## EDGE ARTICLE

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# First experimental evidence for the elusive tetrahedral cations [EP₃]⁺ (E = S, Se, Te) in the condensed phase†

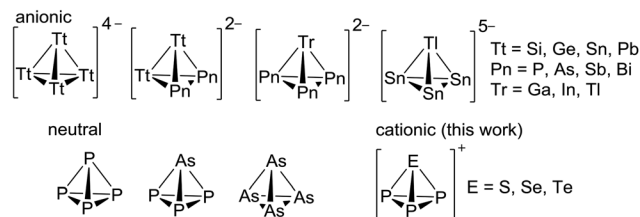Philippe Weis,[a] David Christopher Röhner,[a] Richard Prediger,[a] Burkhard Butschke,[a] Harald Scherer,[a] Stefan Weber[b] and Ingo Krossing [iD] *[a]

Condensed phase access to the unprecedented tetrahedral cations $[EP_3]^+$ (E = S, Se, Te) was achieved through the reaction of $ECl_3[WCA]$ with white phosphorus ($[WCA]^- = [Al(OR^F)_4]^-$ and $[F(Al(OR^F)_3)_2]^-$; $-R^F = -C(CF_3)_3$). Previously, $[EP_3]^+$ was only known from gas phase MS investigations. By contrast, the reaction of $ECl_3[A]$ with the known $P_3^{3-}$ synthon $Na[Nb(ODipp)_3(P_3)]$ (enabling $AsP_3$ synthesis), led to formation of $P_4$. The cations $[EP_3]^+$ were characterized by multinuclear NMR spectroscopy in combination with high-level quantum chemical calculations. Their bonding situation is described with several approaches including *Atoms in Molecules* and *Natural Bond Orbital* analysis. The first series of well-soluble salts $ECl_3[WCA]$ was synthesized and fully characterized as starting materials for the studies on this elusive class of $[EP_3]^+$ cations. Yet, with high $[ECl_3]^+$ fluoride ion affinity values between 775 (S), 803 (Se) and 844 (Te) kJ mol$^{-1}$, well exceeding typical phosphenium ions, these well-soluble $ECl_3[WCA]$ salts could be relevant in view of the renewed interest in strong (also cationic) Lewis acids.

## Introduction

The chemistry of simple tetrahedral main group clusters continues to fascinate researchers worldwide.[1–5] Neutral white phosphorus ($P_4$) is the archetype of this class and a commodity chemical. Even nitrogen was shown to exist shortly as $N_4$ in a plasma and has raised significant theoretical interest.[6] However, the heavier homologous yellow arsenic ($As_4$) is difficult to handle due to its high sensitivity to light. Recent years yielded several new representatives, such as $AsP_3$ (Scheme 1) and $As_2P_2$, $As_3P$ and $SbP_3$.[2,7] In addition, a focus was put on the development of chemical tools to facilitate the handling of $As_4$ with reagents such as $Ag(As_4)_2[Al(OR^F)_4]$ or $As_4$ intercalated in porous carbon that acts as a storage form of yellow arsenic and yields concentrated solutions of $As_4$ that are light stable for several hours.[4,8] These molecules continue to offer interesting follow-up chemistry that is not exhausted yet.[9] For example, the side-on protonation of $P_4$, $[HP_4]^+$ has only been realized very recently.[10] In addition to these neutral molecules, the syntheses and structures of a multitude of Zintl-type anionic tetrahedra

shown in Scheme 1 are known: $[Tt_4]^{4-}$ (Tt = Si, Ge, Sn, Pb) or binary anions such as $[Tt_2Pn_2]^{2-}$ (Pn = P, As, Sb, Bi), $[TrPn_3]^{2-}$ (Tr = Ga, In, Tl) and $[TlSn_3]^{5-}$.[11] These are often accessible by solid-state reactions of the corresponding elements with alkaline metals. Several of these long known tetrahedra were also observed in polar media like liquid ammonia and/or with the presence of cryptands and crown ethers as sequestering reagents.[12] Recent additions detected by NMR spectroscopy include the dissolved Zintl-tetrahedra $[Si_4]^{4-}$, $[Sn_4]^{4-}$ and the protonation product ion $[HSi_4]^{3-}$.[13,14] However, the only reports on any cationic tetrahedra are those on $[SP_3]^+$ and $[SeP_3]^+$ as well as the arsenic homologues that were observed by MS in the gas phase as fragmentation products of $Pn_4E_3$ (Pn = P, As; E = S, Se); the first observation dating back to 1971.[15] Tellurium analogues have not been described in any phase.[16] If turning to coordination chemistry, also no clear evidence for such cations

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Scheme 1 Exemplary overview of commonly known and structurally characterized tetrahedron shaped molecules in the condensed phase. The cations characterized in this work – albeit without crystal structure – are included for comparison.

is published. Only the related complexes $[(triphos)Co(Pn_2E)][BF_4]$ (Pn = P, As; E = S, Se, Te); triphos = 1,1,1-tris(diphenylphosphinomethylethane) are known. Tentatively, these were formulated as coordinated $[P_2E]^+$ and $[As_2E]^+$ cations stemming from the fragmentation of the elusive $[EP_3]^+$ cations.[17] Thus, to the best of our knowledge there is no proven condensed phase evidence for such binary tetrahedral main group cations in any composition.
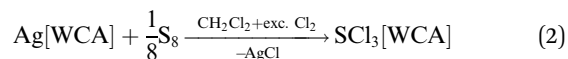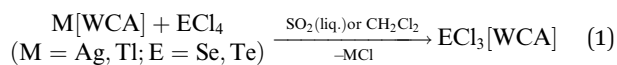
Despite a large number of binary pnictogen–chalcogen cations of nitrogen, arsenic, antimony and bismuth has been published,[18,19] the first binary phosphorus–chalcogen cation isolated in the condensed phase, $[P_3Se_4]^+$, was only published in 2015 by three independent groups *via* three different routes.[20] Binary phosphorus–sulfur and phosphorus–tellurium cations remain unknown.[21] The $[P_3Se_4]^+$ cation adopts a nortricyclanelike structure similar to the heavier analogues $[As_3S_4]^+$ and $[As_3Se_4]^+$ known since 1981.[19] Attempts to synthesize binary phosphorus–selenium cations by reaction of liquid phosphine $PH_3$ with $SeCl_3[AlCl_4]$ yielded insoluble polymeric materials[22] tentatively assigned as "$SeP[AlCl_4]_n$".[23] Moreover, most known $[ECl_3]X$ salts (X = suitable anion) are poorly soluble in solvents compatible with white phosphorus. Therefore, any follow-up chemistry of $[ECl_3]X$ salts is scarce and, to our knowledge, in particular no reactions of any trihalochalcogenonium ion with $P_4$ or any other elemental pnictogen was hitherto published. The synthesis of well soluble $[ECl_3]X$ salts in common solvents is a prerequisite for such investigations and was the starting point for our studies on the tetrahedral $[EP_3]^+$ cations (E = S, Se and Te).

