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Trapping Rare and Elusive Phosphinidene Chalcogenides

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Dedicated to Prof. Risto S. Laitinen on the occasion of his 65th birthday.

Abstract: Four-membered rings with a P₂Ch₂ core (Ch = S, Se) and phosphorus in the +3 oxidation state have been synthesized. The utility of these rings as a source of monomeric phosphinidene chalcogenides was probed by the addition of an *N*-heterocyclic carbene, resulting in a base-stabilized phosphinidene sulphide. Similarly, persistence of the phosphinidene selenide in solution was shown through cycloaddition chemistry with 2,3-dimethylbutadiene at elevated temperatures. The observed reactivity was explained by detailed computational work that established the conditions upon which the P₂Ch₂ rings can liberate phosphinidene chalcogenides.

Phosphinidenes (R-P (1)) are often considered the phosphorus analogues of carbenes based on their electronic structure that contains a monocoordinate, neutral P(I) centre.^[1–9] Phosphinidene chalcogenides (R-P=Ch (2Ch)) are oxidized versions of phosphinidenes (P(I)→P(III)). Despite formally containing a lone pair of electrons at phosphorus, where one would expect an imposition of carbene-like behaviour, olefinic reactivity remains dominant.^[10–14] The presence of phosphinidene sulphides (R-P=S) in solution has been verified using Diels-Alder chemistry, trapping R-P=S with dimethylbutadiene.^[11,12,14–17] Although this is elegant work demonstrating the resilience of R-P=S, the outcome of the reaction precludes a close examination of the P=S functional group with phosphorus in the +3 oxidation state. Alternatively to cycloaddition chemistry, transition metal complexes^[18–23] and unique ligand design^[24,25] have been used to stabilize R-P=Ch. With the exception of single examples demonstrating zwitterionic stabilization of R-P=Ch (Ch = S, Se; **A**, Figure 1), the quest to isolate “free” phosphinidene chalcogenides remains a challenge in phosphorus-chalcogen chemistry.^[26,27] Moreover, these reports chronicle nucleophilic behaviour that stemmed from the terminal chalcogenide,^[26,27] the prevalent resonance form, rather than olefinic as one might expect for a P=Ch functionality.

Figure 1. Top: General structures of phosphinidenes (**1**), phosphinidene chalcogenides (**2Ch**), and P₂Ch₂ rings (**3Ch**). Previously reported ylid-stabilized “P=Ch” moiety (**A**) and known phosphorus-chalcogen rings with a general formula (RPS)_n (**B**, n = 3; **C**, n = 4). Bottom: General synthetic scheme for **3Ch** and their potential equilibrium with **2Ch**.

The R-P=S unit is speculated as a key species in the formation of larger (RPS)_n rings (**B** and **C**, Figure 1),^[28–35] although the smallest member of the series (RPS)₂ (**3S**) has yet to be identified for P(III) as compared to P(V), where numerous examples are known.^[29,36–42] Nevertheless, breaking apart the cyclic structures (RPCh)_n into their monomeric units (n[R-P=Ch]) is one strategy envisioned to establish systematic and stoichiometric access to a low-coordinate P(III) centre. In this context, we report the synthesis of (RPCh)₂ heterocycles (**3S**, Ch = S; **3Se**, Ch = Se) which represent the first four-membered organophosphorus-chalcogen rings with phosphorus in the +3 oxidation state, a species absent in the well-established chemistry of P and S/Se. The success in preparing the (RPS)₂ ring provided means to the isolation of a *N*-heterocyclic carbene (NHC) stabilized phosphinidene sulphide. Access to the monomeric selenide unit was ascertained by a reaction of the (RPSe)₂ ring with 2,3-dimethylbutadiene (dmbd), giving a six-membered Diels-Alder product. A mechanistic investigation using density functional theory revealed that the P(III) centres in **3Ch** can display Lewis acidic behaviour and react with strong nucleophiles such as NHCs, breaking the four-membered ring. The results of computational investigations also supported the notion that the reactivity of **3Ch** with dmbd involves monomeric phosphinidene chalcogenides as intermediates, consistent with the elevated temperatures required to induce reactivity.

