 82.9$ ppm (d, $^1J_{SeP} = -809.2$ 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.
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The reaction of Woollins’ Reagent (WR) with pyridine gives the P(V) species Ph₂PSe₂ stabilised by pyridine coordination. PhPSe₂•py is the first crystallographically characterised mononuclear RPSe₂ system stabilised by an external molecule (py). The species has potential as a selenation reagent for reactions under mild condition as shown by calculations and an experimental comparison to WR.