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Lewis base-free thiophosphonium ion: a cationic sulfur atom transfer reagent†

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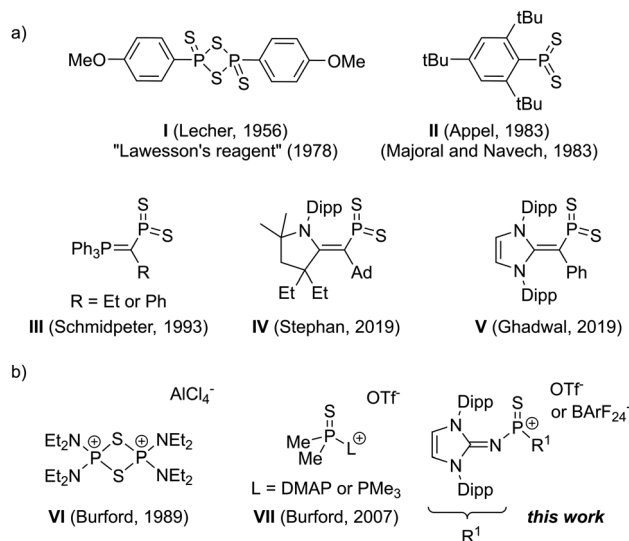
Phosphorus(v) sulfide and Lawesson's reagent are commonly used thionating reagents which are considered to operate after dissociation into highly reactive dithiophosphorane fragments. We report the synthesis and properties of a monomeric thiophosphonium ion $[R_2P=S]^+$. The highly electrophilic species reacts with carbonyls in oxo-for-sulfido exchange reactions at room temperature and undergoes phosphorus–chalcogen bond metathesis reactions with phosphine chalcogenides.

The chemical conversion of carbonyls to thiocarbonyls using sulfur atom transfer reagents is an important method in synthetic organic chemistry.¹ Phosphorus(v) sulfide (P_4S_{10}) and Lawesson's reagent (**I**, Scheme 1) are most commonly used in this context.² Their cyclic structures of alternating sulfur and phosphorus atoms require thermal cleavage into reactive dithiophosphoranes ($R-PS_2$), which can then react with carbonyls *via* four-membered ring intermediates to give the corresponding thiocarbonyls and metathiophosphonates.^{3,4}

Trigonal planar dithiophosphoranes have a natural tendency to dimerise or trimerise forming dithiadiphosphetanes or trithiatriphosphinanes, in which phosphorus adopts a tetrahedral binding mode. Since the discovery of the potential of dithiophosphoranes as thionating reagents,⁵ scientists were eager to isolate the monomeric and thus more reactive species. In 1983, the groups of Appel,⁶ as well as Majoral and Navech,⁷ synthesised the first monomeric dithiophosphorane **II** (Scheme 1) by using a very bulky 2,4,6-tri-*tert*-butylphenyl group, which prevents dimerisation upon blocking both sides of the PS_2 plane but

decomposes at 110 °C *via* isomerisation.^{8,9} The group of Yoshifuji extended the scope of monomeric phenyl-substituted dithiophosphoranes by using amino groups to prevent dimerisation.¹⁰ Furthermore, the group replaced one *tert*-butyl group adjacent to phosphorus in **II** with a methoxy group, resulting in a dithiophosphorane that is monomeric in solution but dimeric in the solid state.⁴ Ylide-substituted monomeric dithiophosphoranes **III** were reported by Schmidpeter and coworkers.¹¹ Very recently, the group of Mardiykov trapped the monomeric form of the Lawesson's reagent in argon matrices at 10 K¹² and the groups of Stephan and Ghadwal reported two examples for vinyl-substituted dithiophosphoranes **IV** and **V**, respectively.¹³

The reactivity of main group carbonyl analogues ($R_2E=O$) has recently gained considerable interest,¹⁴ fueled by the successful isolation of monomeric, Lewis base-free representatives, such as neutral germanones¹⁵ and silanones,¹⁶ cationic



Scheme 1 (a) Dimeric and monomeric dithiophosphoranes. (b) Thiophosphonium dimer **VI**, Lewis base-stabilised thiophosphonium ion **VII** and the Lewis base-free thiophosphonium presented in this work.

