The chemistry of cationic polyphosphorus cages – syntheses, structure and reactivity

Michael H. Holthausen and Jan J. Weigand

The aim of this review is to provide a comprehensive view of the chemistry of cationic polyphosphorus cages. The synthetic protocols established for their preparation, which are all based on the functionalization of \( \text{P}_4 \), and their intriguing follow-up chemistry are highlighted. In addition, this review intends to foster the interest of the inorganic, organic, catalytic and material oriented chemical communities in the versatile field of polyphosphorus cage compounds. In the long term, this is envisioned to contribute to the development of new synthetic procedures for the functionalization of \( \text{P}_4 \) and its transformation into (organo-)phosphorus compounds and materials of added value.

1. Introduction

Discovering novel pathways for the activation and transformation of white phosphorus (\( \text{P}_4 \)) is important for the ongoing search for new, systematic entries to polyphosphorus and organo-phosphorus compounds. Especially in the realm of polyphosphorous cations methods for the preparation of species featuring a high P to substituent ratio are rare. In contrast, a systematic access to highly substituted cations \( \text{R}_n\text{P}_m(n > m) \) is achieved with synthetic protocols mainly based on the utilization of neutral \( \text{catena or cyclic polyphosphanes R}_n\text{P}_m \).\(^1\) Protocols for phosphorus-rich cations \( \text{R}_n\text{P}_m(n < m) \) often involve \( \text{P}_1 \)-precursors and are based on the reduction of either P–Cl\(^2\) or P–H bonds.\(^3\) Multiple P–P bonds are formed in these reactions giving access to elaborate P–P bonded frameworks. However, in most...

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cases the reaction outcome is unpredictable which hampers the targeted preparation of polyphosphorus cations. Thus, a synthetic approach that takes advantage of the tetrahedral $P_4$ framework should allow for a targeted and systematic assembly of phosphorus-rich cations $R_nP_m$ $(n < m)$. Additionally, the application of $P_4$ in such conversions is of high interest, since it constitutes an important raw material in industrial chemistry and is produced on a megaton-scale nowadays. The desire to develop synthetic protocols for the more sustainable production of P-containing bulk chemicals has sparked significant academic and industrial research efforts within the last decades. Progress in the areas of transition metal and main group mediated $P_4$ activation has been reviewed several times. However, no account was given so far on the importance of $P_4$ as a starting material for the preparation of polyphosphorus cations.

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The synthetic protocols established for their preparation, which are all based on the functionalization of $P_4$, and their intriguing follow-up chemistry are highlighted. In addition, this review intends to foster the interest of the inorganic, organic, catalytic and material oriented chemical communities in the versatile field of polyphosphorus cage compounds. In the long term, this is envisioned to contribute to the development of new synthetic procedures for the functionalization of $P_4$ and its transformation into (organo-)phosphorus compounds and materials of added value.

In the following, black dots denote P atoms in order to provide easily comprehensible drawings of complex polyphosphorus frameworks for the reader. These frameworks may give rise to complicated, sometimes higher order, spin systems in their $^{31}P$ NMR spectra. Their designation is derived by assigning letters in alphabetical order starting with the resonance at the highest field. The spin systems were considered to be higher order and consecutive letters are assigned if $\Delta\delta(P_iP_j)/\delta(P_iP_j) < 10$. For $\Delta\delta(P_iP_j)/\delta(P_iP_j) > 10$, the spin system is considered to be pseudo first order and the assigned letters are separated. However, if a group of similar compounds is discussed, only one spin system is mentioned for the sake of clarity. All cationic polyphosphorus cages presented here are obtained by functionalization of $P_4$. Mostly, phosphenium ions or cationic phosphorus species which formally serve as a phosphenium ion source are used for this functionalization. It is of high importance for the reader to be aware of the general reactivity pattern of $P_4$ and the general characteristics of phosphenium ions. Thus, a brief insight into both fields is given in the first two sections.

2. $P_4$ activation pathways

In order to gain an in depth understanding of the reactions of $P_4$ and main group element compounds, it is crucial to understand the properties of the $P_4$ tetrahedron. The bonding in $P_4$ is almost “cluster-like”, strongly delocalized and mostly effected through $3p$ atomic orbitals. Interestingly, $P_4$ shows spherical aromaticity and is virtually unstrained despite acute bond angles of 60°. Generalized reactions of $P_4$ with nucleophiles (Nu$^-$), electrophiles (El$^+$) and ambiphiles (Ab) are shown in Fig. 1. Radical reactions involving $P_4$ are excluded. A nucleophile (Nu$^-$) interacts with the LUMO of $P_4$ ($-1.8$ eV), which leads to the rupture of a $P$–$P$ bond giving butterfly-type bicyclo[1.1.0]tetraphosphane A (Fig. 1). The reactions of $P_4$ with nucleophiles were intensively investigated using an array of organo-alkali and organo-alkali earth reagents. However, in many cases the formation of a derivative of A only constitutes the first step of a reaction sequence which ultimately leads to the degradation of $P_4$ to $P_4$-compounds. Only a few reactions involving a selective cleavage of only a single bond in the $P_4$ tetrahedron are reported.

![Fig. 1 Generalized reactions of $P_4$ with nucleophiles (I, Nu$^-$), electrophiles (II, El$^+$), predominantly nucleophilic ambiphiles (III, Ab), and predominantly electrophilic ambiphiles (IV, Ab); A–D illustrate structural motifs obtained after reaction with the aforementioned species.](image-url)
One is the reaction of Mes*Li (Mes* = 2,4,6-tri-tert-butylphenyl) with one equivalent of P4 yielding a tetraphosphanide intermediate of type A. Subsequent reaction with Mes*Br yields the butterfly-type species 1 (Fig. 2).\textsuperscript{6} Further degradation of 1 is prevented by the sterically demanding Mes*-groups. Nucleophiles based on silicon, main group 5 or main group 6 elements were also employed.\textsuperscript{6} An electrophile may attack at a non-bonding orbital of lone pair character (HOMO – 6, –7.5 eV)\textsuperscript{7} which results in the formation of compounds of type B (Fig. 11I a). Alternatively, an electrophile may attack at a bonding orbital at one of the edges of the tetrahedron (HOMO, –6.7 eV; Fig. 11I b). However, this mode of attack is commonly less productive for main group element centered electrophiles and is not depicted. In total, only very few reactions with electrophiles were reported due to the low nucleophilicity of P4.\textsuperscript{9} One example constitutes the reaction of P4 with two equivalents of the sterically encumbered Lewis acid Ga(t-Bu)3. This yields compound 2; however, mechanistic details regarding its formation were not reported (Fig. 2).\textsuperscript{10}

The utilization of ambiphilic main group element compounds (Ab) for the activation of P4 represents a rather new synthetic approach. Reactions of P4 with ambiphiles can be divided into two categories assuming an asynchronous process with two consecutive steps. The first category comprises reactions of P4 with predominantly nucleophilic ambiphiles. Similar to the reactions of P4 and nucleophiles, intermediate A’ is obtained in the first step of the reaction. Subsequently, A’ rearranges to cyclo-triphasphirene derivative C (Fig. 11III). The rearrangement is attributed to the propensity of Ab to accept electron density from the adjacent P atom which formally leads to the formation of an Ab–P double bond. Carbene are ambiphiles with a predominantly nucleophilic character.\textsuperscript{11} Two types of carbenes, \textit{i.e.} N-heterocyclic carbenes (NHC) and cyclic or acyclic alkyl amino carbenes (cAAC or aAAC), were investigated in reactions with P4 by the research group of Bertrand.\textsuperscript{12}

The formation of an intermediate of type A’ was confirmed by DFT calculations\textsuperscript{12} and of type C by trapping experiments with 2,3-dimethylbutadiene yielding \([2+4]\) cyclo-addition product 3 (Fig. 2, \textit{e.g.} L1 = cAAC).