## Results and discussion

First attempts towards the synthesis of the $[EP_3]^+$ cations were performed in analogy to the published synthesis[2] of $AsP_3$ from $Na[Nb(ODipp)_3(P_3)]$ and $AsCl_3$. Thus, $AsCl_3$ was replaced by isoelectronic $ECl_3[WCA]$ (WCA = weakly coordinating anion). Therefore, we briefly describe the synthesis of a series of well soluble $ECl_3[WCA]$ salts before turning to the investigated routes towards the $[EP_3]^+$ cations.

### Synthesis of well-soluble ECl₃[WCA] salts as starting materials

The large majority of the many known salts $[EX_3]A$ (E = S, Se, Te, X = F, Cl, Br, I) feature halometallate counterions A like $[AlCl_4]^-$, $[MF_6]^-$ (M = Sb, As) and $[AuCl_4]^-$.[24] They were synthesized from melts or in oxidizing media like $SOCl_2$ or $SO_2Cl_2$.[24] Typically, they do exhibit poor solubility in common organic solvents. In addition, many of the media employed for synthesis, would be highly reactive towards reductants such as $P_4$. Therefore, salts $EX_3[WCA]$ (E = S, Se, Te, X = F, Cl, Br, I) soluble in common, non-reactive solvents were needed. Since the WCAs $[Al(OR^F)_4]^-$ and $[F(Al(OR^F)_3)_2]^-$ often lend high solubility to salts of the respective cations, the salts $ECl_3[WCA]$ were prepared by halide abstraction of the chalcogen tetrachlorides with $M[Al(OR^F)_4]$ or $M[F(Al(OR^F)_3)_2]$ (M = Ag, Tl for E = Se; M = Ag for E = Te) in $CH_2Cl_2$ or liquid $SO_2$. Eqn (1) is related to the known synthesis of $TeCl_3[Al(OR^F)_4]$ (2a).[25]

$$M[WCA] + ECl_4 \quad \xrightarrow[-MCl]{SO_2(liq.) \text{ or } CH_2Cl_2} \quad ECl_3[WCA] \quad (1)$$
$$(M = Ag, Tl; E = Se, Te)$$

$$Ag[WCA] + \frac{1}{8}S_8 \quad \xrightarrow[-AgCl]{CH_2Cl_2 + exc. Cl_2} \quad SCl_3[WCA] \quad (2)$$

The compounds $SeCl_3[Al(OR^F)_4]$ (1a), $SeCl_3[F(Al(OR^F)_3)_2]$ (1b), $SeCl_3[FAl(OR^F)_3]$ (1c) and $TeCl_3[F(Al(OR^F)_3)_2]$ (2b) are well accessible and soluble in organic media like $CH_2Cl_2$ and 1,2-$F_2C_6H_4$ (o-dfb). By contrast, $[SCl_3]^+$ salts turned out to be very reactive. Due to the instability of $SCl_4$, it was prepared as an intermediate by the reaction of sulfur with $Cl_2$ in $CH_2Cl_2$ and slowly warming the reaction mixture from $-196\ ^\circ C$ to room temperature. Reaction of this $SCl_4$ intermediate with $Ag[Al(OR^F)_4]$ according to eqn (2) was accompanied by anion decomposition and yielded predominantly $SCl_3[F(Al(OR^F)_3)_2]$ (3). A selective way to 3 in good yields (>90%) simply substitutes $[Al(OR^F)_4]^-$ with the more stable[26–29] anion $[F(Al(OR^F)_3)_2]^-$. Care needs to be taken, to ensure a complete reaction during the synthesis of the $ECl_3[WCA]$ salts. If there is residual $Ag[WCA]$ present in $ECl_3[WCA]$, $Ag(P_4)_2[Al(OR^F)_4]$ or $Ag(P_4)_2[F(Al(OR^F)_3)_2]$ tend to crystallize from the reaction mixtures in subsequent reactions. This could be overcome by using $Tl[WCA]$ as a starting material.[30] Attempts to synthesize $[SeCl_3]^+$ salts from $Li[Al(OR^F)_4]$ and $SeCl_4$ or through metathesis reaction with $SeCl_3[AlCl_4]$ only led to the re-isolation of the starting materials (see ESI Section 3.5†). Since it appeared useful to also test a $[EF_3]^+$ source as starting material, we investigated the preparation of $SF_3[Al(OR^F)_4]$ from $Li[Al(OR^F)_4]$ and $SF_4$, but all efforts of its synthesis failed (see ESI Section 3.5†). Attempts to synthesize 1b by reacting $SeCl_4$ with two equivalents of the strong Lewis acid $Me_3Si–F–Al(OR^F)_3$ and trying to skip the synthesis of $Ag[F(Al(OR^F)_3)_2]$, only led to methylation and the isolation of $SeMeCl_2[F(Al(OR^F)_3)_2]$.[31] Yet, to all prepared salts $ECl_3[WCA]$, optimized routes were found and the products were fully characterized (yields, NMR, IR, Raman; crystal structures of 1a, 1b, 1c and 3). As a side, the crystal structure of $Tl[Al(OR^F)_4]$ was determined and deposited with the CCDC. Due to the well-known properties of the long-known $[ECl_3]^+$ cations, the characterization and discussion of the novel salts $ECl_3[WCA]$ is found in the ESI.†

### Syntheses directed towards the ion [EP₃]⁺

**Reaction of 1a with Na[Nb(ODipp)₃(P₃)].** In analogy to the published route[2] to $AsP_3$ from $Na[Nb(ODipp)_3(P_3)]$ and $AsCl_3$, the reaction of 1a with the $P_3^{3-}$ transfer reagent was tested by weighing equal amounts of the powders into an NMR-tube and condensing a solvent ($CD_2Cl_2$, 1,2,3,4-tfb (=1,2,3,4-tetrafluorobenzene) or o-dfb) onto the sample at $-196\ ^\circ C$. The samples were then kept at $-40\ ^\circ C$ to avoid a reaction of 1a with the arene. However, the formation of the desired $[SeP_3]^+$ was never observed. Instead, $P_4$ was cleanly synthesized as indicated by its exclusive signal in the $^{31}P$-NMR spectra next to the known signal of the $[Nb(ODipp)_3(P_3)]^-$ anion. Due to the highly chlorinating nature of $[SeCl_3]^+$ compared to the relatively inert $AsCl_3$, the selenonium salt presumably formed $PCl_3$ by chlorination of

the $[Nb(ODipp)_3(P_3)]^-$ anion. This was followed by an immediate reaction of $PCl_3$ with the residual $Na[Nb(ODipp)_3(P_3)]$ to form $P_4$ (ESI, Section 3.3†).