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The 1:1 stoichiometric addition of $\text{S}(\text{TMS})_2$ (TMS = trimethylsilyl) to Ar^*PCl_2 ($\text{Ar}^* = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$, Mes = 2,4,6- $(\text{CH}_3)_3\text{C}_6\text{H}_2$; Figure 1) at 25°C resulted in the gradual appearance of a new singlet in $^{31}\text{P}\{^1\text{H}\}$ NMR ($\delta_{\text{P}} = 124$ ppm). After 16 h, the starting material Ar^*PCl_2 ($\delta_{\text{P}} = 160$ ppm) was consumed and the volatiles were removed *in vacuo* to give a yellow powder. Adding a small amount of *n*-pentane and placing the resulting solution at -35°C for overnight gave single crystals of X-ray diffraction quality that were confirmed to be **3S** by a subsequent structure analysis (64% total yield). NMR spectroscopy data recorded on crystalline **3S** redissolved in benzene- d_6 showed the same $^{31}\text{P}\{^1\text{H}\}$ signal as the reaction mixture along with a single set of Ar^* resonances in the ^1H NMR spectrum, which confirmed the equivalence of Ar^*PS fragments on the NMR time scale. In the solid state, **3S** was found to have a high melting point (204°C), and the compound proved to be resistant to oxidation upon short exposure to the ambient environment.

An analogous synthetic procedure was used to make **3Se**. In this instance, a sample of the crude reaction mixture showed the presence of multiple products as determined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. However, the minor products could be removed by washing the crude product with *n*-pentane, yielding a single major product as evidenced by the NMR data ($\delta_{\text{P}} = 24$ ppm, $^1J_{\text{P-Se}} = 46$ Hz). The isolated material (86% yield) was redissolved in CH_2Cl_2 , and a sample of it was used in a CH_2Cl_2 /toluene vapour

diffusion to yield single crystals suitable for X-ray diffraction. The signal in the $^{31}\text{P}\{^1\text{H}\}$ NMR data of redissolved crystalline **3Se** is identical to that observed in the reaction mixture; a corresponding broad triplet was also observed in the $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum ($\delta_{\text{Se}} = 484.6$ ppm, $^1J_{\text{Se-P}} = 45.9$ Hz). Relative to **3S**, **3Se** is far less stable. For example, solution $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy studies showed that **3Se** decomposes when left at room temperature in solution over an extended period of time, while **3S** does not show any noticeable decomposition under similar conditions.

X-ray crystallographic analysis of **3S** showed that, in the solid state, the P_2S_2 core adopts a butterfly conformation (Figure 2) with narrow bond angles ($\text{P-S-P}_{\text{avg}} = 85.96(3)^\circ$, $\text{S-P-S}_{\text{avg}} = 88.96(3)^\circ$) and P-S bond lengths suggestive of single bonds ($\text{P-S}_{\text{avg}} = 2.1461(8)$ Å; sum of Pyykkö & Atsumi single bond covalent radii for P and S is 2.14 Å).^[43,44] The solid state structure of **3Se** is similar to **3S** (Figure 2) in that the P_2Se_2 core is folded with acute bond angles ($\text{P-Se-P}_{\text{avg}} = 85.96(3)^\circ$, $\text{Se-P-Se}_{\text{avg}} = 89.20(3)^\circ$) and P-Se bond lengths slightly longer than that expected for single bonds ($\text{P-Se}_{\text{avg}} = 2.3033(16)$ Å; the sum of Pyykkö & Atsumi single bond covalent radii for P and Se is 2.27 Å).^[43,44] The two structures, however, differ in the relative orientation of the terphenyl ligands i.e. *anti* for **3S** and *syn* for **3Se**. The *syn*-conformation of **3Se** most likely causes some ring strain and steric repulsion, leading to elongation of P-Se bonds.

