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

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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 P₄, 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 P₄ 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 (P₄) is important for the ongoing search for new, systematic entries to polyphosphorus and

polyphosphorus 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 $R_n P_m$ (n > m) is achieved with synthetic protocols mainly based on the utilization of neutral *catena* or *cyclic* polyphosphanes $R_n P_m$. Protocols for phosphorus-rich cations $R_n P_m$ (n < m) often involve 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

organo-phosphorus compounds. Especially in the realm of

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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 P₄ framework should allow for a targeted and systematic assembly of phosphorus-rich cations $R_n P_m$ (n < m). Additionally, the application of P₄ 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 metal⁵ and main group⁶ mediated P₄ activation has been reviewed several times. However, no account was given so far on the importance of P4 as a starting material for the preparation of polyphosphorus cations.

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 P4, 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 P4 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 ³¹P 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 $\Delta \delta(P_i P_{ii}) / {}^n J(P_i P_{ii}) < 10$. For $\Delta \delta(P_i P_{ii}) / {}^n J(P_i P_{ii}) > 10$, 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 P₄. 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 P4 and the general characteristics of phosphenium ions. Thus, a brief insight into both fields is given in the first two sections.

2. P₄ activation pathways

In order to gain an in depth understanding of the reactions of P₄ and main group element compounds, it is crucial to understand the properties of the P₄ tetrahedron. The bonding in P₄ is almost "cluster-like", strongly delocalized and mostly effected through 3p atomic orbitals. Interestingly, P₄ shows spherical aromaticity and is virtually unstrained despite acute bond angles of 60°. Generalized reactions of P₄ with nucleophiles (Nu⁻), electrophiles (El⁺) and ambiphiles (Ab) are shown in Fig. 1. Radical reactions involving P4 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. 1I). The reactions of P₄ with nucleophiles were intensely investigated using an array of organo-alkali and organo-alkali earth reagents.6 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 P4 to P₁-compounds. Only a few reactions involving a selective cleavage of only a single bond in the P4 tetrahedron are reported.

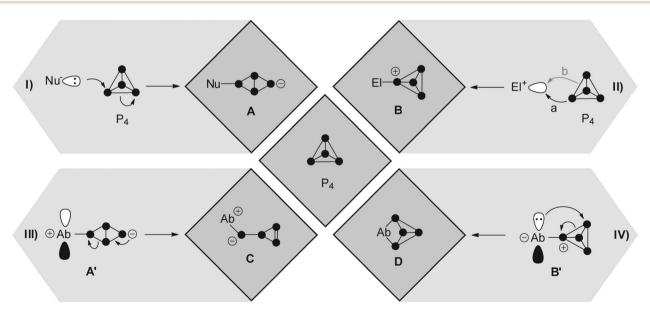


Fig. 1 Generalized reactions of P₄ with nucleophiles (I, Nu⁻), electrophiles (II, El⁺), predominantly nucleophilic ambiphiles (III, Ab), and predominantly electrophilic ambiphiles (IV, Ab); A-D illustrate structural motifs obtained after reaction with the aforementioned species.

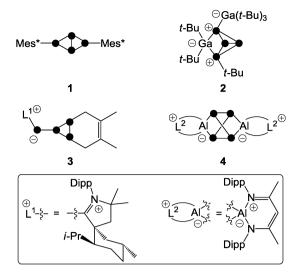


Fig. 2 Examples of polyphosphorus compounds obtained by the functionalization of P₄ by nucleophiles (1), electrophiles (2), predominantly nucleophilic ambiphiles (3), and predominantly electrophilic ambiphiles (4).

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).8 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.⁶ An electrophile may attack at a nonbonding orbital of lone pair character (HOMO -6, -7.5 eV)⁷ which results in the formation of compounds of type B (Fig. 1II a). Alternatively, an electrophile may attack at a bonding orbital at one of the edges of the tetrahedron (HOMO, -6.7 eV; Fig. 1II 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 P4.9 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).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-triphosphirene derivative C (Fig. 1III). 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. Carbenes are ambiphiles with a predominantly nucleophilic character. 11 Two types of carbenes, 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. 12 The formation of an intermediate of type A' was confirmed by DFT calculations¹² and of type C by trapping experiments with 2,3-dimethylbutadiene yielding [2+4] cyclo-addition product 3 (Fig. 2, e.g. $L^1 = cAAC$).

