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Trapping Rare and Elusive Phosphinidene Chalcogenides


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

Abstract: Four-membered rings with a P=Ch 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(II) centre.[1–9] Phosphinidene chalcogenides (R-P=Ch (2Ch)) are oxidized versions of phosphinidenes (P(II)→P(III)). Despite formally containing a lone pair of electrons at phosphorus, where one would expect an imposition of carbone-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.[15,16] 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[17–23] 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. Moreover, these reports chronicle nucleophilic behaviour that stemmed from the terminal chalcogeno[26,27] the prevalent resonance form, rather than olefinic as one might expect for a P=Ch functionality.

The R-P=S unit is speculated as a key species in the formation of larger (RPS)₂ rings (B and C, Figure 1)[28–35] although the smallest member of the series (RPS)₁ (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)₁ into their monomeric units ([nR-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 (RPSe)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.

Figure 1. Top: General structures of phosphinidenes (1), phosphinidene chalcogenides (2Ch), and P₃Ch₃ rings (3Ch). Previously reported yield-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 1:1 stoichiometric addition of S(TMS)$_2$ (TMS = trimethylsilyl) to Ar*=P(2)-P(1) ($\text{Ar}^*=2,6$-Mes$_2$C$_6$H$_3$, Mes=2,4,6-(CH$_3$)$_2$C$_6$H$_2$; Figure 1) at 25°C resulted in the gradual appearance of a new singlet in $^{31}$P($^1$H) NMR (δ$_p$ = 124 ppm). After 16 h, the starting material Ar*P(2)Cl$_2$ (δ$_p$ = 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 $^{31}$P($^1$H) signal as the reaction mixture along with a single set or Ar* resonances in the $^1$H NMR spectrum, which confirmed the equivalence of Ar*PS fragments on the NMR time scale. In the solid state, 3S was found 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 $^{31}$P($^1$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 (δ$_p$ = 24 ppm, J$_{P-Se}$ = 46 Hz). The isolated material (86% yield) was redissolved in CH$_2$Cl$_2$, and a sample of it was used in a CH$_2$Cl$_2$/toluene vapour diffusion to yield single crystals suitable for X-ray diffraction. The signal in the $^{31}$P($^1$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 $^{77}$Se($^1$H) NMR spectrum (δ$_{se}$ = 484.6 ppm, J$_{Se-P}$ = 45.9 Hz). Relative to 3S, 3Se is far less stable. For example, solution $^{31}$P($^1$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$_2$Se$_2$ core adopts a butterfly conformation (Figure 2) with narrow bond angles (P-S-P$_{avg}$ = 85.96(3)$^\circ$, S-P-S$_{avg}$ = 88.96(3)$^\circ$) and P-S bond lengths suggestive of single bonds (P-S$_{avg}$ = 2.1461(8) Å; sum of Pyykkö & Atsumi single bond covalent radii for P and Se is 2.1479(8) Å). 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 $^{31}$P($^1$H) NMR spectrum of the reaction mixture revealed complete consumption of 3S and the formation of a new product (δ$_p$ = 29 ppm). The volatiles were removed in vacuo and the crude material rinsed with n-pentane to give an insoluble yellow powder (73% yield; δ$_p$ = 29 ppm). X-ray structural study performed on single crystals grown by CH$_2$Cl$_2$/$\text{Et}_2$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 (Σ $= 310.5^\circ$) 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 single bond covalent radii for P and S is 1.96 Å).
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 

$^{31}$P-$^{1}H$ NMR spectroscopy even after two days. We therefore examined the chemistry of 3Ch and the possible dimer ⇄ 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 reactive 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 HO MO and LUMO of 3Ch. As discussed in the literature,[10] 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 (P=S) resonance structure makes a high contribution to bonding in 5S.

Although the calculations indicated that a dimer ⇄ 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 $3\text{Se}$ 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 ($\delta_P = 11.1, \delta_{3\text{S},3\text{Se}} = 184.1$ Hz). The resulting compound ($6\text{Se}$, 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 $7\text{Se}$ (Figure 3). After 16 h of stirring with Me-I in Et$_2$O at 25°C, the starting material was fully consumed, and a new singlet appeared in the $31^\text{P}(1^\text{H})$ spectrum ($\delta_P = 46.9, \delta_{3\text{S},3\text{Se}} = 212.3$ Hz). The crude white powder was washed with n-pentane, and the precipitate was redissolved in CH$_2$Cl$_2$ and layered with Et$_2$O to give single crystals suitable for X-ray diffraction (64% total yield). The structure (Figure 4) confirmed the product to be the salt $7\text{Se}$ with a six-membered ring and tetrahedral geometry around the phosphorus atom. It is notable that the P-Se bond is significantly shorter in $7\text{Se}$ (2.3113(15) Å) than in $3\text{Se}$ (2.225(2) Å), indicating relief of strain upon dissociation of the dimeric structure.

The reaction between $3\text{Se}$ 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 $3\text{Se}$ and dmbd directly to $6\text{Se}$. The lack of reactivity is not surprising considering that bonding analyses indicated that the P-Ch bonds in $3\text{Ch}$ are single bonds. In contrast, $2\text{Se}$ has a P=Se double bond and it was found to be a probable intermediate leading to $6\text{Se}$. Specifically, the Diels–Alder reaction between two equivalents of $2\text{Se}$ 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 $3\text{Se}$ to $2\text{Se}$ is endergonic, the facile reactivity of $2\text{Se}$ 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 ($3\text{Ch}$) 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 shown that 5S forms from 3S via base-assisted cleavage of the P$_2$S$_2$ 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 $3\text{Ch}$ are in progress.

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