**Reactions of ECl₃[WCA] with P₄.** Thus, we turned to a different reaction sequence: when reacting $SeCl_3[AlCl_4]$ with $P_4$ in $CH_2Cl_2$, a mixture of almost exclusively $PCl_3$ and $PCl_4[AlCl_4]$ (see ESI Section 3.4.2†) was obtained, next to a red precipitate, supposedly $Se_{red}$. Yet, the $^{31}P$-NMR spectra of this reaction did include a tiny resonance at $\delta^{31}P = -360.8$ hinting towards the formation of $[SeP_3]^+$. Upon changing to the well soluble salts $ECl_3[WCA]$ ($[WCA]^- = [Al(OR^F)_4]^-$, $[F(Al(OR^F)_3)_2]^-$; **1a** to **3**), product ion mixtures containing mainly $[EP_3]^+$ ($[SeP_3]^+$ (**4**), $[TeP_3]^+$ (**5**), $[SP_3]^+$ (**6**)) – easily distinguishable by their characteristic NMR signals (Fig. 1) – and the chlorinated $[P_5Cl_2]^+$ cation were obtained (molar ratio $[EP_3]^+ : [P_5Cl_2]^+ = 0.3$ (E = S), 1.1 (E = Se), 0.3 (E = Te)).

Multiple efforts testing both, the $[Al(OR^F)_4]^-$ and the $[F(Al(OR^F)_3)_2]^-$ anion, to crystallize the obtained product ions **4**, **5** and **6** as pure salts from the complex reaction mixtures were unsuccessful in many solvents. Since the crystal structure of **1c** did show no superstructure and no disorder, as contrasted by the other $[SeCl_3]^+$ salts, **1c** was tested for the synthesis of **4**. This was also futile (see ESI Section 3.4.2†): the $[FAl(OR^F)_3]^-$ anion is not able to withstand the fluorophilic nature of phosphorus cations, and decomposes with formation of several P–F bond

containing compounds in the $^{31}P$-NMR ($PF_4(OR^F)$, dynamic $PF_3$ complexes, unknown $PF_2X$, $PFX_2$).

*Towards optimized reaction conditions.* The ratio of $[EP_3]^+$ to $[P_5Cl_2]^+$ in the reaction is highest for $[SeCl_3]^+$ amongst the $[ECl_3]^+$ starting materials. Equal amounts of both cations were obtained in the reaction with $[SCl_3]^+$ and with $[TeCl_3]^+$. Keeping the reaction temperature at $-40\ °C$ leads to $[SeP_3]^+$ being around 48% (compared to 28% with the starting conditions) of the total intensity of the cation signals in the $^{31}P$ spectrum (23% including unremoved $PCl_3$, see ESI Table S7†) and increases the ratio $[SeP_3]^+ : [P_5Cl_2]^+$ from 1.1 to 1.9 : 1 (Fig. 2).[32] Slow anion decomposition was observed in the ambient temperature $^{19}F$-NMR spectra. This can be avoided by keeping the reaction at $-40\ °C$. Screenings of the reaction in different solvents did show no significant improvement for the selectivity of the reaction and led to further side reactions (see ESI Section 3.4.1†). In agreement with this, the calculated Gibbs reaction energies in solvents of different relative dielectric permittivity ($CH_2Cl_2$, $o$-dfb, $SO_2$) using the COSMO model revealed no significant solvent dependency (discussion below, Table 2). Experiments using $CS_2$ to enhance the solubility of $P_4$ have shown no formation of **4** at all. Raman spectra obtained from reactions on a small scale have only shown fluorescence. Only bulk material obtained from experiments on a larger scale did yield Raman spectra. The vibrational bands can be assigned to the $[Al(OR^F)_4]^-$ anion and tentatively to the
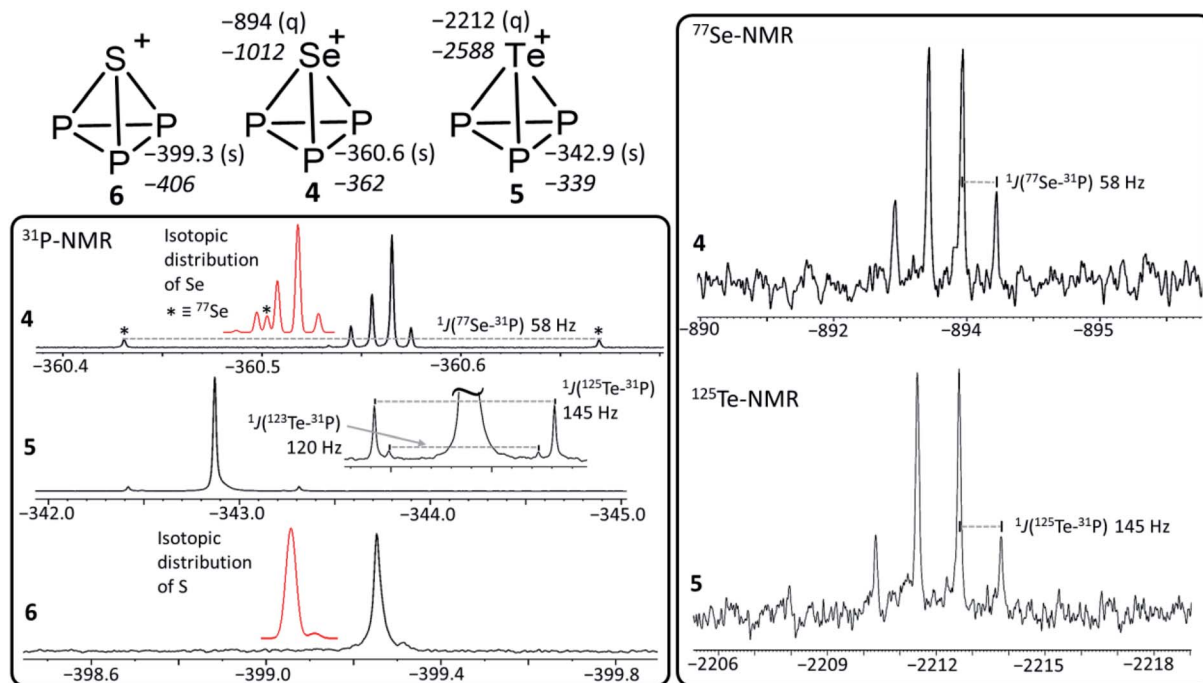