Given the acute bond angles in **3Ch**, we hypothesised that the structures might be amenable to liberating **2Ch**. To test this hypothesis, trapping reactions were carried out by dropwise addition of a THF solution of two stoichiometric equivalents of NHC (1,3-isopropyl-4,5-dimethylimidazol-2-ylidene) to a THF solution of **3S** at 25°C over 15 min (Figure 3). A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture revealed complete consumption of **3S** and the formation of a new product ($\delta_{\text{P}} = 29$ ppm). The volatiles were removed *in vacuo* and the crude material rinsed with *n*-pentane to give an insoluble yellow powder (73% yield; $\delta_{\text{P}} = 29$ ppm). X-ray structural study performed on single crystals grown by $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ vapour diffusion confirmed that the product is a base-stabilized phosphinidene sulphide (**5S**, Figure 4). The metrical parameters of **5S** (Figure 4) show that the phosphorus atom is significantly pyramidal ($\Sigma 310.5^\circ$) with two essentially equal P-C bonds (1.869(4) and 1.853(5) Å). The most notable feature in the structure is, however, the P-S bond (2.029(14) Å) that is more than 0.1 Å shorter than that in **3S**, suggestive of some multiple bond character (the sum of Pyykkö & Atsumi double bond covalent radii for P and S is 1.96 Å).^[43,44]

Figure 2. Solid state structures for **3S** (left) and **3Se** (right) with thermal ellipsoids at 50% probability. Selected bond lengths [Å] and bond angles [$^\circ$]. **3S**: P(1)-S(1) 2.1489(2), P(1)-S(2) 2.1517(8), P(2)-S(1) 2.1359(8), P(2)-S(2) 2.1479(8), P(1)-C(1) 1.849(2), P(2)-C(25) 1.863(2), C(1)-P(1)-S(1) 105.11(7), C(1)-P(1)-S(2) 102.97(7), S(1)-P(1)-S(2) 88.74(3), C(25)-P(2)-S(1) 110.59(7), C(25)-P(2)-S(2) 101.17(7), S(1)-P(2)-S(2) 89.18(3), P(2)-S(1)-P(1) 86.14(3), P(2)-S(2)-P(1) 85.77(3), P(1)-S(1)-S(2)-P(2) 34.335(4). **3Se**: P(1)-Se(1) 2.3113(14), P(1)-Se(2) 2.3060(16), P(2)-Se(1) 2.2931(16), P(2)-Se(2) 2.3033(16), P(1)-C(1) 1.851(5), P(2)-C(25) 1.853(5), C(1)-P(1)-Se(1) 103.74(15), C(1)-P(1)-Se(2) 103.72(16), Se(1)-P(1)-Se(2) 88.93(6), C(25)-P(2)-Se(1) 106.10(18), C(25)-P(2)-Se(2) 108.39(17), Se(1)-P(2)-Se(2) 89.45(6), P(2)-Se(1)-P(1) 82.17(6), P(2)-Se(2)-P(1) 82.06(5), P(1)-Se(1)-Se(2)-P(2) 45.442(8).

Figure 3. Trapping of $\text{Ar}^*\text{-P=S}$ and $\text{Ar}^*\text{-P=Se}$ by treatment of **3S** and **3Se** with an NHC and dmbd, respectively.