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 \mathbf{B}' (Fig. 1). Subsequently, **B**' rearranges to a bicyclo[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 +I are a class of substances that are widely used in such transformations. 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).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, 14 disilenes, 15 phosphasilenes, 16 and a bis(stannylene) 17 was reported. Reactions of P_4 with phosphenium cations (R_2P^+) 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. 18 Phosphenium ions reveal a lone pair of electrons and a formally vacant p-type orbital, and thus, they constitute carbene analogues.¹¹ The stability of phosphenium ions strongly depends on their substituents. While aryl- or alkylphosphenium ions R_2P^+ (7⁺, Fig. 3) are strongly electrophilic and generally elusive, a large series of phosphenium ions bearing amino-substituents $(R_2N)_2P^+$ (R =alkyl, aryl) are known. 18 Three methods for their preparation are mainly reported throughout the literature. Halide abstraction from the corresponding halo-phosphane precursor is the most commonly used synthetic protocol. 18 Further methods

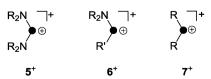


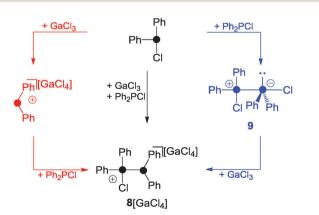
Fig. 3 Distinct types of phosphenium ions featuring two (5⁺) or one (6⁺) stabilizing amino-substituents and elusive, non-stabilized phosphenium ion $\mathbf{7}^+$ (R, R' = alkyl, aryl).

constitute the protolysis of P–N single bonds by Brønsted acids and the coordination of strong Lewis acids to P–N double bonds. 18

The increased stability of phosphenium ions $(R_2N)_2P^+$ (5⁺, Fig. 3) stems from a lowered electrophilicity due to donation of π -electron density from the lone pair of electrons at the nitrogen atoms to the vacant p-type orbital at the P atom. ¹⁹ Phosphenium 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 phosphenium ion bearing only alkyl- or aryl-substituents has not been isolated to date. The reaction of phosphanes bearing organo- and chloro-groups $R_nPCl_{(3-n)}$ (n=1,2) and a halide abstracting agent (e.g. Me₃SiOTf, GaCl₃, or AlCl₃) in the appropriate stoichiometry usually results in the formation of phosphanylphosphonium ions. This is best exemplified by the reaction of Ph_2PCl and $GaCl_3$ in a 2:1 stoichiometry which yields $8[GaCl_4]$ (Scheme 1). $Parallel{2}$

Two mechanisms for the formation of 8⁺ are conceivable. Firstly, Ph₂PCl reacts with GaCl₃ as a halide abstracting agent giving a transient Ph₂P⁺-phosphenium ion. This reacts with the second equivalent of Ph₂PCl yielding 8⁺. The second and in the author's opinion more likely mechanism proceeds via the zwitterionic intermediate 9 which features a Ph₂PCl molecule donating electron density from its lone pair of electrons to the lobes of the antibonding $\sigma^*(P-Cl)$ orbital of a second molecule of Ph₂PCl. Subsequently, chloride abstraction by GaCl₃ yields 8⁺ without an intermediary formation of a free Ph₂P⁺-phosphenium ion. The phosphoniumyl-moiety in 8⁺ is easily substituted when 8⁺ is reacted with phosphanes of higher basicity than the leaving group. This is illustrated by the reaction of 8⁺ with Ph₃P yielding 10⁺ and Ph₂PCl (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-4,5dimethylimidazol-2-ylidene (L³) which yields the imidazoliumylsubstituted phosphane 11⁺.²³



Scheme 1 Synthesis of $8[GaCl_4]$ by the reaction of Ph_2PCl and $GaCl_3$ in 2:1 stoichiometry and possible reaction sequences giving $8[GaCl_4]$ either via free Ph_2P^+ -phosphenium ion (red) or zwitterion 9 (blue).