**Fig. 1** Summary of the experimental and calculated (in *italics*) NMR data of **4**, **5** and **6** (top left) including a graphical representation of the structures of $[EP_3]^+$ (E = S, Se, Te). $^{77}Se$ (top right) and $^{125}Te$ (bottom right) spectra of **4** and **5** as well as the $^{31}P$ spectra of **4**, **5** and **6** (bottom left). The red traces in the $^{31}P$-NMR box indicate the isotopic distributions of Se and S calculated with a standard mass spectrometry program. Of all noticeable S and Se isotopes, only $^{77}Se$ is NMR active ($^{33}S$ has an abundancy of only 0.7%). Thus, only the NMR signal of $[^{77}Se^{31}P_3]^+$, labelled by an asterisk in the isotopic distribution, is visibly splitted to a doublet in the NMR trace of **4**. Apparently, the $^{31}P$-chemical shift of $[EP_3]^+$ follows the weight of the isotopes for the lighter elements S and Se, with higher isotope weights leading to incrementally slightly higher field shifted $^{31}P$-NMR resonances. However, for Te, where the relative weight differences between isotopomers are smallest among the three cations, the high-field shift in the $^{31}P$-NMR is so small that the signals due to all Te-isotopes fall onto one visible line (with the exception of the two NMR active nuclei $^{123}Te$ and $^{125}Te$ that couple and give doublets).
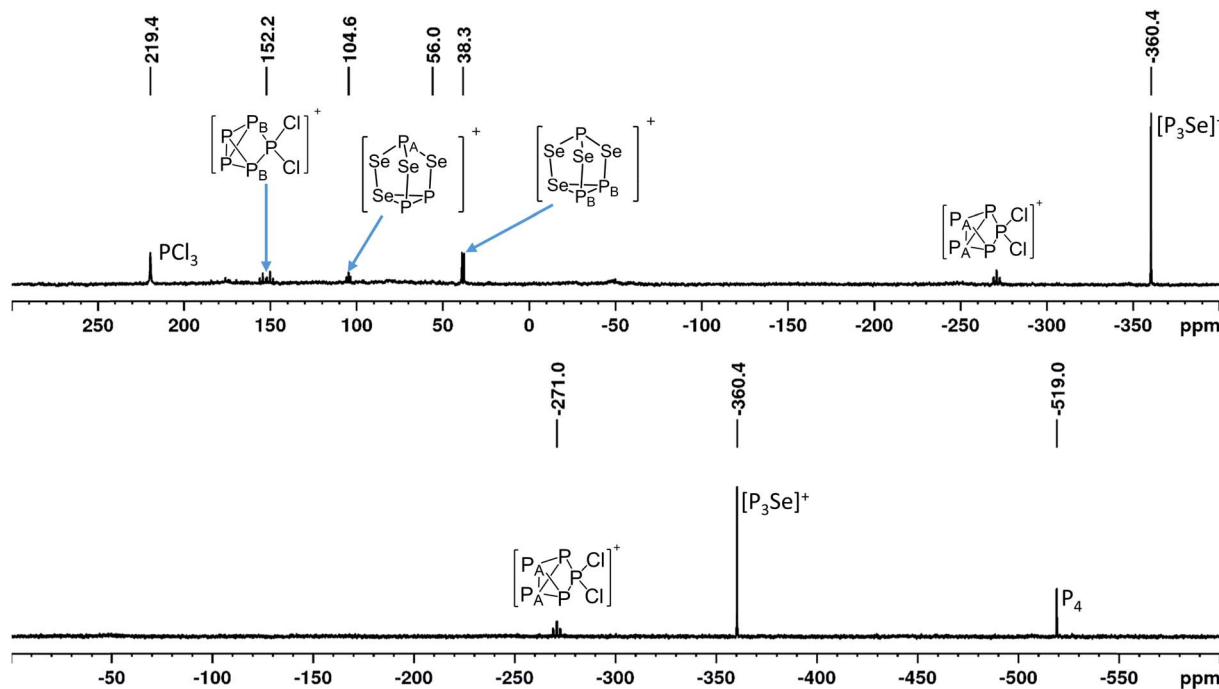
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**Fig. 2** Product ion mixture obtained from the larger scale reaction of **1a** with $P_4$ at −40 °C. Combined views of the measured range of the $^{31}P$-NMR spectra (81.0 MHz, $CD_2Cl_2$, RT) from 300 to −400 ppm (top) and 0 to −600 ppm (bottom).

overlapping vibrational bands of the $[SeP_3]^+$, $[P_5Cl_2]^+$ and $[P_3Se_4]^+$ cations, as well as some $Se_2Cl_2$ showing its most intense band[33] at 361 cm$^{-1}$ (ESI, Section 3.4.3.2†). An exact assignment of all vibrational bands is not possible due to the unavoidable occurrence of $[P_5Cl_2]^+$ having strong overlaps with the predicted bands of $[P_3Se]^+$. Electro-spray-MS spectra of solutions containing **4** showed the presence of the $[SeP_3]^+$ ($m/z = 172.83$) and the $[P_5Cl_2]^+$ ($m/z = 225.0$) cation (ESI, Section 3.4.3.2†).

*On the occurrence of $[P_5Cl_2]^+$.* The formation of **4**, **5** and **6** is necessarily accompanied by the formation of $PCl_3$ (eqn (3)). From NMR investigations it became clear that the $[EP_3]^+$ cations are unreactive towards $PCl_3$. On the other hand, the formation of $[P_5L_2]^+$ (L = organic residue or halide) cations is typically ascribed to the insertion of an intermediate carbene-like $[PL_2]^+$ into $P_4$.[1,5,27,34] However, this intermediate $[PCl_2]^+$ was never

observed in the condensed phase, but assumed to be a complex $[(S)Ag–Cl–PCl_2]^+$ (S = solvent) delivering $[PCl_2]^+$ *in situ*.[35] To completely rule out the $[P_5Cl_2]^+$ presence as a byproduct ion resulting from the reaction of residual $Ag^+$ with $PCl_3$ and $P_4$, ion **4** was synthesized from a silver-free $SeCl_3[Al(OR^F)_4]$ prepared from $SeCl_4$ *via* the thallium salt[36] $Tl[Al(OR^F)_4]$ according to eqn (1). Yet, these experiments revealed a similar quantity of $[P_5Cl_2]^+$ as side product ion. Thus, the formation of $[P_5Cl_2]^+$ does not occur due to silver impurities of the starting material and may arise by reaction of $P_4$ with $[ECl_3]^+$ as in eqn (4).
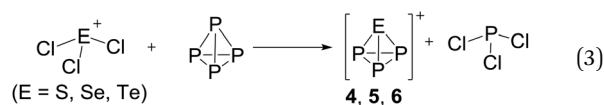
$$\begin{array}{c} Cl{-}\overset{+}{\underset{Cl}{E}}{-}Cl \\ (E = S, Se, Te) \end{array} + \begin{array}{c} P{-}P \\ P{-}P \end{array} \longrightarrow \left[ \begin{array}{c} E \\ P{-}P \\ P{-}P \end{array} \right]^+ + Cl{-}\overset{Cl}{\underset{Cl}{P}}{-}Cl \qquad (3)$$
$$\textbf{4, 5, 6}$$