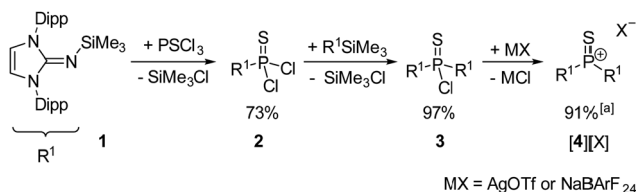
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Scheme 2 Synthesis of [4][OTf] and [4][BARF₂₄]. Dipp = 2,6-diisopropylphenyl, OTf[−] = trifluoromethanesulfonate, BARF₂₄[−] = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. ^ayield for MX = NaBARF₂₄.

oxophosphonium¹⁷ and anionic boryloxy¹⁸ compounds. However, heavier monomeric phosphathiocarbonyls, namely thiophosphonium cations [R₂P=S]⁺, have not yet been isolated. These cationic species should exhibit a highly electrophilic phosphorus center and a more polar P=S double bond compared with the neutral dithiophosphoranes. In fact, the group of Burford showed that these properties translate into a pronounced tendency to form dimers **VI**^{19,20} and Lewis-base adducts **VII**.²¹ Herein, we report the synthesis and characterisation of a Lewis base-free thiophosphonium ion, which can be regarded as a monomeric, more reactive form of the Lawesson's reagent, as indicated by the efficient transfer of the sulfur atom to both carbonyls and phosphorus compounds.

The synthesis of thiophosphonium salts [4][X] ([X][−] = trifluoromethanesulfonate, [OTf][−] or tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, [BARF₂₄][−]) is based on our synthetic protocol for oxophosphonium salts (Scheme 2).¹⁷ Bulky π-donating 1, 3-bis(2,6-diisopropylphenyl)imidazolin-2-imine substituents (R¹) were employed to provide both kinetic and thermodynamic stabilisation of the electrophilic P=S double bond. The reaction of PSCl₃ with (R¹)SiMe₃ (**1**) upon elimination of Me₃SiCl gave the monosubstituted thiophosphoryl chloride (R¹)PSCl₂ (**2**). The subsequent reaction of **2** with a second equivalent of **1** gave the disubstituted thiophosphoryl chloride (R¹)₂PSCl (**3**) with an overall isolated yield of 71% over both steps. A single-crystal X-ray diffraction (XRD) study of **3** (Fig. 1, left) confirmed the formation of the desired species. Treatment of **3** with AgOTf or NaBARF₂₄ resulted in precipitation of AgCl or NaCl,

respectively, and the formation of the corresponding thiophosphonium salts [4][OTf] or [4][BARF₂₄]. The Lewis base-free, trigonal-planar nature of thiophosphonium ion [4]⁺ is confirmed by the shift of the ³¹P NMR signal (116.6 ppm) to higher frequency with respect to the thiophosphoryl chloride precursor **3** (25.9 ppm). The choice of the anion (OTf[−] or BARF₂₄[−]) does not affect the ³¹P NMR shift, which suggests that the anion is separated from the phosphorus center in solution. The phosphorus atom of [4]⁺ is deshielded compared with other imidazoline-2-imine substituted trigonal planar phosphorus(v) cations (iminophosphonium: 79.9 ppm,²² oxophosphonium: 59.1 ppm,¹⁷ phosphorandiylium: 50.7 ppm²³) but appears at lower frequency compared to the dithiophosphorane **II** (295.3 ppm).⁶

An XRD study of single crystals obtained from a concentrated CH₂Cl₂ solution confirmed that [4][BARF₂₄] is a monomeric, Lewis base-free thiophosphonium salt (Fig. 1, right). In the solid-state structure, the electrophilic N₂PS unit is surrounded by the bulky 2,6-diisopropylphenyl (Dipp) substituents and thus well separated from the BARF₂₄[−] anions. The phosphorus atom is in a perfectly planar environment (sum of angles: 360°) comprising a short P–S bond (1.897 Å), which is in the range of the P–S bonds in dithiophosphorane **II** (1.90 Å)⁶ and **III** (R=Ph, 1.92 Å and 1.93 Å),¹¹ and shorter than that of the thiophosphonium dimer **VI** (2.11 Å).¹⁹