Scheme 2 Substitution of the phosphoniumyl-moiety of **8**⁺ by Lewis-bases.

Scheme 3 S_N2-type substitution of the phosphoniumyl-moiety in 12⁺.

Detailed investigations of mixtures of phosphanyl-phosphonium ion ${\bf 12}^+$ and Ph_3P revealed second-order kinetics for the exchange process of Ph_3P consistent with a S_N2 -type pathway (Scheme 3).²⁴

This was further supported by quantum chemical calculations which suggested the phosphoranide-type transition state ${\bf 13}^+$ for the substitution process. ²⁴ In contrast, the phosphanyl-phosphonium ion ${\bf 14}^+$, which is formed *via* the reaction of phosphenium ion ${\bf 15}^+$ and PMe₃, was reported to favour a dissociative S_N1-type reaction pathway in substitution reactions (Scheme 4). ²⁵

For phosphanylphosphonium ions such as those described above the term "ligand stabilized phosphenium ions" is frequently used in the literature while the described substitution reactions are also called "ligand exchange" reactions. Independent of any such controversy, however, these distinct points of view are based on the labile P-P bond observed in phosphanylphosphonium ions. This allows for the transfer of R₂P⁺-moieties (formally phosphenium ions) between distinct Lewis bases (*e.g.* phosphanes, carbenes or P₄). Thus, for reasons of simplification, phosphanylphosphonium ions will be regarded as "sources of phosphenium ions" throughout this review.

Phosphanylphosphonium ions were frequently used as phosphenium ion sources. The reaction of a mixture of Me_2PCl

Scheme 4 S_N1-type dissociation of phosphanylphosphonium ion 14⁺.

Fig. 4 Polyphosphorus cations 16⁺, 17⁺ and 18²⁺ obtained via the formal insertion of R_2P^+ -phosphenium ions (R = Me, Ph) into the P-P bond of (Ph₂P)₂, (PhP)₄ and (PhP)₅.

and Me₃SiOTf with diphosphane (Ph₂P)₂ gave diphosphanylphosphonium ion 16⁺ as a triflate salt (Fig. 4).²⁶ Species 16⁺ is formally derived from the insertion of a Me₂P⁺-phosphenium ion into the P-P bond of the diphosphane (Ph₂P)₂. Mixtures of Ph₂PCl and Me₃SiOTf with the cyclo-phosphanes (PhP)₄ or (PhP)₅ give in both cases the *cyclo*-tetraphosphanylphosphonium ion 17⁺.

A ring expansion is observed in the reaction with (PhP)4 whereas a 5-membered ring is retained in the reaction involving (PhP)₅ via an unknown redistribution process.²⁶ Both reactions proceed via the formal transfer of a Ph₂P⁺-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 sixmembered alternative. The highly reactive, cyclic six-membered dication 18²⁺ is only obtained by employing a melt approach.²⁷ Solvent-free mixtures of Ph2PCl and GaCl3 provide room temperature molten media. These melts represent a powerful source of phosphenium ions Ph₂P⁺.²⁸

4. Cationic homoleptic polyphosphorus cages

For decades the investigation of homoleptic polyphosphorus cations was limited to mass spectroscopy29 and quantum chemical calculation 30 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 P_n^+ cations $\mathbf{19}^+$ (n = 5) and $\mathbf{20}^+$ (n = 7) may be described as electron-deficient Wade clusters whereas larger P_n⁺-cages $(n \ge 9)$ feature electron-precise Zintl-type structures. According to Wade's rules, a square pyramidal structure is anticipated for cation 19⁺ (Fig. 5, nido-cluster). Such a structure was confirmed as the most stable isomer by means of quantum chemical calculations. 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 di-coordinated P atom. The most stable isomer of P₇⁺-cage 20⁺ is a tricapped trigonal prism that is missing two of the capping vertices (arachno-cluster). A second isomer, which is only slightly higher in energy $(20'^+, 2.0 \text{ kcal mol}^{-1})$, shows the P₅-cage motif of $19'^+$ and a three-membered P ring which are both fused by a bridging