The second category comprises reactions of P4 with predominantly electrophilic ambiphiles. By analogy with the reactions involving electrophiles, the first step of the reaction is an electrophilic attack of Ab yielding an intermediate B’ (Fig. 1). Subsequently, B’ rearranges to a cyclo[1.1.0]tetraphosphane D featuring a bridging Ab moiety (IV). This reaction sequence equals the formal insertion of the ambiphile in one of the P–P bonds of the P4 tetrahedron. P4 functionalization involving a predominantly electrophilic ambiphile is an experimentally more widespread approach. Monovalent group 13 element compounds with the oxidation state \(+1\) are a class of substances that are widely used in such transformations.\textsuperscript{13} The first type of such a structural motif was achieved by Roesky and coworkers by reacting P4 with two equivalents of Al(I) compound AlL2 (L2 = CH[(CMe)(2,6-i-Pr2C6H3N)]2).\textsuperscript{13} The formal insertion of AlL2 into one P–P bond of P4 is assumed to give an intermediate of type B’ in the first step. However, the insertion of a second equivalent of AlL2 into the opposing P–P bond of the P4 tetrahedron occurs rapidly yielding the two-fold insertion product 4 (Fig. 2). In addition, P4 activation by predominantly electrophilic silylenes,\textsuperscript{14} disilenes,\textsuperscript{15} phosphasilenes,\textsuperscript{16} and a bis(stannylene)\textsuperscript{17} was reported. Reactions of P4 with phosphenium cations (R3P+) are also classified as P4 functionalization with predominantly electrophilic ambiphiles. They will be thoroughly discussed within this review from an experimental as well as a mechanistic point of view.

### 3. Syntheses and characteristics of phosphenium ions

The term phosphenium ion describes a cation featuring a di-coordinated, positively polarized P atom.\textsuperscript{18} Phosphenium ions reveal a lone pair of electrons and a formally vacant p-type orbital, and thus, they constitute carbene analogues.\textsuperscript{11} The stability of phosphenium ions strongly depends on their substituents. While aryl- or alkylphosphenium ions R2P+ (‘) are strongly electrophilic and generally elusive, a large series of phosphenium ions bearing amino-substituents (R3N)2P+ (\(R = \text{alkyl, aryl}\)) are known.\textsuperscript{18} Three methods for their preparation are mainly reported throughout the literature. Halide abstraction from the corresponding halo-phosphate precursor is the most commonly used synthetic protocol.\textsuperscript{18} Further methods
constitute the protolysis of P–N single bonds by Bronsted acids and the coordination of strong Lewis acids to P–N double bonds.16

The increased stability of phosphonium ions \( \text{R}_3\text{N}+\text{P}^- \) (5\(^\text{t}\), Fig. 3) stems from a lowered electrophilicity due to donation of \( \pi \)-electron density from the lone pair of electrons at the nitrogen atoms to the vacant p-type orbital at the P atom.19 Phosphonium ions of type 6 featuring one amino-substituent are borderline cases between both of the aforementioned types and are only scarcely investigated. Only a few fully characterized derivatives are reported to date bearing either (pseudo-) halogens20 or sterically demanding aryl-moieties21 as the second substituent R’ on phosphorus (Fig. 3).

A phosphonium ion bearing only alkyl- or aryl-substituents has not been isolated to date.18 The reaction of phosphanes bearing organo- and chloro-groups \( \text{R}_n\text{PCl}_{(3-n)} \) (\( n = 1, 2 \)) and a halide abstracting agent (e.g. \( \text{Me}_3\text{SiOTf}, \text{GaCl}_3, \text{or AICl}_3 \)) in the appropriate stoichiometry usually results in the formation of phosphanylpseudo phosphonium ions.1 This is best exemplified by the reaction of \( \text{Ph}_2\text{PCl} \) and \( \text{GaCl}_3 \) in a 2:1 stoichiometry which yields \( \text{[GaCl}_4\text{]} \) (Scheme 1).22

Two mechanisms for the formation of \( 8^+ \) are conceivable. Firstly, \( \text{Ph}_2\text{PCl} \) reacts with \( \text{GaCl}_3 \) as a halide abstracting agent giving a transient \( \text{Ph}_2\text{P}^+= \)phosphate ion. This reacts with the second equivalent of \( \text{Ph}_2\text{PCl} \) yielding \( 8^+ \). The second and in the author’s opinion more likely mechanism proceeds via the zwitterionic intermediate 9 which features a \( \text{Ph}_2\text{PCl} \) molecule donating electron density from its lone pair of electrons to the lobes of the antibonding \( \sigma^*(\text{P–Cl}) \) orbital of a second molecule of \( \text{Ph}_2\text{PCl} \). Subsequently, chloride abstraction by \( \text{GaCl}_3 \) yields \( 8^+ \) without an intermediary formation of a free \( \text{Ph}_2\text{P}^+= \)phosphate ion. The phosphoniumyl-moiety in \( 8^+ \) is easily substituted when \( 8^+ \) is reacted with phosphanes of higher basicity than the leaving group.1 This is illustrated by the reaction of \( 8^+ \) with \( \text{Ph}_3\text{P} \) yielding \( 10^+ \) and \( \text{Ph}_2\text{PCl} \) (Scheme 2, left).23 Other Lewis bases are also suitable as nucleophiles. This is illustrated by the reaction of \( 8^+ \) with 1,3-di-iso-propyl-4,5-dimethylimidazol-2-ylidene (\( \text{L}_3 \)) which yields the imidazoliumyl-substituted phosphate 11.23

Detailed investigations of mixtures of phosphanylphosphonium ion \( 12^+ \) and \( \text{Ph}_3\text{P} \) revealed second-order kinetics for the exchange process of \( \text{Ph}_3\text{P} \) consistent with a \( \text{S}_{\text{N}2} \)-type pathway (Scheme 3).24

This was further supported by quantum chemical calculations which suggested the phosphoranide-type transition state \( 13^+ \) for the substitution process.24 In contrast, the phosphanylpseudo phosphonium ion \( 14^+ \), which is formed via the reaction of phosphonium ion \( 15^+ \) and \( \text{PMe}_3 \), was reported to favour a dissociative \( \text{S}_{\text{N}1} \)-type reaction pathway in substitution reactions (Scheme 4).25

For phosphanylpseudo phosphonium ions such as those described above the term “ligand stabilized phosphonium ions” is frequently used in the literature while the described substitution reactions are also called “ligand exchange” reactions.1 Independent of any such controversy, however, these distinct points of view are based on the labile P–P bond observed in phosphanylpseudo phosphonium ions. This allows for the transfer of \( \text{R}_2\text{P}^+= \)moieties (formally phosphonium ions) between distinct Lewis bases (e.g. phosphanes, carbenes or \( \text{P}_3 \)). Thus, for reasons of simplification, phosphanylpseudo phosphonium ions will be regarded as “sources of phosphonium ions” throughout this review.