Density functional theory calculations at the B3LYP-D3BJ/def2-TZVP level of theory were performed on [(R¹)₂PS]⁺ ([4]⁺) and [(R¹)₂PSe]⁺ ([5b]⁺). The results from our previous computations on [(R¹)₂PO]⁺ ([5a]⁺) are included in the following discussion for comparison.¹⁷ The frontier orbitals (see Fig. 2 for [5a]⁺ and [4]⁺; see S42 in the ESI† for all three analogues) of the three chalcogenophosphonium ions are similar with an increasing contribution of the chalcogen lone pairs to the HOMO for the

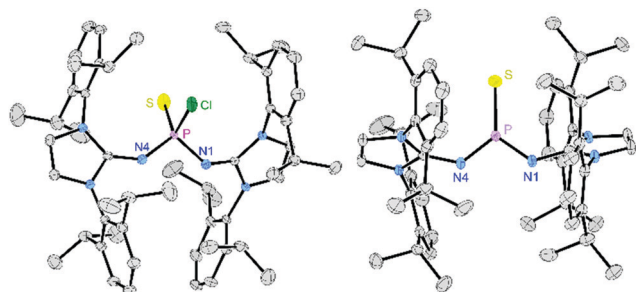


Fig. 1 Solid-state structure of **3** (left) and [4][BARF₂₄] (right). Hydrogen atoms, solvent molecules and the anion of [4][BARF₂₄] are omitted for clarity. Ellipsoids are drawn at 50% probability. Only one of the two crystallographically independent molecules of **3** and only one part of the disordered isopropyl group and N₂PSCl moiety is depicted. Selected bond lengths [Å] and angles [°] of [4][BARF₂₄]: P–N1 1.5578(12), P–N4 1.5606(12), P–S 1.8967(5), N1–P–N4 108.02(6), N1–P–S 124.79(5), N4–P–S 127.17(5).

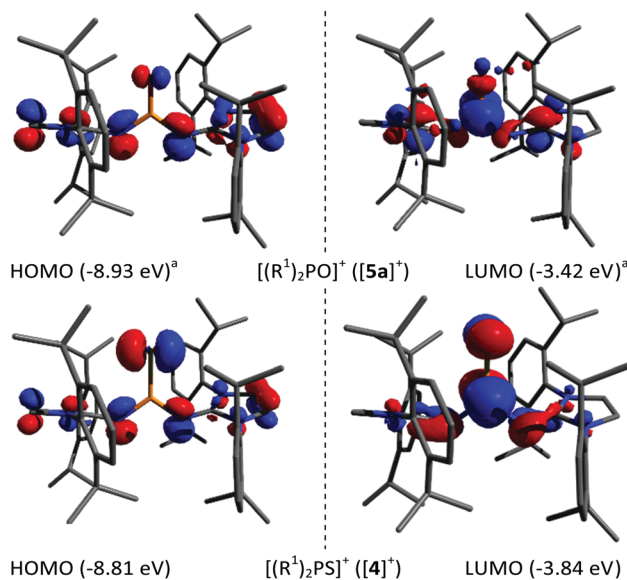


Fig. 2 Selected molecular orbitals of [5a]⁺ (top)¹⁷ and [4]⁺ (bottom) at the B3LYP-D3BJ/def2-TZVP level of theory (±0.05 isosurface). ^aliterature data.¹⁷



Table 1 Calculated Wiberg bond indices (WBI), natural bond orbital (NBO) charges and fluoride ion affinities (FIA) for the chalcogenophosphonium cations **[5a]**⁺, **[4]**⁺ and **[5b]**⁺ using B3LYP-D3BJ/def2-TZVP