**Table 1** Experimental and calculated (B3-LYP/DKH2/cc-PVQZ level, based on (RIJ)MP2/def2-QZVPP structures) $^{31}P/^{77}Se/^{125}Te$-NMR shifts, NICS values, bond lengths in the optimized structures and $^1J(P, E)$ coupling constants. The chemical shifts are given in ppm. Calculated data is given in *italics*

| Compound | $\delta(^{31}P)^a$ | NICS$^b$ | NICS/e$^b$ | $d$(P–E) [pm] | $d$(P–P) [pm] | $\delta(E)_{exp.}{}^c$ | $^1J(P, E)$ |
|---|---|---|---|---|---|---|---|
| $P_4$ | −520 *−520* | −61.9 | *−3.10* | — | 219.94(3)[37] *219.3* | — | — |
| $AsP_3$ | −484 (ref. 2) *−484* | −61.3 | *−3.07* | 230.4(1)[37] *230.4* | 219.5(3)[37] *219.4* | — | — |
| $SbP_3$ | −462 (ref. 2) *−452* | −58.6 | *−2.93* | *250.0* | *219.8* | — | — |
| $[SP_3]^+$ | −399 *−406* | −60.6 | *−3.03* | *214.8* | *220.2* | — | — |
| $[SeP_3]^+$ | −361 *−362* | −60.3 | *−3.02* | *228.1* | *220.5* | −894 *−1012* | $^1J(^{31}P, ^{77}Se) = 58$ Hz |
| $[TeP_3]^+$ | −342 *−339* | −59.4 | *−2.97* | *246.9* | *220.9* | −2212 *−2588* | $^1J(^{31}P, ^{125}Te) = 145$ Hz, $^1J(^{31}P, ^{123}Te) = 120$ Hz |

$^a$ $^{31}P$ chemical shifts were referenced to the chemical shift of $P_4$ in $CH_2Cl_2$. $^b$ NICS values are calculated at the cage center. NICS/e denotes the NICS per valence electron. $^c$ $^{77}Se$ and $^{125}Te$ chemical shifts were referenced against the chemical shifts of $SePMe_3/TePMe_3$ more details on the referencing of the chemical shifts is given in the ESI in Section 4.2.
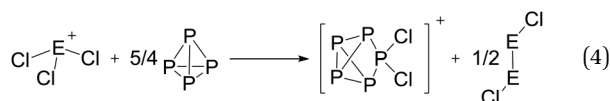
**Table 2** *Ab initio* CCSD(T)/$\infty \zeta$ reaction enthalpies and free reaction enthalpies for the formation of $[EP_3]^+$ (E = S, Se (parentheses), Te [brackets]) and the fluoride ion affinities (FIAs) of $[EP_3]^+$ and $[EX_3]^+$ (E = S, Se, Te; X = F, Cl, Br, I) cations [all given in kJ mol$^{-1}$]. Further details are given in the ESI in Tables S14 and S15

| Reaction | E = | $\Delta_r H^{298}$ (g) | $\Delta_r G^{298}$ (g) | $\Delta_r G^{298}$ (CH$_2$Cl$_2$)$^b$ | $\Delta_r G^{298}$ (o-dfb)$^b$ | $\Delta_r G^{298}$ (SO$_2$)$^b$ | Cation | FIA | E = |
|---|---|---|---|---|---|---|---|---|---|
| $P_4 + [EF_3]^+ \rightarrow [EP_3]^+ + PF_3$ | S | −550 | −554 | −477 | −475 | −474 | $[EF_3]^+$ | 909 | S |
| | (Se) | (−560) | (−563) | (−468) | (−464) | (−463) | | (941) | (Se) |
| | [Te] | [−407] | [−408] | [−319] | [−315] | [−314] | | [962] | [Te] |
| $P_4 + [ECl_3]^+ \rightarrow [EP_3]^+ + PCl_3$ | S | −339 | −343 | −324 | −325 | −325 | $[ECl_3]^+$ | 775 | S |
| | (Se) | (−291) | (−295) | (−269) | (−268) | (−268) | | (803) | (Se) |
| | [Te] | [−167] | [−170] | [−143] | [−143] | [−142] | | [844] | [Te] |
| $P_4 + [EBr_3]^+ \rightarrow [EP_3]^+ + PBr_3$ | S | −263 | −267 | −271 | −272 | −273 | $[EBr_3]^+$ | 735 | S |
| | (Se) | (−206) | (−210) | (−209) | (−210) | (−210) | | (762) | (Se) |
| | [Te] | [−97] | [−99] | [−96] | [−97] | [−97] | | [805] | [Te] |
| $P_4 + [EI_3]^+ \rightarrow [EP_3]^+ + PI_3$ | S | −165 | −168 | −184 | −186 | −187 | $[EI_3]^{+a}$ | 675$^a$ | S |
| | (Se) | (−115) | (−118) | (−127) | (−129) | (−129) | | (704) | (Se) |
| | [Te] | [−29] | [−32] | [−39] | [−41] | [−41] | | [753] | [Te] |
| $\frac{5}{4}P_4 + [ECl_3]^+ \rightarrow [P_5Cl_2]^+ + \frac{1}{2}E_2Cl_2$ | S | −297 | −267 | −227 | −225 | −225 | $[EP_3]^+$ | 828 | S |
| | (Se) | (−256) | (−226) | (−182) | (−181) | (−180) | (F bound *via* P) | (819) | (Se) |
| | [Te] | [−152] | [−121] | [−84] | [−82] | [−82] | | [798] | [Te] |

$^a$ Efforts to synthesize $[SI_3]^+$ previously yielded $[S_2I_4]^{2+}$ instead.[43] $^b$ The free reaction energies in solvents were calculated at the (RIJ)BP86/def2-TZVPP level using the COSMO model.

$$Cl{-}\overset{+}{\underset{Cl}{E}}{-}Cl \ + \ 5/4 \ P_4 \longrightarrow \left[ \begin{array}{c} P{-}P{-}Cl \\ P{-}P{-}Cl \end{array} \right]^+ + \ 1/2 \ \underset{Cl}{\overset{Cl}{E{-}E}} \quad (4)$$

The reaction course according to eqn (4) is further supported by the observation of a yellow volatile material (Se$_2$Cl$_2$) present in the traps of the vacuum line after pumping on the mixtures as well as the Se$_2$Cl$_2$ Raman band observed in solid product mixtures at 361 cm$^{-1}$ (ESI, Section 3.1†). Efforts to suppress this side reaction by slowly adding P$_4$ to the reaction at low temperatures showed no significant improvement towards a clean reaction (ESI, Table S7†).