Phosphanylpseudo phosphonium ions were frequently used as phosphonium ion sources. The reaction of a mixture of \( \text{Me}_2\text{PCl} \)

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\begin{align*}
\text{Scheme 1} & \quad \text{Synthesis of } \text{[GaCl}_4\text{]} \text{ by the reaction of } \text{Ph}_2\text{PCl} \text{ and } \text{GaCl}_3 \text{ in } 2:1 \text{ stoichiometry and possible reaction sequences giving } \text{[GaCl}_4\text{]} \text{ either via free } \text{Ph}_2\text{P}^+= \text{phosphate ion (red) or zwitterion } 9 \text{ (blue).}
\end{align*}
\]

\[
\begin{align*}
\text{Scheme 2} & \quad \text{Substitution of the phosphoniumyl-moiety of } 8^+ \text{ by Lewis-bases.}
\end{align*}
\]

\[
\begin{align*}
\text{Scheme 3} & \quad \text{S}_{\text{N}2} \text{-type substitution of the phosphoniumyl-moiety in } 12^+. \\
\end{align*}
\]

\[
\begin{align*}
\text{Scheme 4} & \quad \text{S}_{\text{N}1} \text{-type dissociation of phosphanylpseudo phosphonium ion } 14^+. \\
\end{align*}
\]
4. Cationic homoleptic polyphosphorus cages

For decades the investigation of homoleptic polyphosphorus cations was limited to mass spectroscopy\(^{29}\) and quantum chemical calculation\(^{10}\) in the gas phase. Homoleptic \(P_n^+\) cations are paramagnetic if the number of P atoms \(n\) is even. In the case of an odd number of P atoms the respective cation is diamagnetic. In general, the paramagnetic series of polyphosphorus cations is less stable. In the odd-membered series, the smaller \(n\) feature electron-precise Zintl-type structures. According to Wade’s rules, a square pyramidal structure is anticipated for cation \(19^+\) (Fig. 5, \textit{nido}-cluster). Such a structure was confirmed as the most stable isomer by means of quantum chemical calculations.\(^\text{30a}\) The structural motif of the second most stable isomer \(19^{+*}\) (34.7 kcal mol\(^{-1}\) higher in energy) does not follow Wade’s rules and shows a \(d\)-coordinated P atom. The most stable isomer of \(P_5^+\)-cage \(20^+\) is a tricapped trigonal prism that is missing two of the capping vertices (\textit{arachno}-cluster). A second isomer, which is only slightly higher in energy (\(20^{+*}, 2.0\) kcal mol\(^{-1}\)), shows the \(P_5\)-cage motif of \(19^{+*}\) and a three-membered P ring which are both fused by a bridging phosphonium moiety. The \(P_5^{+}\)-cage \(21^+\), which is composed of two \(P_4\)-moieties fused by a phosphonium moiety, is one of the most stable homoleptic polyphosphorus cations according to quantum chemical calculations (Fig. 5).\(^\text{30b}\)

Krossing and co-workers were the first to report evidence for the existence of homoleptic polyphosphorus cations in the condensed phase.\(^\text{31}\) The attempted oxidation of \(P_4\) with \(I_2\) or \(Br_2\) in the presence of \(\text{Ag(CH}_2\text{Cl}_2)[A]\) \((A = \text{Al(OC(CF}_3)_3)_4\) was suggested to proceed via the intermediary formation of \(P_5^{+}\)-cage cation \(19^+\) (Scheme 5).\(^\text{32}\) However, cation \(19^+\) is highly reactive and reacts with the solvent to give phosphonium cation \(22^+\) as one of the main products. Cation \(22^+\) forms via elimination of \(P_4\) and two-fold insertion into C–Cl bonds of \(\text{CDCl}_3\) molecules which was used as solvent. In the case of \(I_2\) as oxidant, \(P_4\) reacts partially to give \(P_3\) which was suggested to react with intermediate \(19^+\) to give \(P_4\) and the bis(phosphanyl)-substituted phosphonium ion \(23^+\). Experimental evidence confirming the presence of \(19^+\) in the reaction mixtures was not obtained; however, the suggested reaction pathways are in accordance with quantum chemical calculations.\(^\text{32}\) The nitrosonium salt [\(\text{NO}[A]\)] \((A = \text{Al(OC(CF}_3)_3)_4\) was also investigated as a possible one electron oxidant. However, the reaction of \(P_4\) with [\(\text{NO}[A]\)] yields \(P_5\text{NO}^+\)-cage compound \(24[A]\) via insertion of the nitrosonium cation into a P–P bond (Scheme 6).\(^\text{33}\)

Although X-ray structure determination of compound \(24[A]\) was not successful, the molecular structure is confirmed by spectroscopic data and computational investigations. The theoretical

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**Fig. 4** Polyphosphorus cations \(16^+\), \(17^+\) and \(18^{+*}\) obtained via the formal insertion of \(R_2P^+\)-phosphenium ions \((R = \text{Me, Ph})\) into the P–P bond of \((\text{PhP})_2\), \((\text{PhP})_4\) and \((\text{PhP})_5\).

**Fig. 5** Anticipated structures of homoleptic, diamagnetic polyphosphorus cations \(19^+\), \(20^+\) and \(21^+\).

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and Me$_3$SiOTf with diphosphane \((\text{PhP})_2\) gave phosphanylphosphonium ion \(16^+\) as a trflate salt (Fig. 4).\(^\text{26}\) Species \(16^+\) is formally derived from the insertion of a \(\text{Me}_2\text{P}^+\)-phosphenium ion into the P–P bond of the diphosphane \((\text{PhP})_2\). Mixtures of \(\text{Ph}_3\text{P}Cl\) and Me$_3$SiOTf with the \textit{cyclo}-phosphanes \((\text{PhP})_4\) or \((\text{PhP})_5\) give in both cases the \textit{cyclo}-tetraphosphanylphosphonium ion \(17^+\).

A ring expansion is observed in the reaction with \((\text{PhP})_4\) whereas a 5-membered ring is retained in the reaction involving \((\text{PhP})_5\) via an unknown redistribution process.\(^\text{26}\) Both reactions proceed via the formal transfer of a \(\text{Ph}_2P^+\)-phosphenium ion from the intermediary formed phosphanylphosphonium ion \(8^+\). In both cases \(17^+\) is exclusively formed which demonstrates the thermodynamic preference of the five-membered ring over the six-membered alternative. The highly reactive, cyclic six-membered dication \(18^{+*}\) is only obtained by employing a melt approach.\(^\text{27}\) Solvent-free mixtures of \(\text{Ph}_3\text{P}Cl\) and \(\text{GaCl}_3\) provide room temperature molten media. These melts represent a powerful source of phosphonium ions \(\text{Ph}_2P^+\).\(^\text{28}\)
5. Cationic polyphosphorus cages featuring halogen-substituents

The oxidation of Ag(I) complex 25[A] (A = Al(OC(CF3)3)4) featuring two intact P4 ligands with elemental iodine at low temperatures gives rise to interesting binary PI cations. The P3I2+ cage 26a+ was observed in the reaction mixture at −78 °C together with PI1+ and P4 (Scheme 7).36 However, on raising the temperature above −40 °C, decomposition of 26a+ was observed, leading to the formation of P3I6+ (23+) and unidentified by-products.

6. Cationic polyphosphorus cages featuring alkyl- and aryl-groups

A versatile approach to cationic polyphosphorus cages featuring alkyl- and aryl-groups represents the utilization of dichlorophosphanes RPCl2 (R = alkyl, aryl) instead of PX3 (X = I, Br, Cl).39 Mixtures of dichlorophosphanes RPCl2 and a strong Lewis acid (GaCl3, AlCl3) as a halide abstracting reagent can be utilized as the source for the phosphonium ion RPCl+. In the presence of P4, insertion into one of the P–P bonds takes place, giving access to...
GaCl3 in fluorobenzene applying varying stoichiometries gave the presence of Lewis acids revealed the formation of chloro-investigations of mixtures of mono- and dichlorophosphanes in the presence of Lewis acids revealed the formation of chloro-phosphanylchlorophosphonium ions of type 27⁻ (Fig. 6).³² In most cases, characteristic ³¹P coupling constants were observed by ³¹P NMR spectroscopy at ambient temperature.

However, the spectra of mixtures of dichlorophosphanes and Lewis acids in CH₂Cl₂ were less informative and showed in most cases only broad resonances.³³ A systematic study based on Raman and ³¹P NMR spectroscopy of mixtures of RPCl₂ and GaCl₃ in fluorobenzene applying varying stoichiometries gave important insight into these reactions.³⁹ Depending on the ratio of the reactants and the substituent R in RPCl₂, mixtures of the structurally distinct species 28⁺, 29⁻ and 30⁺ were formed (Fig. 6).