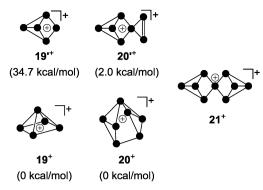
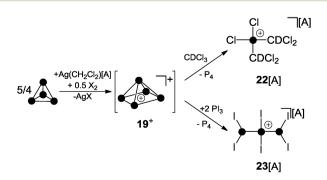


Fig. 5 Anticipated structures of homoleptic, diamagnetic polyphosphorus cations 19+, 20+ and 21+.

phosphonium moiety. The P₉⁺-cage 21⁺, which is composed of two P₄-moieties fused by a phosphonium moiety, is one of the most stable homoleptic polyphosphorus cations according to quantum chemical calculations (Fig. 5). 30b

Krossing and co-workers were the first to report evidence for the existence of homoleptic polyphosphorus cations in the condensed phase. 31 The attempted oxidation of P₄ with I₂ or Br₂ in the presence of $Ag(CH_2Cl_2)[A]$ (A = $Al(OC(CF_3)_3)_4$) was suggested to proceed via the intermediary formation of P5+-cage cation 19⁺ (Scheme 5).³² However, cation 19⁺ is highly reactive and reacts with the solvent to give phosphonium ion 22⁺ as one of the main products. Cation 22⁺ forms via elimination of P₄ and two-fold insertion into C-Cl bonds of CDCl3 molecules which was used as solvent. In the case of I2 as oxidant, P4 reacts partially to give PI3 which was suggested to react with intermediate 19⁺ to give P₄ 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.32 The nitrosonium salt [NO][A] (A = Al(OC(CF₃)₃)₄) was also investigated as a possible one electron oxidant. However, the reaction of P4 with [NO][A] yields P_4NO^+ -cage compound 24[A] *via* insertion of the nitrosonium cation into a P-P bond (Scheme 6).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



Scheme 5 Oxidation of P₄ with I₂ or Br₂ in the presence of Aq(CH₂Cl₂)[A] via P_5^+ -cage intermediate **19**⁺; A = Al(OC(CF₃)₃)₄.

Scheme 6 Reaction of P₄ and NO[A] yielding P₄NO⁺-cage **24**[A] and subsequent reaction with P_4 yielding P_9^+ -cage compound 21[A]; A = $Al(OC(CF_3)_3)_4$

investigations suggested a two-step mechanism indicating the HOMO of P₄ and a π^* -type LUMO at NO⁺ as the interacting frontier orbitals (II b, Fig. 1).33 Similar results were obtained utilizing the carborate salt NO[HCB₁₁Cl₁₁].³⁴ The reaction of P₄NO⁺-cage compound 24[A] with additional 1.5 equivalents of P₄ was reported to yield P₉⁺-cage compound 21[A] which is the first isolated salt of a homoleptic phosphorus cation (Scheme 6).35

The reaction proceeds very likely *via* extrusion of 1/n (PNO)_n and intermediary formation of a P₃⁺-species. The P₉⁺ cation 21⁺ is obtained upon reaction of the latter with 1.5 equivalents of P₄ via an unknown reaction mechanism. The ³¹P NMR spectrum of cation 21⁺ shows a characteristic A₂A'₂BC₂C'₂ spin system which confirms the D_{2d} symmetric Zintl-type structure. Despite the electron precise Lewis formula of eight neutral, threecoordinated and one cationic, four-coordinated P atom the charge is almost evenly distributed over all nine atoms according to quantum chemical calculations.³⁵

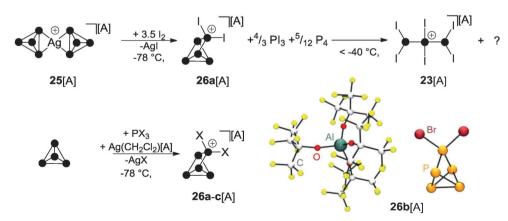
5. Cationic polyphosphorus cages featuring halogen-substituents

The oxidation of Ag(I) complex 25[A] (A = $Al(OC(CF_3)_3)_4$) featuring two intact P4 ligands with elemental iodine at low temperatures gives rise to interesting binary PI cations. The P₅I₂⁺-cage 26a⁺ was observed in the reaction mixture at −78 °C together with PI₃ 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.