*Further side product ions.* The known[20] $[P_3Se_4]^+$ additionally occurs as a side product ion. Performing the reaction at −40 °C lowers the amount of obtained $[P_3Se_4]^+$, but does not allow to completely get rid of this side product ion. Depending on the solvent, the higher chlorinated oxidized $[PCl_4]^+$ was also observed (ESI, Section 3.4.1†). An unknown side product/product ion including five chemically equivalent phosphorus atoms and three chemically equivalent tellurium atoms occurs during the synthesis of **5**. Analogously, in the synthesis of **6**, side-products of unknown origin occurred (ESI, Section 3.4.3†).

### Quantum chemical calculations on $[EP_3]^+$

Since it proved impossible to crystallize any $[EP_3]^+$ salt, we turned to quantum chemical calculations, to shed some light on energetics, structure, properties and bonding.

#### Calculated structure and NMR-shifts

*Molecular structures.* The molecular structures of the title tetrahedra were calculated at the (RIJ)MP2/def2-QZVPP level, which gives very good agreement with experimental data for P$_4$ and PnP$_3$ (Pn = As, Sb). Apparently, the calculated $[EP_3]^+$ bond

lengths $d_{PP}$ are slightly elongated, if compared to the neutral tetrahedra and increase from S to Se to Te.

*Calculated NMR-shifts.* The calculated NMR-shifts of **4**, **5** and **6**, as well as that of the neutral molecules AsP$_3$ and SbP$_3$ for comparison, were obtained using a fully decontracted basis set with (RIJ)B3-LYP(DKH2)/cc-pVQZ single point calculations, using the (RIJ)MP2/def2-QZVPP structures. They were referenced against P$_4$ (Table 1). The calculated $^{31}$P chemical shifts of all $[EP_3]^+$ ions deviate by less than 7 ppm from the experimental values. This is similar to the deviation of the calculated NMR shifts from the known AsP$_3$ and SbP$_3$ shifts (less than 10 ppm).[2] However, the calculated $^{77}$Se and $^{125}$Te chemical shifts show larger deviations from the experimental values. Yet, the trends in chemical shifts are well reproduced, as investigated on a larger test set of Se- and or Te-containing molecules spanning a range of 2300 ppm (Se) and even 5000 ppm (Te) (ESI, Section 4.2†). With such a broad range of chemical shifts, the choice of the reference compound is crucial, although the calculated absolute shielding tensors remain the same. Yet, no truly close relative to $[EP_3]^+$ is known experimentally to serve as a reference to tie to the calculated shift. The best compromise was to use EPMe$_3$ (E = Se, Te). We note, that the observed resonances of **4** and **5** underlie an extreme high-field shift to untypical regions for inorganic Se(IV) and Te(IV) compounds compared to their $[ECl_3]^+$ counterparts. This raises the question, whether the chalcogen atoms in the $[EP_3]^+$ cations can be formally rationalized as deriving from an E$^{4+}$ cation being exposed to the ring current of a 6π Hückel-aromatic $[P_3]^{3-}$ ring or if the chalcogen atoms exhibit a lower formal oxidation state (see next section).

**Bonding within $[EP_3]^+$.** Since the $[EP_3]^+$ cations present a hitherto unknown class of cations in the condensed phase, an investigation of its bonding motifs is appropriate. With the unusually high-field shifted Se- and Te-NMR resonances at

a)  b)  c)  d)
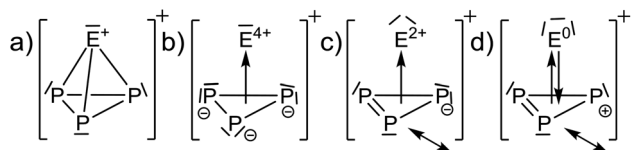
**Scheme 2** Extreme, limiting sketches that might contribute to the $[EP_3]^+$ structures. (a) Formally electron precise structure, (b) cluster bonding as described by $\pi$-donation from a $6\pi$ Hückel-aromatic $P_3^{3-}$ unit. (c) Similar, but $\pi$-donation from a $4\pi$ antiaromatic $P_3^-$ and (d) synergistic $\pi$-donation from a $2\pi$ Hückel-aromatic $P_3^+$ unit to an $E^0$ and back bonding from p-type AOs of $E^0$ to $\pi^*$-MOs of $P_3^+$.

$-894$ (Se) and $-2212$ (Te, Table 1), one could draw the following extreme, limiting sketches in Scheme 2a–d that might contribute to the $[EP_3]^+$ structures.

Thus, with the cluster-like description as in Scheme 2b and c, one would expect that the E atoms experience a large high-field shift due to the proximity to an aromatic ring current. Thus, it first needed to be investigated, if diamagnetic ring currents are present.

*NICS values.* Calculated nuclear independent chemical shift (NICS) values at the cage centers of the $[EP_3]^+$ cations suggest pronounced diamagnetic ring currents with a very slightly decreased order of magnitude, if compared with $P_4$ and $AsP_3$ (Table 1). This suggests a delocalized cluster-like bonding.

*Population analyses and MO diagram.* Calculated NBO, PABOON and AIM charges (Fig. 3) only agree that the positive charge on the E atom of the $[EP_3]^+$ cluster increases in going

from S to Se and Te and that on P decreases in the same direction. The similarity of the calculated MO diagrams to the known[7] MO diagrams of $P_4$ and $AsP_3$ clearly shows that the $[EP_3]^+$ cations can be understood as clusters related to $AsP_3$ and $P_4$. This is in accordance with the generally at very high field observed NMR shifts as well as the NICS values in Table 1, and similar to the known tetrahedra $P_4$, $AsP_3$, $Si_4^{4-}$ and $Sn_4^{4-}$.[2,14] However, closer inspection reveals some differences. First, due to the cationic nature, all orbital energies are lowered by 6 to 7 eV in comparison to the neutral tetrahedra. Second, the lowering of the symmetry from $T_d$ to $C_{3v}$ in $AsP_3$ splits the $t_2$-MOs of $P_4$ giving a pair of e and $a_1$ MOs. The sequence of orbital energies for this pair of e (higher $E$) and $a_1$ MOs (lower $E$) in $AsP_3$ matches those in $[EP_3]^+$ only for Se and Te. For the $[SP_3]^+$ system, these orbitals are reversed in energy and the $a_1$ MO is now higher in energy than the e MO (Fig. 3).