The classical Lewis acid–base adducts of type 30⁺ are only formed in reaction mixtures involving dichlorophosphanes RPCl₂ featuring alkyl-substituents R. The formation of non-classical adducts of type 30⁻ is not observed and is unlikely according to quantum chemical calculations.³⁹ This is further supported by the isolation and structural characterization of 30a (R = t-Bu), which was proven to form a classical Lewis acid–base adduct. An increasing amount of phosphophosphonium ions of type 28⁻ is formed with decreasing steric demand of the substituent R (t-Bu > Cy > i-Pr). The formation of cations of type 29⁻ is observed when the basicity and the steric requirements of the dichlorophosphanes are further reduced (R = Et, Me, Ph). Such cations are the result of adduct formation between GaCl₃ and the phosphane moiety of phosphophosphonium ions of type 28⁻. Most mixtures show dynamic exchange indicating a possible interconversion of species 28⁺, 29⁻ and 30⁻.³⁹ The exchange rates of these processes strongly depends on the concentration of GaCl₃. In the reaction mixtures equilibrium dissociation of the GaCl₄⁻ anion to free GaCl₃ and Cl⁻ occurs. The dynamic exchange is linked to these chloride anions which nucleophilically attack phosphophosphonium species yielding the phosphane starting materials in a back reaction. By using an excess of GaCl₃ the GaCl₄⁻ forms higher gallates (Ga₃Cl₇⁻ or Ga₄Cl₁⁰⁻) and the concentration of free chloride anions is reduced.⁴³

Quantum chemical calculations were carried out to determine which of the observed species serves as the phosphonium ion source in a reaction with P₄. According to these results,⁴⁴ the formation of RP₃Cl⁻ cagés via a free phosphonium ion RPCl⁻ can be excluded. Attempts to calculate a feasible reaction mechanism from adducts 30 or 30⁻ as sources of phosphonium ions were not successful. Thus, the reaction of P₄ with methyl-substituted phosphophosphonium derivative 28e⁻ was investigated (Fig. 7). A single step insertion of the phosphonium moiety into a P–P bond of the P₄ tetrahedron is viable and the calculated energy profile of the reaction path is denoted in black. In addition, a two-step reaction pathway is feasible as well (energy profile is shown in red).

The two step reaction pathway proceeds via a butterfly-type compound 31 as an intermediate (bottom, Fig. 7). The single step transfer of the phosphonium moiety in 28e[GaCl₄⁻] and insertion thereof into a P–P bond of P₄ shows an energy barrier of 27.4 kcal mol⁻¹ (TS1) and is energetically viable. In the light of recent mechanistic studies on the reaction of isoelectronic silylenes with P₄,⁷⁶ this is best understood as a combined electrophilic and nucleophilic attack of the phosphonium moiety. On the one hand the P–P bond of P₄ (HOMO) nucleophilically attacks the p-type orbital of the phosphonium moiety. On the other hand the lone pair of electrons of the phosphonium moiety donates electron density to the LUMO of the P₄ tetrahedron which corresponds to p-orbitals situated perpendicular to the P₄ lone pairs.⁷ It was found that a lower barrier reaction pathway is possible if 28e⁻ does not act as a nucleophile. Instead, a chloro-substituent of the GaCl₄⁻ anion nucleophilically attacks the P₄ tetrahedron along with the electrophilic attack of the phosphonium moiety of 28e⁻ on P₄. This leads to the slightly endothermic formation of the intermediate 31 (15.6 kcal mol⁻¹) via transition state TS2 (17.7 kcal mol⁻¹). Compound 31 reveals a butterfly-type structure featuring a chloro-substituent in an exo-position and a phosphanyl-substituent in an endo-position. Finally, 31 reacts via TS3 (16.3 kcal mol⁻¹), which shows only a very low energy barrier. This step proceeds via the intra-molecular nucleophilic attack of the phosphanyl-substituent on the chloro-substituted P atom. This eliminates the GaCl₄⁻ anion and leads to the formation of the P₅⁻ cagé cation 32e⁺.

Despite their different compositions 1 : 1 mixtures of RPCl₂ and a Lewis acid ECl₃ (E = Al, Ga) in fluorobenzene are potent sources of reactive phosphonium ion RPCl⁻ equivalents, which insert formally into P–P bonds of P₄.⁴³ Dissolution of P₄ in these mixtures yielded white to yellowish precipitates of the corresponding RP₃Cl⁻ cagé salts for a large range of different alkyl- and aryl-substituents R (32a–h[GaCl₃], Scheme 8).

All compounds are obtained in almost quantitative yield and high purity. In contrast to the halogen-substituted species 26a–c[A], they are stable in the solid state or when dissolved in non-coordinating solvents at ambient temperature.⁴⁶,⁴⁷ The cations 32a–h⁺ show characteristic ³¹P NMR spectra. Iterative line shape
analysis of the observed spin systems gave chemical shifts and coupling constants in accordance with $C_4$ symmetric RP$_5$Cl$^+$-cages with four chemically non-equivalent phosphorus nuclei. All cages possess a mirror plane which includes the tetra-coordinated P atom and both P atoms opposing the former. Due to the reduced symmetry compared to the $C_{2V}$-symmetric P$_5$X$_2$+-cages 26a–c an ABM$_2$X spin system is observed for 32a–d and an ABMX$_2$ spin system for 32e–h. Due to the similar geometry of the P$_5$+-core in all cations, the respective $^1J$(PP) and $^2J$(PP) coupling constants deviate only marginally. However, the chemical shifts are strongly dependent on the substituent R attached to the RP$_5$Cl$^+$-cage (Fig. 8). The P$_A$ and P$_B$ atoms exhibit characteristic low field resonances at approximately −275 ppm. The assignment of the A and B part to the respective P nuclei is based on the observed coupling pattern. First, the non-symmetrically substituted P$_5$+-cage is divided by a plane spanned by the tetra-coordinated and both adjacent P atoms into a HCl- and HR-hemisphere (Fig. 9).

The H$_{Cl}$-hemisphere contains the chloro-substituent and the H$_{R}$-hemisphere the alkyl- or aryl-substituent. Within the series of cations 32a–h$^+$ the P atom located in the H$_{Cl}$-hemisphere shows values of $^1J$(PP) and $^2J$(PP) coupling constants which are reminiscent of those of P$_5$X$_2$+-cages 26a–c.$^{36,37}$ Accordingly, the P atom located in the H$_{R}$-hemisphere reveals one- and

Scheme 8  Preparation of compounds 32a–h[EC1$_4$] from P$_{4}$, RPCl$_2$ and ECl$_3$ (E = Ga, Al; R = alkyl, aryl) in fluorobenzene.

Fig. 7  Calculated reaction pathways for the reaction of 28e[GaCl$_4$] and P$_4$: calculated differences of the enthalpies at 298.15 K ($\Delta H_{298}$) are given for the optimized structures of MP2/6-31G(d) and the optimized structures of 28e[GaCl$_4$]+ P$_4$ were defined as 0 kcal mol$^{-1}$.