	[5a] ⁺	[4] ⁺	[5b] ⁺
WBI of P–O/S/Se	1.315 ^a	1.585	1.546
WBI of P–N	1.126 ^a	1.104	1.105
NBO charge of P [e]	+2.307 ^a	+1.732	+1.642
NBO charge of O/S/Se [e]	−1.030 ^a	−0.502	−0.423
NBO charge of N [e]	−1.013 ^a	−0.987	−0.990
FIA [kJ mol ^{−1}]	634 ^a	616	614

^a literature data.¹⁷

heavier congeners. The LUMOs of **[4]**⁺ and **[5b]**⁺ have π^* character with equal contributions from the P and S/Se atoms. According to the Wiberg bond indices (WBI) (Table 1), the phosphorus–chalcogen bond in **[4]**⁺ has the highest double bond character in this series, which can be rationalised by the similar atom size and thus better orbital overlap of sulfur and phosphorus. The natural bond orbital analysis reveals a concomitant decreasing positive charge for the phosphorus and negative charge for the chalcogen atom in the order O > S > Se, which is associated with a lower polarity of the phosphorus–chalcogen bond. As a common metric to determine the Lewis acidity, the fluoride ion affinities (FIA) were calculated using Christie's method.²⁴ The FIA correlate with the electronegativity of the chalcogen atom and give smaller values for **[4]**⁺ (616 kJ mol^{−1}) and **[5b]**⁺ (614 kJ mol^{−1}) compared to **[5a]**⁺ (634 kJ mol^{−1}),¹⁷ ranking the electrophilicity of chalcogenophosphonium ions in the range of phosphonium cations.²⁵ Our attempt to experimentally determine the Lewis acidity of **[4]**⁺ using the Gutmann–Beckett parameter²⁶ was unsuccessful since no adduct between POEt₃ and **[4]**⁺ was detected.

Inspired by the structural similarity of the trigonal planar thiophosphonium ion **[4]**⁺ with the monomeric form of the Lawesson's reagent, we wanted to explore the ability of **[4]**⁺ to act as thionating reagent.

Preliminary studies were performed by treating **[4][BARF₂₄]** with different amounts of benzaldehyde which gave mixtures of phosphorus containing products as indicated by ¹H and ³¹P NMR spectroscopy. The stoichiometric reaction resulted in incomplete conversion of **[4][BARF₂₄]** suggesting that the oxophosphonium ion is formed as an intermediate, which then undergoes subsequent reactions with benzaldehyde or thiobenzaldehyde. The reaction between the literature-known oxophosphonium salt **[5a][BARF₂₄]**¹⁷ and benzaldehyde was confirmed to give a complex mixture of products in a separate experiment (Fig. S29 in the ESI†). To avoid this subsequent reaction, triethylphosphine oxide was used as a trapping reagent, because it readily forms the Lewis base adduct **[6a]**⁺ with **[5a]**⁺,¹⁷ but does not react with **[4]**⁺ at room temperature. Indeed, adding one equivalent of benzaldehyde to a solution containing **[4][BARF₂₄]** and an excess of POEt₃ resulted in sulfur atom transfer and formation of **[6a][BARF₂₄]** in more than 70% yield determined by ³¹P{¹H} NMR (Scheme 3). Thiobenzaldehyde could not be detected by NMR spectroscopy and GC/MS analysis owing to its tendency to oligomerise.²⁷ The thionation of benzaldehyde with **[4]**⁺ proceeds



Scheme 3 Conversion of carbonyls to thiocarbonyls using **[4][BARF₂₄]** and POEt₃ as trapping reagent. **[BARF₂₄]**[−] anions are omitted for clarity.

within minutes at room temperature, while the same reaction requires refluxing in toluene for 15 hours with the Lawesson's reagent.²⁷ Although this indicates that the thiophosphonium ion **[4]**⁺ is very reactive, the carbonyl substrate scope turned out to be rather narrow. *N*-Methyl-2-pyrrolidinone undergoes thionation to 1-methylpyrrolidine-2-thione at room temperature in 59% yield determined by ³¹P{¹H} NMR. However, other carbonyl compounds such as benzophenone, methyl benzoate, γ -butyrolactone and acetone did not react with **[4]**⁺ at room temperature. The limited substrate scope can be rationalised by the steric shielding of the reactive P=S double bond. The thionation reactions with the thiophosphonium cation **[4]**⁺ are complementary to those with monomeric aryl-substituted dithiophosphoranes reported by the groups of Navech⁹ and Yoshifuji.⁴ The reaction is assumed to proceed *via* a four-membered thiadiphosphetane rings, which is equally conceivable for the cationic system.