Figure 4. Solid state structures for **5S** (left) and **7Se** (right) with thermal ellipsoids at 50% probability. Selected bond lengths [Å] and angles [°]. **5S**: P(1)-C(1) 1.869(4), P(1)-S(1) 2.0289(14), P(1)-C(25) 1.853(5), C(1)-P(1)-S(1) 113.02(13), C(2)-C(1)-P(1) 125.5(3), C(6)-C(1)-P(1) 115.6(3), C(1)-P(1)-C(25) 98.60(19), C(25)-P(1)-S(1) 98.91(13). **7Se**: P(1)-C(1) 1.833(5), P(1)-Se(1) 2.2249(16), P(1)-C(25) 1.792(6), P(1)-C(26) 1.827(6), C(27)-C(28) 1.346(8), C(1)-P(1)-Se(1) 111.99(18), C(2)-C(1)-P(1) 119.9(4), C(6)-C(1)-P(1) 120.4(4), C(1)-P(1)-C(25) 114.5(3), C(1)-P(1)-C(26) 115.0(3), C(25)-P(1)-Se(1) 106.3(2), C(25)-P(1)-C(26) 102.1(3), P(1)-C(26)-C(27) 111.0(4), Se(1)-C(29)-C(28) 111.5(4).

A similar base stabilization approach was undertaken to obtain **5Se**. Unfortunately, this chemistry proved to be less straightforward, and a single major product could not be isolated. Nevertheless, the hypothesis for accessing an as yet unknown R-P=Se fragment in solution remained, so we opted to explore the Diels-Alder chemistry known for trapping compound **2S**. However, the addition of dmbd to **3Se** in a 2:1 stoichiometric ratio at 25°C showed no consumption of the starting material in $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy even after two days. We therefore examined the chemistry of **3Ch** and the possible dimer $\rightleftharpoons$ monomer equilibrium with computational methods using density functional theory at the PBE1PBE/TZVP level (see SI). For simplicity, the Ar* groups were replaced by the parent terphenyl ligand in all calculations.

The frontier orbitals of **3Ch** revealed that the compounds are amphoteric and capable of reacting not only with Lewis acids but also with Lewis bases as the *p*-type atomic orbitals of phosphorus make a large contribution on both the HOMO and LUMO of **3Ch**. Thus, NHCs (1,3-methylimidazol-2-ylidene) were found to add to the P(III) centres in **3S**, leading to a stepwise breakup of the P_2S_2 ring and the formation of **5S** via **3S**-NHC (Figure 5). The reaction is exergonic by 106 kJ mol $^{-1}$ and has an activation energy of 42 kJ mol $^{-1}$ for the second addition step. This indicates that the formation of **5S** is spontaneous and fast even at room temperature, in agreement with experimental observations. Another possible pathway for the formation of **5S** is the reaction between **2S** and NHC, provided that **3Ch** dissociates to **2Ch** in solution. For this reason, the possible dimer $\rightleftharpoons$ monomer equilibrium was put to the fore (Figure 5). Potential energy scans revealed that the dissociation of **3S** and **3Se** is endergonic by 67 and 82 kJ mol $^{-1}$, respectively. Furthermore, the reaction was found to proceed through a high-energy transition state with activation barriers of 113 and 147 kJ mol $^{-1}$ for **3S** and **3Se**, respectively. This immediately suggests that the monomer **2S** is an unlikely intermediate en route to **5S**.

Figure 5. Reaction coordinate diagrams for the conversion of **3S** to **2S/5S** (top) and **3Se** to **2Se/6Se** (bottom). Gibbs energies are reported in kJ mol $^{-1}$ and relative to **3Ch**.

As a corollary of the above, the dimers **3Ch** are the preferred end products from the reaction between $\text{Ch}(\text{TMS})_2$ and Ar^*PCl_2 even though the monomers **2Ch** are most likely the species initially formed in the process.

The tendency of **2Ch** to dimerize follows directly from their electronic structure. As discussed in the literature,^[11] the HOMO and LUMO of **2Ch** are both P-S π^* -orbitals. Thus, the interaction of two molecules of **2Ch** allows for two pairwise donor-acceptor interactions, leading to the formation of two new P-S bonds and, consequently, **3Ch**. As this process involves the occupation of the initially empty P-S antibonding LUMOs of **2Ch**, all P-S bonds in **3Ch** are single bonds. This is clearly seen in the calculated P-S Wiberg bond indices that are close to unity for **3S** (0.95) and **3Se** (0.96), while those of **2S** (1.89) and **2Se** (1.91) are significantly higher; a similar trend is also seen in the delocalization indices calculated for **2Ch** and **3Ch**. For comparison, the Wiberg bond index for the P-S bond in **5S** is 1.22, which, together with the calculated natural atomic charges, indicates that the ylidic ($\text{P}^+=\text{S}^-$) resonance structure makes a high contribution to bonding in **5S**.