Fig. 8  Plot of the $^{31}$P NMR chemical shifts of RP$_5$Cl$^+$-cages 32a–h$^+$ versus their alkyl- or aryl-substituent.
two-bond P–P coupling constants similar to the values observed for the respective R₂P₅⁺-cages. In addition, the former group of P atoms experiences the spatial proximity of the chloro-group, and, therefore, shows similar chemical shifts (marked in green, Fig. 8). In contrast, the P atoms in the H₆⁺-hemisphere show resonances in a much larger chemical shift range. This is attributed to the distinct electronic parameters of the substituents. They affect the chemical shifts of the P atoms mostly likely through “cross-ring through space” interactions of the lone pairs on P atoms and the respective group R.⁴⁵ For RP₅Cl⁺-cages featuring alkyl-substituents R (32a–e) the resonances of the P atoms adjacent to the phosphoniou moiety (marked in blue, Fig. 8) are shifted stepwise to lower field with a decreasing positive inductive effect of the substituent (from 44 ppm (32a⁺) to 81 ppm (32e⁺)). This is in agreement with the increased shielding of a P atom caused by additional alkyl-moieties in the γ-position relative to the P nuclei. This trend was previously termed γ-effect.⁴⁶ In contrast, the chemical shifts of tetra-coordinated P atoms (marked in red, Fig. 8) exhibit an almost inverse trend (from 99 ppm (32a⁺) to 69 ppm (32e⁺)). This high-field shift correlates with an increasing number of hydrogen atoms at the α-carbon of the substituent. This constitutes a characteristic feature of phosphoniou moieties and was termed a-effect.⁴⁷ Overall, these influences are reflected in a change of the spin system between 32e–h⁺ featuring aryl- and methyl-substituents (ABMX₂ spin system) and those bearing alkyl-substituents 32a–d⁺ (ABM₂X spin system).

Employing dichlorophosphanes R₂NPCl₂ (R = Cy, i-Pr) in combination with GaCl₃ in reactions with P₄ gave distinct results. In mixtures of R₂NPCl₂ (R = Cy, i-Pr) and GaCl₃ the corresponding phosphonium ions 33a,b⁺ are the only observable species.⁴⁹ Indicative of their formation is a resonance in the ³¹P NMR which is shifted to remarkable low field.¹⁸ It is highly influenced by the nature of the respective anion [compare 33a[GaCl₄]⁺: δ = 310 ppm, 33a[Ga₂Cl₇]⁺: δ = 350 ppm]. The GaCl₄⁻ salt of 33a⁺ can be isolated and constitutes a rare example of a structurally characterized mono-amino substituted phosphonium ion (Scheme 9). Upon reacting phosphonium ions 33a,b⁺ with P₄ insertion into a P–P bond is observed giving the Cₛ-symmetric RP₅Cl⁺-cage cations 34a,b⁺. However, these cages are in equilibrium with the respective free phosphonium ions and P₄ which hampers the isolation of pure compounds 34a,b[GaCl₄]. The observation of an equilibrium can be attributed to the relative stability of free 33a,b⁺. A similar reversibility of the phosphonium ion insertion was observed in the case of RP₅Cl⁺ compounds. The addition of coordinating solvents like acetonitrile to solutions of 32[ECl₄] (E = Ga, Al) decomposes the respective metallate anion via chloride liberation. Nucleophilic attack of free chloride anions on 32⁺ yields mainly the starting materials P₄ and RPCl₂ (R = alkyl, aryl) in a back reaction.

It is interesting to note that a reaction between the two-fold amino-substituted phosphonium ion [i-Pr₂N]P⁺ (35⁺) and P₄ was not observed.²⁶a This is attributed to a significantly lowered electrophilicity of 35⁺ compared to 33a,b⁺.²⁹ Also, diaminophosphonium ions of type 35⁺ reveal frontier orbitals comparable to those of alkyl-anions with the HOMO mainly located at the N atoms, and, thus, are not amphiphilic at the P moiety.

R₃Pₛ[GaCl₄] cage compounds 36[GaCl₄] featuring two alkyl- or aryl-substituents R are obtained in high yield via the reaction of chlorophosphanes R₂PCl, GaCl₃, and P₄ (Scheme 10).⁴⁹

The Lewis acid–base adduct 37 and phosphanylphosphonium ion 38⁺ are commonly formed in mixtures of chlorophosphanes and GaCl₃ in various stoichiometries.²² Both convert into each other via equilibria involving free R₂PCl and GaCl₃.⁴⁹,²²b Cations of type 38⁺ serve as phosphonium ion sources in the presence of P₄ allowing for the formation of R₂P₅⁺-cage cations 36⁺. Most likely, this proceeds in analogy to quantum chemical calculations on the mechanism of the formation of MeP₅Cl⁺ cage 32e⁺.⁴⁹ In contrast to dichlorophosphanes, however, the reaction conditions for the formation of R₂P₅⁺-cages 36a–h⁺ depend strongly on the substituent R. In the case of chlorophosphanes featuring aryl
substituents R, the reactions proceed smoothly at ambient temperature in fluorobenzene solution. A significant decrease in reaction time is observed with increasing steric bulk of the substituents (Dipp > Mes > C₆F₅ > Ph). For the preparation of R₂P₅⁺-cages 36a–d featuring alkyl-substituents R, solvent-free conditions are necessary. Mixtures of R₂PCl (R = Cy, i-Pr, Et, Me) and GaCl₃ in a 1:1 stoichiometry form melts at ambient temperature. Upon addition of P₄ to these melts, the formation of the corresponding cage compounds 36a–h[GaCl₄] is observed. With increasing steric demand of the substituents R (Cy > i-Pr > Et > Me) extended reaction times and higher temperatures (100 °C to 150 °C) are required. The different reactivity of alkyl- and aryl-substituted phosphines in the synthesis of R₂P₅-cage compounds of type 36[GaCl₄] can be rationalized in terms of the different Lewis acidities of the corresponding phosphonium ions. The Lewis acidity is reflected e.g. by their distinct fluoride ion affinities (e.g. Me₂P⁺: FIA = 959 kJ mol⁻¹, Ph₂P⁺: FIA = 838 kJ mol⁻¹). This necessitates a more Lewis acidic environment for the transfer of a phosphonium ion featuring alkyl-groups, which is realized in a solvent free medium.

The molecular structures of all compounds of the series 36a–h[GaCl₄] were determined by single crystal X-ray structure determination. This allowed for an in-depth evaluation of the influence of substituents of distinct steric demand on the structural parameters of the P₅⁺-cage in the solid state (Fig. 10).

The phosphonium P atoms of cations of type 36⁺ show a distorted tetrahedral environment. If the steric demand of the substituent R is increased a stepwise increase in the corresponding C–P–C angle is observed from the sterically very bulky substituted Dipp₂P₅⁺ (36h⁺) to the methyl-substituted derivative 36e⁺. This is accompanied by a decreasing P–P–P angle at the phosphonium moiety and stepwise increase in P–P bond lengths involving the phosphonium P atom.

As a consequence, the tetraphosphabicyclo[1.1.0]butane moieties display a more pronounced folding (distance between both P atoms adjacent to the phosphonium P atom decreases) and the P₅⁺-cages are stretched (distance between the bridgehead P–P bond and the phosphonium P atom increases).