A proposed reaction mechanism indicates the partial oxidation of the P₄ ligands in 25⁺ by I₂ to give PI₃. The latter reacts with Ag[A] (A = Al(OC(CF₃)₃)₄) via halide abstraction to give AgI and formally the phosphenium ion PI2+. This highly reactive, predominantly electrophilic ambiphile reacts with white phosphorus via insertion in one of the P-P bonds of the P4 tetrahedron yielding the P₅I₂⁺-cage 26a⁺. Likewise, according to the observations described in Section 3, a mechanism involving the formation of phosphanylphosphonium ion P₂I₅⁺ can also be considered. Here, P2I5+ is assumed to transfer a PI2+ phosphenium ion to P₄ and, thus, serves as a phosphenium ion source. Upon warming the reaction mixture, the excess of PI₃ reacts with P4 to yield diphosphane P2I4 in a conproportionation reaction. The diphosphane reacts with 26a+ via transfer of the phosphenium ion PI2+. This gives P4 and the P3I6+ cation 23⁺ which is formed upon insertion of the PI₂⁺ ion into the P-P bond of P2I4. On the basis of these observations, a synthetic protocol for the targeted preparation of P₅X₂⁺-cages was developed (Scheme 7). 36,37 Thus, white phosphorus reacts with PX_3 (X = I, Br) in the presence of $Ag(CH_2Cl_2)[A]$ as a halide abstracting agent and salts of cage cations 26a⁺ and 26b⁺ can be isolated in good yield. However, utilizing PCl₃, the formation of the respective cation 26c⁺ was observed only in trace amounts since it readily decomposes in the reaction mixture.³⁸ The molecular structure of 26b+ is shown in Scheme 7. The structural motif of the P₅-core of the P₅X₂⁺-cage was unprecedented and was not previously observed as part of the many known polyphosphides and organo-polyphosphanes.

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 phosphenium ion RPCl⁺. In the presence of P₄, insertion into one of the P-P bonds takes place, giving access to



Scheme 7 Oxidation of Ag(i) complex 25[A] with I₂ at low temperatures giving intermediary P₅I₂⁺-cage 26a⁺ (top), targeted syntheses of P₅X₂⁺-cages **26a-c**⁺ (X = I, Br, Cl) by the reaction of P_4 , PX_3 and P_4 and P_5 and P_6 and molecular structure of **26b**[A] (bottom); P_6 and P_6 are P_6 and P_6 and P_6 and P_6 are P_6 and P_6 and P_6 are P_6 and P_6 are P_6 and P_6 are P_6 and P_6 and P_6 are P_6 are P_6 and P_6 are P_6 and P_6 are P_6 are P_6 and P_6 are P_6 and P_6 are P_6 and P_6 are P_6 are P_6 are P_6 are P_6 and P_6 are P_6 are

a series of RP₅Cl⁺-cages featuring distinct substituents R.³⁹ Mixtures of dichlorophosphanes and AlCl₃ were previously utilized for the in situ formation of phosphenium ion salts [RPCl][AlCl₄] and subsequent syntheses of various phosphorus heterocycles. 40 However, neither free phosphenium ions nor respective phosphenium ion sources could be verified. In some cases, the formation of Lewis acid-base complexes of the type $mRPCl_2 \cdot nAlCl_3$ (n = 1, 2; m = 1, 2) was suggested.⁴¹ Detailed investigations of mixtures of mono- and dichlorophosphanes in the presence of Lewis acids revealed the formation of chlorophosphanylchlorophosphonium ions of type 27⁺ (Fig. 6).⁴² In most cases, characteristic ¹/(PP) 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.42 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 nonclassical 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 acidbase adduct. An increasing amount of phosphanylphosphonium 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 phosphanylphosphonium 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 phosphanylphosphonium species yielding