The HOMO LUMO gaps decrease in the order $[SP_3]^+$ (6.2 eV) > $[SeP_3]^+$ (5.9 eV) > $[TeP_3]^+$ (5.4 eV) and are comparable to $P_4$ and $AsP_3$ (6.4 eV and 6.0 eV with the same method). This speaks for a stable structure and bonding within $[EP_3]^+$. Closer inspection of the MOs in view of the descriptions in Scheme 2 would be in agreement with the suggestion that the back bonding component from p-type AOs of $E^0$ to $\pi^*$-MOs of $P_3^+$ (Scheme 2d), which might be assigned to the e MO at $-14.89$ (S)/$-14.24$ (Se)/$-13.37$ (Te) eV in Fig. 3, is inferior for the heavier elements. Thus, apparently the sizes of the heavier p-type AOs do not fit similarly well as that of sulfur and the respective MO energies increase from S to Te.
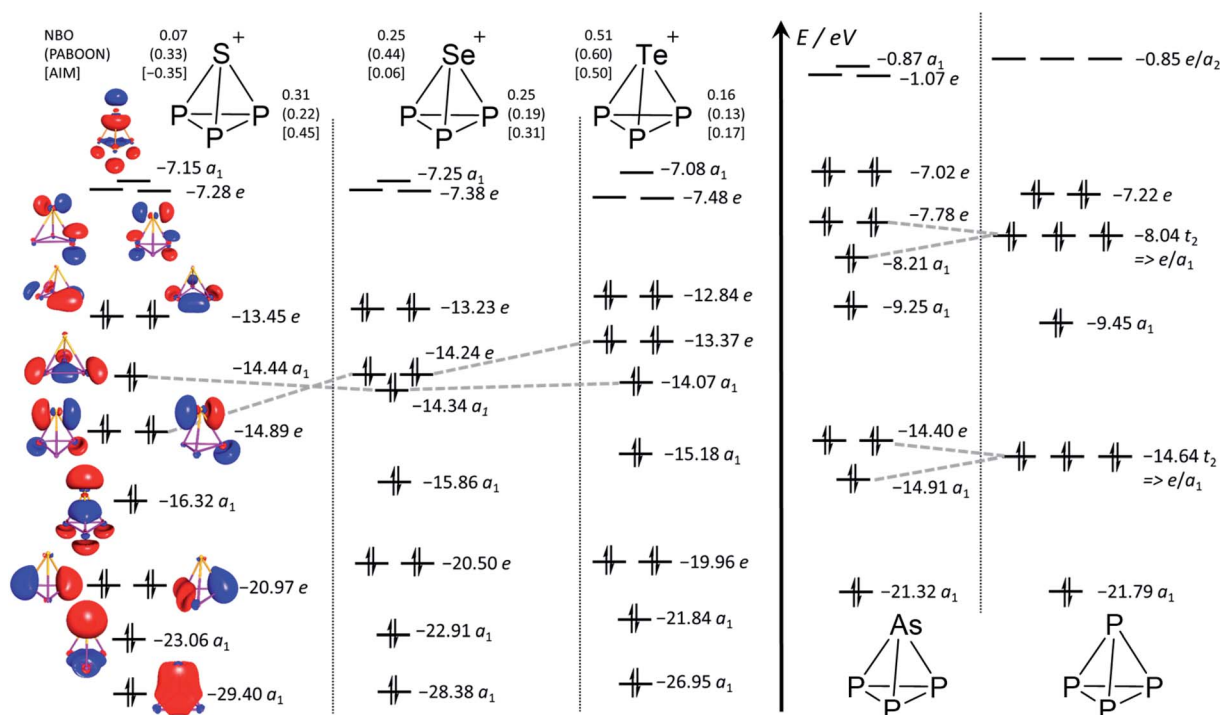


**Fig. 3** Calculated MO Diagrams and NBO,[38] PABOON and AIM[39] charges of $[EP_3]^+$ ((RIJ)B3-LYP/def2-TZVPP). The corresponding MO diagrams of $P_4$ and $AsP_3$ were also generated and are in accordance with the previously published MO diagrams (*cf.* also ESI Section 4.1†).[7] The grey broken lines delineate the switch of the $a_1$ and e MO energies in going from E = S to Se and Te as well as the splitting of the $t_2$ MOs in $P_4$ upon symmetry lowering in $AsP_3$.

*Further AIM analyses.* Contour plots of the Laplacian of the electron density (Section 4.2, ESI†) show a similar situation for all $[EP_3]^+$ cations. They are closely related to the neutral molecules $AsP_3$ and $P_4$, with $[P_3S]^+$ being similar to $P_4$ and $[P_3Se]^+$ and $[P_3Te]^+$ being more similar to $AsP_3$. Exohedral lone pairs of the clusters are absent for any of the tetrahedra, which confirms the nature of the tetrahedra as delocalized clusters rather than electron precise molecules. The electron densities ($\rho_{XCP}$) residing at the critical points XCP (X = R (ring), C (cluster), B (bond)) of the $[EP_3]^+$ cations have similar values to $P_4$ and $AsP_3$ and are included with the ESI.† It is worth noting that the calculated increasing bond ellipticities for E = Se and Te would be in agreement with a description as in Scheme 2d and suggest a larger electronic separation of the 'E'- and '$P_3$'-parts for the heavier elements and its interpretation as resulting from π-interactions.