The ³¹P NMR spectra of cage cations 36⁺ show A₂MX₂ or A₂MX₃ spin systems in accordance with their C₂ᵥ symmetry and are comparable to those observed for the P₅X₂⁺ cages 36a–c⁺ (Fig. 11). The observation of two different spin systems for R₂P₅⁺-cages of type 36⁺ may be explained in terms of different steric and electronic influences of the alkyl- or aryl-substituent R. In the series of alkyl-substituted R₂P₅⁺-cages (36a⁺ to 36d⁺) the resonances of the phosphonium P atoms are shifted to higher field and the resonances of the adjacent P atoms are shifted to lower field. This can be explained in terms of a combination of a-effect and γ-effect (vide infra). The resonances of the tetra-coordinated P atoms in aryl-substituted cations 36e–h⁺ are shifted to higher field compared to those of the corresponding P atoms in cages 36a–d⁺. This is due to a positive mesomeric effect, namely the donation of π-electron density from the aryl substituents to the lobes of the antibonding σ*(P–P) orbitals at the phosphonium moiety. Some main group centered, predominantly electrophilic ambiphiles react with P₄ via multiple insertions into P–P bonds of the P₄ tetrahedron. This is exemplified by SiP₃-cage compound 40.
which is obtained by the reaction of \( \text{P}_4 \) with zwittryionic siylene 39. This compound reacts with a second equivalent of 39 to give the \( \text{Si}_2\text{P}_4 \)-cage compound 41 (Scheme 11).\(^{11}\) The second insertion takes place at a P–P bond opposing the initially inserted main group element. The related product 4 was obtained by the reaction of \( \text{P}_4 \) with a low valent Al(1) species (Fig. 2).\(^{13}\)

Distinct results were obtained in the investigation of multiple insertions of phosphonium ions into P–P bonds of \( \text{P}_4 \). In this context, solvent-free mixtures of \( \text{P}_4 \), \( \text{Ph}_2\text{PCl} \) and \( \text{GaCl}_3 \) in various stoichiometries and at different temperatures were investigated. A 1 : 1 : 1 mixture yields quantitatively the \( \text{Ph}_2\text{P}_5 \)-cage compound 36[\( \text{GaCl}_4 \)] after 45 min at 60 °C (Scheme 12).\(^{31}\)

The \( \text{Ph}_3\text{P}_6^{2+} \)-cage cation 42\(^{2+} \) is observed in a mixture of 1 : 8 : 5 stoichiometry (\( \text{P}_4 \) : \( \text{Ph}_2\text{PCl} : \text{GaCl}_3 \)) as the main product after a reaction time of seven hours at 70 °C. The \( ^{31} \text{P} \) NMR spectrum of 42\(^{2+} \) shows a characteristic ABMM’XX’ spin system which is in accordance with the insertion of a second \( \text{Ph}_3\text{P}^- \)-phosphenium ion into a P–P bond adjacent to the phosphonium moiety in 36f. Two second-order resonances corresponding to an AA’XX’X’’’ spin system are expected for the isomer of 42\(^{2+} \) formed via formal insertion into two opposing P–P bonds of \( \text{P}_4 \). Such a species is not formed in the melt reaction. The formation of dication 42\(^{2+} \) can only be observed if the ratio of \( \text{Ph}_2\text{PCl} \) and \( \text{GaCl}_3 \) is higher than 0.5. In these mixtures, the dominant gallium species is \( \text{GaCl}_4^- \); hence, the melt can be considered as basic medium. In a more Lewis acidic melt, composed of \( \text{P}_4 \), \( \text{Ph}_2\text{PCl} \) and \( \text{GaCl}_3 \) in a 1 : 3 : 6 stoichiometry, the tricationic \( \text{Ph}_4\text{P}_5^{3+} \)-cage 43\(^{3+} \) is formed exclusively. Large single crystals of 43\(^{3+} \) as a heptachlorodigallate salt are formed in the respective melt after 12 h at 100 °C. Cation 43\(^{3+} \) features a nortricyclanetype (tricyclo[2.2.1.0\( ^2.6 \)]heptane) framework. It is composed of a basal ring of three-coordinated P atoms, three tetra-coordinated P atoms at the bridging positions and a three-coordinated P atom at the apex of the cage. This skeleton is reminiscent of the trianionic phosphide \( \text{P}_7^{3-} \)\(^{52}\) several polyphosphazanes \( \text{R}_3\text{P}_3^{3-} \)\(^{33}\) and many polyphosphorus-chalcogenides like e.g. \( \text{P}_4\text{S}_4 \).\(^{54}\) The \( ^{31} \text{P} \) NMR spectrum of 43\(^{3+} \) shows an AA’BB’XX’ spin system resulting from the \( C_3 \) symmetry of the cage. A \( \delta \) or \( \gamma \) P–P bond coupling to the apex of the cage is not observed which might be a result of the adjacent phosphonium P atoms. This leads to a first-order quartet resonance for the apical P atom. The highly electrophilic cation 43\(^{3+} \) is stable only in the presence of excess \( \text{GaCl}_3 \). This prevents the detrimental presence of chloride anions which decompose 43\(^{3+} \) by nucleophilic attack and subsequent degradation via 42\(^{2+} \) to 36f. This illustrates that the consecutive insertion of up to three \( \text{Ph}_3\text{P}^- \)-moieties into P–P bonds of \( \text{P}_4 \) is directed by the Lewis acidity of the reaction mixture.

### 7. Cationic polyphosphorus cages featuring four-membered heterocycles

Cyclic diaminohalophosphanes are important precursors for the preparation of cyclic phosphonium ions via halide abstraction.\(^{55}\) Within this class of compounds, phosphazanes, like the diphosphadiazane 44, are of particular interest (Scheme 13). These compounds feature two chloro-substituted P moieties and, thus, offer a versatile reactivity.\(^{36}\) The diphosphadiazenion ion 45\(^+ \) is generated from 44 upon chloride abstraction with \( \text{GaCl}_3 \). Solutions of 45\(^+ \) are characterized by a bright red colour and the \( ^{31} \text{P} \) NMR spectrum shows a broad resonance at characteristic low field (\( \delta = 242.3 \text{ ppm} \)) indicating the formation of a di-coordinated P moiety. Subsequent addition of \( \text{P}_4 \) to this solution leads to discoloration and quantitative formation of the \( P_3 \)-cage compound 46[\( \text{GaCl}_4 \)].\(^{37}\) The molecular structure of cation 46 shows a planar four-membered (NP)\(_2 \) ring and an almost orthogonal oriented P–Cl bond (Scheme 13). This arrangement is also reflected by the \( A_2\text{MVXXZ} \) spin system observed in the \( ^{31} \text{P} \) NMR spectrum of \( C_5 \)-symmetric cation 46.\(^{36}\) Interestingly, the \( P_3 \)-cage does not couple with the chloro-substituted P atom resulting in the observation of a singlet resonance for the latter. This P–Cl functionality was used for the \textit{in situ} generation of a phosphonium ion upon addition of three equivalents of \( \text{GaCl}_3 \) to the reaction mixture. The resulting dicationic intermediate
was not detected. However, upon addition of $P_4$, the formation of the corresponding insertion product $47^{2+}$ is observed. The $^{31}$P NMR spectrum of $47^{2+}$ shows an $A_2X_2$ spin system which is consistent with two $C_{2v}$-symmetric $P_5^+$-cages bridged by two imido-groups. The dication can be isolated as heptachlorodigallate salt $47[P(GaCl_3)]_2$ and the molecular structure of the $N_2P_{10}$-cage was confirmed by single crystal structure determination (Scheme 13). This illustrates that the stepwise insertion of the disguised bifunctional Lewis acid $([DippNP])_2^{2+}$ into $P-P$ bonds of two $P_4$ tetrahedra can be mediated by the Lewis acidity of the reaction mixture. The utilization of an excess of GaCl$_3$ allows for the preparation of the more electrophilic, higher charged species $47^{3+}$, similar to the reaction sequence yielding $43^{3+}$ (Scheme 12).

It is interesting to note that related NHC analogues, five-membered 1,3,2-diazaphospholenium ions, do not react with $P_4$ under various reaction conditions $^{58}$ similar to acyclic, diamino-phosphenium ion (i-Pr$_2$N)$_2P^+$ ($vide infra$). This indicates that the strained four-membered ring geometry present in diphosphadiazene ions is crucial for its reactivity towards $P_4$.

Other cyclic, four-membered phosphorus containing heterocycles can be employed in reactions with $P_4$ as well. $^{59}$ The cyclic chlorophosphane $48$, featuring a SiCl$_2$-backbone, $^{60}$ reacts with GaCl$_3$ to give the corresponding Lewis acid–base adduct $49$ (Scheme 14).