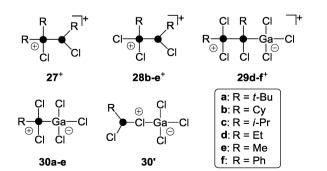


Fig. 6 Phosphanylphosphonium ion derivatives 27⁺-29⁺ and Lewis acidbase adduct 30 (classical) and 30' (non-classical); R = alkyl, aryl.

the phosphane starting materials in a back reaction. By using an excess of GaCl₃ the GaCl₄⁻ forms higher gallates (Ga₂Cl₇⁻ or Ga₃Cl₁₀⁻) 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 phosphenium ion source in a reaction with P₄. According to these results, ⁴⁴ the formation of RP₅Cl⁺-cages via a free phosphenium ion RPCl⁺ can be excluded. Attempts to calculate a feasible reaction mechanism from adducts 30 or 30' as sources of phosphenium ions were not successful. Thus, the reaction of P4 with methylsubstituted phosphanylphosphonium derivative 28e+ was investigated (Fig. 7). A single step insertion of the phosphenium 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 butterfly-type compound 31 as an intermediate (bottom, Fig. 7). The single step transfer of the phosphenium 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 P4,7a this is best understood as a combined electrophilic and nucleophilic attack of the phosphenium moiety. On the one hand the P-P bond of P4 (HOMO) nucleophilically attacks the p-type orbital of the phosphenium moiety. On the other hand the lone pair of electrons of the phosphenium moiety donates electron density to the LUMO of the P4 tetrahedron which corresponds to p-orbitals situated perpendicular to the P₄ lone pairs. The 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 phosphenium 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 intramolecular nucleophilic attack of the phosphanyl-substituent on the chloro-substituted P atom. This eliminates the GaCl₄anion and leads to the formation of the P₅⁺-cage cation 32e⁺.

Despite their different compositions 1:1 mixtures of RPCl₂ and a Lewis acid ECl_3 (E = Al, Ga) in fluorobenzene are potent sources of reactive phosphenium ion RPCl+ equivalents, which insert formally into P-P bonds of P4.39 Dissolution of P4 in these mixtures yielded white to yellowish precipitates of the corresponding RP5Cl+-cage salts for a large range of different alkyl- and aryl-substituents R (32a-h[GaCl₄], 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. 36,37 The cations 32a-h⁺ show characteristic ³¹P NMR spectra. Iterative line shape

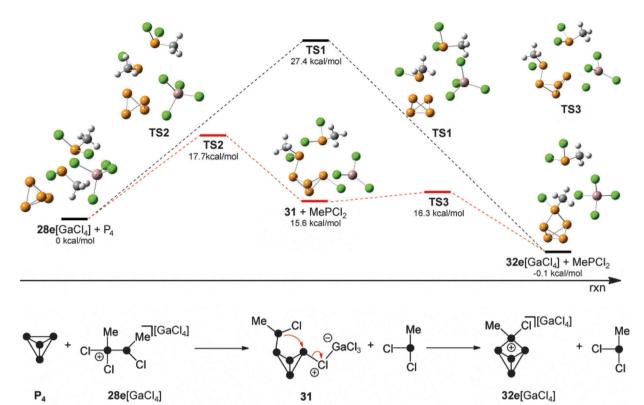
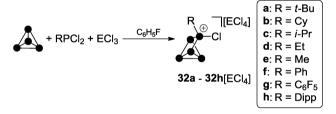


Fig. 7 Calculated reaction pathways for the reaction of **28e**[GaCl₄] and P₄; calculated differences of the enthalpies at 298.15 K (ΔH_{298}) are given for the optimized structures of MP2/6-31G(d) and the optimized structures of **28e**[GaCl₄] + P₄ were defined as 0 kcal mol⁻¹.