Although the calculations indicated that a dimer $\rightleftharpoons$ monomer equilibrium is unlikely at room temperature, it is plausible that some **2Ch** could be liberated by heating **3Ch**. It is also expected that the steric bulk of the Ar* substituent will destabilize the dimer more than the monomer, potentially lowering the barrier for the dissociation of **3Ch** below of that predicted by our calculations. Consequently, the trapping

reaction between **3Se** and dmbd was repeated at 50 °C, which resulted in complete consumption of the starting materials after 16 h and the appearance of a singlet in the $^{31}\text{P}\{^1\text{H}\}$ spectrum ($\delta_{\text{P}} = 11$, $^1J_{\text{Se-P}} = 184.1$ Hz). The resulting compound (**6Se**, Figure 3) was a colourless oil, which prevented straightforward structural characterization by X-ray crystallography. For this reason, the product was derivatized using a stoichiometric amount of Me-I, targeting the quaternization of phosphorus and the formation of **7Se** (Figure 3). After 16 h of stirring with Me-I in Et₂O at 25 °C, the starting material was fully consumed, and a new singlet appeared in the $^{31}\text{P}\{^1\text{H}\}$ spectrum ($\delta_{\text{P}} = 46$, $^1J_{\text{P-Se}} = 212.3$ Hz). The crude white powder was washed with *n*-pentane, and the precipitate was redissolved in CH₂Cl₂ and layered with Et₂O to give single crystals suitable for X-ray diffraction (64% total yield). The structure (Figure 4) confirmed the product to be the salt **7Se** with a six-membered ring and tetrahedral geometry around the phosphorus atom. It is notable that the P-Se bond is significantly shorter in **7Se** (2.3113(15)) than in **3Se** (2.225(2) Å), indicating relief of strain upon dissociation of the dimeric structure.

The reaction between **3Se** and dmbd was also examined computationally (Figure 5). Despite numerous attempts, we were not able to identify a Diels-Alder-type transition state (concerted or stepwise) that would connect **3Se** and dmbd directly to **6Se**. The lack of reactivity is not surprising considering that bonding analyses indicated that the P-Ch bonds in **3Ch** are single bonds. In contrast, **2Se** has a P=Se double bond and it was found to be a probable intermediate leading to **6Se**. Specifically, the Diels-Alder reaction between two equivalents of **2Se** and dmbd is exergonic by 104 kJ mol⁻¹ with an activation barrier of only 66 kJ mol⁻¹ (concerted mechanism). Thus, even though the conversion of **3Se** to **2Se** is endergonic, the facile reactivity of **2Se** with dmbd more than compensates this and transforms the overall reaction exergonic by 22 kJ mol⁻¹.

In conclusion, we have detailed the synthesis of four-membered phosphorus-chalcogen rings (**3Ch**) that are the first representatives of such cyclic inorganic systems with phosphorus in the +3 oxidation state. We have also demonstrated access to monomeric phosphinidene-chalcogenides; the sulphur derivative being stabilized with an *N*-heterocyclic carbene (**5S**) and the selenium congener trapped with 2,3-dimethylbutadiene (**6Se**). Computational work has showed that **5S** forms from **3S** via base-assisted cleavage of the P₂S₂ ring. In contrast, the formation of **6Se** from **3Se** and dmbd most likely proceeds via monomeric phosphinidene selenide **2Se**, a previously unknown member of the phosphinidene chalcogenide family. Further experimental and computational studies of the chemistry of **3Ch** are in progress.

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