![Scheme 13: Stepwise synthesis of $N_2P_{10}$-cage compound $47[P(GaCl_3)]_2$ via insertion of phosphenium ions generated in situ by the reaction of diphospha-diazene $44$ with GaCl$_3$.](image1)

![Scheme 14: Preparation of $P_5^+$-cage cation $51^+$ from $P_4$, GaCl$_3$ and chlorophosphane $48$ (top) and preparation of zwitterionic $P_5$-cage compound $53$ from $P_4$ and zwitterionic phosphenium ion $52$.](image2)
The formation of related phosphonium ion $50^+$ is observed only upon addition of a second equivalent of GaCl$_3$. This can be explained by the suppression of detrimental concentrations of nucleophilic chloride anions through the formation of Ga$_2$Cl$_7^-$. Cation $50^+$ is not stable in solution and decomposes via Lewis acid mediated Me$_3$SiCl elimination. However, the insertion reaction with P$_4$ requires only the use of one equivalent of GaCl$_3$. In 1 : 1 : 1 mixtures of 48, GaCl$_3$ and P$_4$ the corresponding P$_3^-$-cage compound $51[\text{GaCl}_4]$ is formed slowly within four days presumably due to the presence of small amounts of $50^+$ formed from 49 in a series of equilibrium reactions.$^{59}$ The related zwitterionic phosphonium ion $52$ features a formally anionic AlCl$_2$-backbone.$^{60}$ It reacts with P$_4$ in toluene giving the formally neutral P$_2$-cage compound $53$. A conversion of only 30% to the respective product is observed in the reaction mixture, presumably due to the low electrophilicity of 52. However, the developed synthetic protocol includes removal of unreacted starting materials 52 and P$_4$ by sublimation which can be used in additional synthetic cycles increasing the overall isolated yield.

8. Cationic polyphosphorus-chalcogen cages

A multitude of phosphorus-chalcogenides have been characterized to date and many of their structural motifs are displayed even in undergraduate textbooks.$^{61}$ However, until recently, only very few examples of polyphosphorus-chalcogen cations were known which was due to the lack of established synthetic routes for their preparation. To the best of our knowledge only three distinct protocols have been reported so far. The first is based on the reaction of P$_4$S$_3$ with in situ generated phosphonium ion PI$_2^+$ (Scheme 15).$^{48}$

The phosphonium ion formally inserts into a P–P bond of the basal P$_3$-ring accompanied by migration of one of the iodo-substituents to an adjacent P atom giving cation $54^+$. However, $54^+$ is not stable and subsequently disproportionates via an unknown reaction pathway to form $55^+$ and $56^+$. This process involves the extrusion of a very reactive iodo-phosphinidene [PI] and redistribution of the sulfur atoms.

The second protocol is based on halide abstraction from $\alpha$-P$_4$S$_3$I$_2$ with Ag(CH$_2$Cl)$_2$[Al(OC(CF$_3$)$_3$)$_4$] and yields the spirocyclic cage cation $58^+$ (Scheme 16).$^{62}$ The initial step involves the formation of $57^+$ via iodide abstraction from $\alpha$-P$_4$S$_3$I$_2$. Cation $57^+$ subsequently reacts with a second equivalent of $\alpha$-P$_4$S$_3$I$_2$ and this in association with the formal extrusion of phosphinidene [PI] gives rise to spirocyclic cage $58^+$. However, detailed information on the mechanism of the formation of $58^+$ was not gained. The structural motif of this cation is unprecedented and contains the first tetra-coordinated P atom exclusively bonded to P and S atoms.$^{62}$

Recently, a third approach garnered interest which is based on using cationic polyphosphorus cages as starting materials for the preparation of cationic polyphosphorus-chalcogen cages. They constitute potentially versatile reagents due to the multitude of distinctly substituted derivatives which are all conveniently obtained in one step procedures from white phosphorus.$^{49}$ Chalcogenation reactions of R$_2$P$_5$-cage compounds $36a[\text{GaCl}_4]$ and $36f[\text{GaCl}_4]$ with elemental grey selenium yield the corresponding polyphosphorus-selenium cages $59a[\text{GaCl}_4]$ and $59f[\text{GaCl}_4]$ (Scheme 17). Both are obtained at elevated temperatures (110−150 °C) following a solvent-free protocol. In some cases,
the addition of one equivalent of GaCl₄ is beneficial since it lowers the melting point of the respective melt. Both cations are formed upon insertion of two selenium atoms into two P–P bonds adjacent to the phosphonium moieties in 36a,f.

Their structural motif resembles that of nortricyclane, with a basal P₃-ring, the tetra-coordinated P atom and the selenium atoms occupying the bridging positions, and one P atom defining the apex of the cage. This class of compounds feature interesting ³¹P and ⁷⁷Se NMR characteristics. Cages 59a,f reveal an AM₂OX spin system for the C₃-symmetric isotopomer without a ⁷⁷Se nucleus. These resonances are superimposed by the C₄-symmetric isotopomer featuring one ⁷⁷Se atom in one of the bridging positions. This isotopomer gives rise to an AMNOXZ spin system which is highly influenced by higher order effects. However, in the case of 59a, the spin systems of both isotopomers were successfully simulated allowing for the exact determination of chemical shifts and coupling constants.

A series of experiments employing varying temperatures, reaction times and stoichiometries gave meaningful insights into the mechanism of the chalcogenation. These experiments indicate that the insertion of Se atoms into P–P bonds of 36a,f proceeds in a stepwise manner via the intermediates 60a,f. In the case of alkyl-substituted cage 36a the insertion of a second equivalent grey selenium is fast, yielding the respective product 59a quantitatively. If the aryl-substituted starting material 36f is employed, the intermediate formation of dication 61⁺ is observed. This species forms via the transfer of a [Ph₂P⁺] moiety from a second equivalent of 36f to the reactive intermediate 60f. Due to the higher stability of the corresponding phosphonium ion Ph₂P⁺, this transfer is faster than the insertion of the second selenium atom. Subsequently, one of the [Ph₂P⁺]-moieties of 61⁺ is substituted by a selenium atom giving rise to 59f. The formally liberated Ph₂P⁺-phosphonium ion is not stable and reacts with a GaCl₄⁻ anion to give the Lewis acid–base adduct 37 (Ph₂PCI–GaCl₄). This is in accordance with the observation of only 50% conversion and the quantitative formation of P₆ and 37 or the respective oxidation product Ph₂P(Se)Cl-GaCl₄ in the case of reactions involving 36f as a starting material. The targeted preparation of 61⁺ as GaCl₄⁻ salt is achieved by utilizing a 2:1 stoichiometry of 36f and grey selenium. Another synthetic approach for the preparation of 61⁺ is the targeted substitution of one [Ph₂P⁺]-moiety in the tricationic cage 43⁺. This is achieved by reacting 43⁺ with grey selenium under solvent-free conditions (Scheme 17).

Dication 61⁺ was comprehensively characterized by X-ray crystallography (Fig. 12) as well as ³¹P and ⁷⁷Se NMR spectroscopy. The ³¹P NMR spectrum reveals a characteristic AA'MOXX'-spin system for the isotopomer without a ⁷⁷Se nucleus which is superimposed by the respective AA'MOXX'Z-spin system of the ⁷⁷Se containing species.