 $\begin{array}{lll} \textbf{Scheme 8} & \text{Preparation of compounds } \textbf{32a-h}[\text{ECl}_4] \text{ from } P_4\text{, } RPCl_2 \text{ and } ECl_3 \text{ } (E=Ga,Al;\ R=alkyl,\ aryl) \text{ in fluorobenzene.} \\ \end{array}$

analysis of the observed spin systems gave chemical shifts and coupling constants in accordance with $C_{\rm S}$ symmetric RP₅Cl⁺cages with four chemically non-equivalent phosphorus nuclei. All cages possess a mirror plane which includes the tetracoordinated P atom and both P atoms opposing the former. Due to the reduced symmetry compared to the C_{2V} -symmetric $P_5X_2^+$ cages 26a-c⁺ an ABM₂X spin system is observed for 32a-d⁺ and an ABMX₂ spin system for 32e- \mathbf{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 RP₅Cl⁺cage (Fig. 8). The PA and PB 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 P₅⁺-cage is divided by a plane spanned by the tetra-coordinated and both adjacent P atoms into a H_{Cl}- and H_R-hemisphere (Fig. 9).

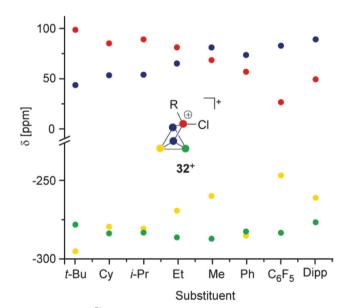


Fig. 8 Plot of the 31 P NMR chemical shifts of RP₅Cl⁺-cages **32a-h**⁺ versus their alkyl- or aryl-substituent.

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 1 J(PP) and 2 J(PP) coupling constants which are reminiscent of those of P_5X_2 ⁺-cages 26a–c⁺. 36,37 Accordingly, the P atom located in the H_R -hemisphere reveals one- and

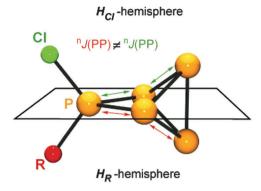


Fig. 9 Definition of the H_{Cl} - and H_{R} -hemisphere in cations **32a-h**⁺. The tetra-coordinated and the adjacent P atoms span a plane. The tricoordinated P atom above the plane is within the H_{CI}-hemisphere, and the P atom below the plane is in the H_R-hemisphere.

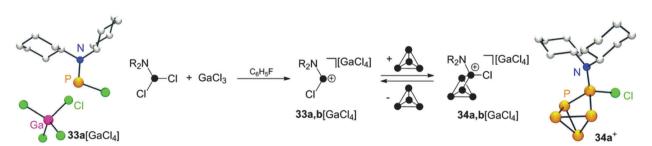
two-bond P-P coupling constants similar to the values observed for the respective R₂P₅⁺-cages. In addition, the former group of P atoms experiences the spatial proximity of the chloro-group, and, therefore, shows similar chemical shifts (marked in green, Fig. 8). In contrast, the P atoms in the H_R-hemisphere 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 most 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 phosphonium 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 tetracoordinated P atoms (marked in red, Fig. 8) exhibit an almost inverse trend (from 99 ppm (32a⁺) to 69 ppm (32e⁺)). This highfield shift correlates with an increasing number of hydrogen atoms at the α -carbon atom of the substituent. This constitutes a characteristic feature of phosphonium 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 = Cv, 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 phosphenium ions 33a,b⁺ are the only observable species.^{20a} 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]: $\delta = 310$ ppm, 33a[Ga₂Cl₇]: $\delta = 350$ ppm). The GaCl₄ salt of 33a+ can be isolated and constitutes a rare example of a structurally characterized mono-amino substituted phosphenium ion (Scheme 9). Upon reacting phosphenium ions 33a,b⁺ with P₄ insertion into a P-P bond is observed giving the C_S-symmetric RP₅Cl⁺-cage cations 34a,b⁺. However, these cages are in equilibrium with the respective free phosphenium 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 phosphenium ion insertion was observed in the case of RP₅Cl⁺ compounds. The addition of coordinating solvents like acetonitrile to solutions of $32[ECl_4]$ (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.

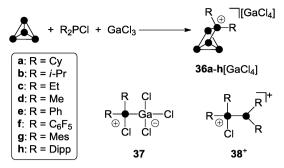
It is interesting to note that a reaction between the two-fold amino-substituted phosphenium ion [(i-Pr₂N)₂P]⁺ (35⁺) and P₄ was not observed. 20a This is attributed to a significantly lowered electrophilicity of 35⁺ compared to 33a,b⁺. 19 Also, diaminophosphenium ions of type 35⁺ reveal frontier orbitals comparable to those of allyl-anions⁴⁸ with the HOMO mainly located at the N atoms, and, thus, are not ambiphilic at the P moiety.