**Formation energetics of $[EP_3]^+$.** To provide reliable values, the thermodynamics of the product ion mixture formation was assessed using the gold standard of quantum chemistry, the coupled cluster level of theory with single, double and a numerical evaluation of the triples excitation extrapolated to the complete basis set limit (CCSD(T)/∞ζ, see ESI†), an approach we have shown to be accurate within about 5 kJ mol$^{-1}$.[29,40] Reaction enthalpies and Gibbs energies with and without solvation calculated towards the formation of $[EP_3]^+$ from $[EX_3]^+$ (X = F–I) and $P_4$ are collected in Table 2. They are in agreement with the observed formation of ions **4** to **6** from $[ECl_3]^+$, but also agree with the competing formation of the chlorinated side product ion $[P_5Cl_2]^+$ (eqn (4) and Table 2). Thus, for E = Se, $[P_5Cl_2]^+$ formation is exergonic ($\Delta_rG° = -180$ to $-182$ kJ mol$^{-1}$ in solution) as is the formation of $[EP_3]^+$ ($\Delta_rG° = -268$ to $-269$ kJ mol$^{-1}$ in solution). Apparently, the competing formation of $[P_5Cl_2]^+$ has kinetic reasons. With all our tested conditions, any clear discrimination between both routes was impossible. This suggests that the activation barriers to reach the two product ions $[P_5Cl_2]^+$ and $[EP_3]^+$ starting from $ECl_3^+$ and $P_4$ have similar height and cannot be selectively favored by all the tested measures. This raised the question, as to whether it would be favorable to change the chloride ligands in $[ECl_3]^+$ for other halides to improve selectivity. Inspection of Table 2 shows that the driving force for $[EP_3]^+$ formation from $P_4$ and $[EX_3]^+$ lowers in the sequence F > Cl > Br > I but also S > Se > Te. Only the fluoro-chalcogenonium salts $EF_3[A]$ would provide a considerably higher impetus to yield $[EP_3]^+$, presumably due to formation of the very stable $PF_3$ gas. However, the $[EF_3]^+$ ions are extreme Lewis acids, as shown by their calculated very high fluoride ion affinities (FIAs, Table 2). Their Lewis acidity increases from S (909 kJ mol$^{-1}$) to Te (FIA 961 kJ mol$^{-1}$). These FIA values are close to that of the extremely Lewis acidic small silylium ion $[SiMe_3]^+$ (+958 kJ mol$^{-1}$).[41] The latter, *in situ* generated from $Me_3SiCl$ and $Ag[Al(OR^F)_4]$, reacts with the $[Al(OR^F)_4]^-$ anion under fluoride abstraction to give the adduct $Me_3Si-F-Al(OR^F)_3$ and the epoxide $C_4F_8O$.[26,42] Thus, at least $[SeF_3]^+$ and $[TeF_3]^+$ should be, according to our experience, unstable with the aluminates used as counterions in this study. By contrast and in agreement with the experiment, the FIA

values of the $[EP_3]^+$ ions of 798 to 828 kJ mol$^{-1}$ are in a range that is typically tolerated by the $[Al(OR^F)_4]^-$ anion.

$[SF_3]^+$ with a FIA of 915 kJ mol$^{-1}$, similar to the one of $[CCl_3]^+$ (904 kJ mol$^{-1}$)[44] that is stable as $[Al(OR^F)_4]^-$ salt and in solution at temperatures of $-20$ °C,[45] might be accessible with the aluminate counterions. Therefore, we have tried to prepare the salt $SF_3[Al(OR^F)_4]$, but all efforts failed and no $[EF_3]^+$ salts could be tested. However, this might be a reaction path that could be pursued in future; given the use of a suitable WCA tolerant towards extremely Lewis acidic cations – for example a halogenated carborane anion. As to whether the strongly exergonic Gibbs energy for the formation of the $[EP_3]^+$ cations from $[EF_3]^+$ salts and $P_4$ would guarantee a selective reaction, remains to be tested. However, we do not expect that fluorometallates $[MF_6]^-$ (M = P, As, Sb), with considerably lower FIA values of $MF_5$ (389 to 495 kJ mol$^{-1}$) than $Al(OR^F)_3$ (543 kJ mol$^{-1}$),[41] would stabilize salts of $[EP_3]^+$, but rather form fluoro-phosphorus compounds and $MF_5$.

## Conclusion

Investigations on the existence of tetrahedral $[EP_3]^+$ (E = S, Se, Te) in condensed phases required the here reported synthesis and characterization of well-soluble salts $ECl_3[WCA]$. We note, that these cations are very strong Lewis acids with FIA values of 775 (S); 803 (Se) and 844 (Te) kJ mol$^{-1}$ that could be relevant in view of the renewed interest[46] in strong[47] (also cationic[48]) Lewis acids.[49] They should be compared to classical phosphenium ions $[PR_2]^+$ with FIA values of 721 (R = NMe$_2$), 789 (R = Mes) and 828 (R = Ph).[50] The easily and in high yield accessible salts $ECl_3[WCA]$ were tested for their reaction with the known $P_3^{3-}$ precursor $Na[Nb(P_3)(ODipp)_3]$, related to the synthesis of $AsP_3$ from $AsCl_3$. Only a clean generation of $P_4$ occurred. This is due to the strongly chlorinating nature of the $[ECl_3]^+$ cations that immediately reacted with the niobate to give $PCl_3$. Subsequently, the $PCl_3$ was transformed by the $P_3$-niobate to $P_4$. Contrary, the reaction of the salts $ECl_3[WCA]$ with $P_4$, led to reaction mixtures containing mainly the $[EP_3]^+$ cations, $PCl_3$ and $[P_5Cl_2]^+$ as well as other byproducts/byproduct ions. Even under optimized reaction conditions, the clean formation of $[EP_3]^+$ and $PCl_3$ from $[ECl_3]^+$ and $P_4$ is rivaled by side reactions. High level quantum chemical calculations show that the formation of $[EP_3]^+$ and of $[P_5Cl_2]^+$ are both strongly exergonic and independent of the solvent choice. Apparently, the similar activation energies of the reactions prevent the separation of both pathways by all tested reaction conditions. Experimental $^{31}$P-, $^{77}$Se- and $^{125}$Te-NMR spectra as well as calculations of the chemical shifts prove the presence of the first cationic tetrahedra in the condensed phase. The selenium analogue $[SeP_3]^+$ was also unambiguously detected by ESI-MS of the obtained samples, while IR- and Raman spectra show the expected mixtures of cations in agreement with the optimized NMR conditions. The $[EP_3]^+$ ions are the first tetrahedral cations stabilized in the condensed phase, contrasted by the many anionic and the long known neutral tetrahedra. These cationic tetrahedra are also the first clear evidence for binary P–S and P–Te cations in the condensed phase, with the 2015 published

$[P_3Se_4]^+$ being the first phosphorus chalcogen cation at all. Theoretical investigations show, that the $[EP_3]^+$ tetrahedra can be understood as clusters similar to $P_4$ and $AsP_3$ as indicated by their MO diagrams, AIM analyses and calculated NICS values. The unusually high-field shifted $^{77}Se$- and $^{125}Te$-NMR shifts may arise from a synergistic $\pi$-interaction between formal $E^0$ and $P_3^+$ fragments.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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