A similar reactivity was observed for reactions of the P₅⁺-cage 36a or the P₇⁺-cage 43⁺ with elemental ₃₇Se. The polyphosphorus cation 43⁺ and cationic polyphosphorus-chalcogen cages 61⁺, and 59f are formally derived from the stepwise isolobal exchange of [Se] atoms by [Ph₂P⁺] units in the bridging positions of the nortricyclane-type structure of P₄Se₂. This allows for an in-depth study of the ³¹P NMR characteristics of the whole series of compounds and a correlation with the observed structural features in the solid state. Fig. 13 shows the dependence of the chemical shifts of 43⁺, 61⁺ and 59f, the related sulfur-containing cages 62a and 63⁺, and P₇Ch₃ (Ch = Se, S) on the number of chalcogen atoms in the corresponding molecules. The stepwise exchange of tetra-coordinated P atoms in 43⁺ by Se or S atoms is accompanied by a high-field shift of the resonances of the P atoms of the basal three-membered ring. The chemical shifts of basal P atoms in nortricyclane-type cages are influenced by the exocyclic angles of the P₃-ring. The observed high-field shift correlates well with decreasing exocyclic angles observed in the solid state structures of the respective compounds. The resonances of apical P atoms exhibit the widest range of chemical shifts and reveal a stepwise down-field shift upon the substitution of tetra-coordinated P atoms by chalcogen atoms. This is consistent with different electronegativities of directly bonded phosphorus or chalcogen atoms. Moreover, apical P atoms show a high dependency of their chemical shift on elongation or compression of the nortricyclane framework. Elongation is accompanied by a decrease in the P–P–P angles involving the apical P atom. This increases the s-orbital contribution to the lone pair of electrons and leads to an upfield shift of the corresponding resonance in the ³¹P NMR spectrum. On this basis, the observed downfield shift indicates a stepwise elongation of the cages which is observed in the respective molecular structures in the solid state.

![Fig. 12 Nortricyclane type molecular structures of the related, polyphosphorus cations 59⁺, 61⁺ and 43⁺.](image-url)
9. Nucleophilic fragmentation of cationic polyphosphorus cages

The activation of white phosphorus with carbenes, which belong to the class of predominantly nucleophilic ambiphiles, displays one of the most diverse fields of P4 chemistry.6 The cyclo-triphosphirenne derivative C constitutes a key intermediate in all transformations, independent of the characteristic of the respective carbene employed (Fig. 1). However, intermediate C is elusive and distinct reaction pathways occur depending on the electronic and steric features of carbene L. Bertrand and co-workers reacted P4 with carbenes L5 and L4 in a 1:2 stoichiometry and obtained E/Z isomers 64a,b via an intermediate of type C.12 Bicyclic species 65 is the result of a cyclo-addition reaction involving the phosphorus double bond of an intermediate of type C and the alkyl amino carbene L4.66 Compound 66 results from a ring-opening reaction of an intermediate C with two equivalents of L4.66 This reaction is accompanied by the formation of 67 as a side product. This P2-species is formed by the formal [2+2] fragmentation of P4 by carbene L4. A [3+1]-fragmentation of the P4 tetrahedron was achieved using the sterically less demanding carbene L4 in a reaction with P4 in a 3:1 stoichiometry.66 The P2-fragment was identified as 68 and isolated as chloride salt. The presence of chloride anions is explained by the decomposition of CHCl3 solvent molecules.

A compound of unknown constitution featuring a P2 moiety was indicated in the 31P NMR spectrum of the respective reaction mixture.66

A combination of phosphenium ion and carbene mediated P4 activation constitutes a novel, potentially versatile approach for the preparation of cationic polyphosphorus cages. This strategy allows for the preparation of polyphosphorus cations featuring imidazolium-substituents. These substituents are valuable for two purposes. First, they serve well for the stabilization of cations by delocalization of the positive charge.70 Second, they stabilize low-coordinated P moieties by reducing the nucleophilicity of directly bonded P atoms.71 The reaction of P5+-cage compound 32b[GaCl4] with carbene L7 in a 1:1 stoichiometry yields the bicyclo[1.1.0]tetraphosphane 69[GaCl4] (Scheme 19).67 The bicyclic framework is substituted with an imidazoliumyl-group in an exo-position and a phosphanyl-group in an endo-position. This is reminiscent of the intermediate 31 observed in the formation of RP3Cl+-cages. Cation 69 features an ACExM spin system indicating a non-symmetrical molecular structure due to hindered rotation around the P-P bond involving the Dipp-substituted P atom. The endo,exo-substitution of 69 causes a short intermolecular distance between the Dipp- and the imidazoliumyl-substituted P atoms in the solid state (see molecular structure in Scheme 19). This spatial proximity is also indicated in solution by an extraordinarily large \( J(PP) \) coupling constant of 244.6 Hz in the 31P NMR spectrum.

The reaction of 32b[GaCl4] with carbene L7 in a 1:3 stoichiometry proceeds via a quantitative [3+2]-fragmentation of the P5+-cage (Scheme 20).67

The P2 fragment was identified as the neutral P2 species 70 featuring an inversely-polarized phosphaalkene moiety. The di-coordinated P atom bears a phosphanyl-substituent which originates from the tetra-coordinated P atom of starting material 32h-. The P3 fragment was identified as GaCl4--salt of cation 71 which features a chain of three di-coordinated P atoms terminated by two imidazoliumyl-substituents. This compound is characterized by a deep green colour that results from \( n \to \pi^* \) and \( \pi \to \pi^* \) transitions similar to those observed in diphosphenes.69 Quantum chemical calculations elucidated the bonding in 71+.67 The frontier orbital arrangement of the cation is closely related.
to the classical π-system of the C₃-allyl anion. Thus, 71⁺ features a local triphosphaallylanion moiety substituted with imidazoliumyl-groups. The mechanism of the [3+2] fragmentation is explained by the reaction sequence in Scheme 21 on the basis of experimental evidence and quantum chemical calculations.⁶⁷ The reaction of 32h⁺ with the first equivalent of L⁷ yields the experimentally verified species 69⁺. The nucleophilic attack of a second carbene L⁷ occurs at a P atom adjacent to the phosphonium moiety in 32h⁺ and initiates a P–P bond cleavage. This reaction step is the reverse of the last step in the formation of RP₄Cl⁺-cages (Fig. 7) and is in accordance with the observed reversibility of phosphonium ion insertion into P–P bonds of P₄ (vide infra). The nucleophilic attack of a second carbene L⁷ occurs at the endo-substituted P atom of 69⁺ and initiates a P–P bond cleavage in the respective P₃-ring.

This yields intermediate 72⁺ according to quantum chemical calculations.⁶⁷ Subsequently, this intermediate intramolecularly
eliminates the P₂ fragment 70. This yields the elusive triphosphirene derivative 73⁺ which is related to the key intermediate C (Fig. 1) of carbene-induced P₄ activation.¹²,⁶⁶ The nucleophilic attack of a third carbene L⁷ on the PP double bond of 73⁺ initiates a ring-opening and yields the second fragment 7¹⁺. The ease of fragmentation (high yields, multi-gram scale) together with the facile accessibility of cationic phosphorus cages from P₄ and the multitude of carbenes available render this approach suitable for the preparation of a plethora of interesting polyphosphorus compounds.

### Abbreviations

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<th>Abbreviation</th>
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<tr>
<td>aAAC</td>
<td>Acyclic alkyl amino carbene</td>
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<tr>
<td>Ab</td>
<td>Ambiphile</td>
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<td>FIA</td>
<td>Fluoride ion affinity</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>i-Pr</td>
<td>Iso-propyl</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>Me</td>
<td>Methyl</td>
</tr>
<tr>
<td>Mes⁺</td>
<td>2,4,6-Tri-tert-butylphenyl</td>
</tr>
<tr>
<td>NHC</td>
<td>N-Heterocyclic carbene</td>
</tr>
<tr>
<td>Nu</td>
<td>Nucleophile</td>
</tr>
<tr>
<td>OTf</td>
<td>Triflate, trifluoromethylsulfonate</td>
</tr>
<tr>
<td>t-Bu</td>
<td>tert-Butyl</td>
</tr>
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### Acknowledgements

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### References


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58 Unpublished results.