Given the polar nature of the P–S bond in **[4]**⁺, we were wondering if it would undergo bond metathesis reactions with other polar P–X (X=O, Se, Te) bonds such as those of Et₃PX (Scheme 4).

The reaction between **[4]**⁺ and Et₃PX required prolonged heating, consistent with the limited steric access of the P–S bond and the fact that four-membered P₂SX ring intermediates are assumed to be formed in the chalcogen exchange process. Heating a fluorobenzene solution of **[4][BARF₂₄]** and two equivalents of Et₃PO at 180 °C for 29 hours resulted in 96% conversion to **[6a][BARF₂₄]** and Et₃PS. The conversion did not change significantly upon further heating of the mixture, suggesting an equilibrium state. Indeed, the same set of compounds was obtained by reacting **[5a][BARF₂₄]** with Et₃PS under equal



Scheme 4 Phosphorus–chalcogen bond metathesis reactions. **[BARF₂₄]**[−] anions are omitted for clarity.

conditions, which confirms the reversibility of this phosphorus–chalcogen bond metathesis.

The metathesis reaction between $[4][\text{BArF}_{24}]$ and Et_3PSe gave the selenophosphonium salt $[5b][\text{BArF}_{24}]$ and Et_3PS . $[5b][\text{BArF}_{24}]$ is the second example of a Lewis base-free selenophosphonium salt²⁸ and was unambiguously identified by its ^{31}P NMR resonance at 104.2 ppm, which is in the same range like that of $[4]^+$ (116.6 ppm) and shows characteristic ^{77}Se satellites with an exceptionally large $^1J_{\text{PSe}}$ coupling constant of 999 Hz. The corresponding doublet in the ^{77}Se NMR spectrum appears at 119.8 ppm. Schmidpeter and co-workers reported the first selenophosphonium salt, which is stabilised by phosphonium ylidyl groups and has a significantly smaller $^1J_{\text{PSe}}$ coupling constant of 847 Hz.²⁸ $[5b][\text{BArF}_{24}]$ could not be isolated because it decomposes thermally into the phosphonium ion $[7]^+$ and elemental selenium, as indicated by the characteristic ^{31}P NMR resonance of $[7]^+$ at 307.5 ppm²⁹ and the precipitation of gray selenium. This observation confirms the reported trend for phosphine chalcogenides of decreasing phosphorus–chalcogen bond energies $\text{O} > \text{S} > \text{Se}$.³⁰ In line with this trend, $[4][\text{BArF}_{24}]$ is reduced by Et_3PSe to give the phosphonium salt $[7][\text{BArF}_{24}]$ and Et_3PS with concomitant precipitation of elemental tellurium in quantitative yield. The intermediate formation of tellurophosphonium $[5b]^+$ was not observed since it appears to decompose rapidly at 120 °C.

In conclusion, we have synthesised and isolated the first Lewis base-free thiophosphonium ion $[4]^+$ by using bulky, electron-donating N-heterocyclic imine substituents attached to the phosphorus atom. $[4]^+$ contains a highly electrophilic, trigonal-planar phosphorus center and a polar $\text{P}=\text{S}$ double bond that undergoes thionation reactions with benzaldehyde and N-methyl-2-pyrrolidinone at room temperature. The mild reaction conditions of this process also support the notion that Lawesson's reagent requires the dissociation into reactive dithiophosphorane fragments prior to its reaction with carbonyls. In addition, the chalcogen exchange reactions between $[4]^+$ and triethylphosphine chalcogenides demonstrate the potential of trigonal planar phosphorus cations in bond metathesis reactions, which is under current investigation in our laboratory.

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Conflicts of interest

There are no conflicts to declare.

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