R₂P₅[GaCl₄] cage compounds 36[GaCl₄] featuring two alkylor 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.^{22b} Both convert into each other via equilibria involving free R₂PCl and GaCl₃. ^{49,22b} Cations of type 38+ serve as phosphenium 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⁺. ³⁹ 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



Scheme 9 Reaction of R_2NPCl_2 (R = Cy, i-Pr) with $GaCl_3$ and P_4 and equilibrium of $\mathbf{34a,b^+}$ with $\mathbf{33a,b^+}$ and P_4 (middle) and molecular structure of 33a[GaCl₄] (left) and 34a⁺ (right).



Scheme 10 Preparation of compounds 36a-h[GaCl₄] from P₄, R₂PCl and GaCl₃ in fluorobenzene (R = aryl) or according to a solvent free approach (R = alkyl) and species 37 and 38+ commonly observed in mixtures of R₂PCl and GaCl₃.

substituents R, the reactions proceeds smoothly at ambient temperature in fluorobenzene solution. A significant decrease in reaction time is observed with increasing steric bulk of the substituents (Dipp $> Mes > C_6F_5 > Ph$). For the preparation of R₂P₅⁺-cages 36a-d⁺ featuring alkyl-substituents R, solventfree conditions are necessary. Mixtures of R₂PCl (R = Cy, i-Pr, Et, Me) and GaCl₃ in a 1:1 stoichiometry form melts at ambient temperature.²⁸ Upon addition of P₄ to these melts, the formation of the corresponding cage compounds 36a-d[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 phosphanes in the synthesis of R₂P₅-cage compounds of type 36[GaCl₄] can be rationalized in terms of the different Lewis acidities of the corresponding phosphenium ions. The Lewis acidity is reflected e.g. by their distinct fluoride ion affinities (e.g. Me_2P^+ : FIA = 959 kJ mol⁻¹, Ph_2P^+ : FIA = 838 kJ mol⁻¹). This necessitates a more Lewis acidic environment for the transfer of a phosphenium 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).

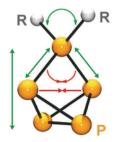


Fig. 10 Influence of the steric demand of substituents R on the structural parameters of the P₅⁺-cage core in cations of type **36**⁺; upon increasing the steric demand of R green arrows indicate increasing angles and distances and red arrows indicate declining angles and distances.

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 $Dipp_2P_5^+$ (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 A₂M₂X or A_2MX_2 spin systems in accordance with their C_{2V} symmetry and are comparable to those observed for the $P_5X_2^+$ cages 26a-c⁺ (Fig. 11). The observation of two different spin systems for $R_2P_5^+$ -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 $\sigma^*(P-P)$ orbitals at the phosphonium moiety.^{47a} 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 SiP₄-cage compound 40,

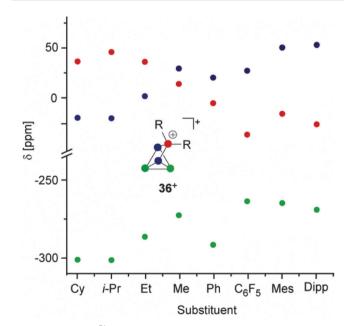


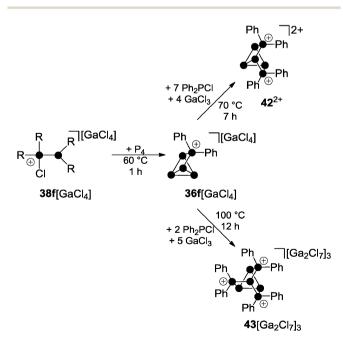
Fig. 11 Plot of the ^{31}P NMR chemical shifts of $R_2P_5^+$ -cages **36a-h**⁺ versus their alkyl- or aryl-substituent.

Scheme 11 Stepwise insertion of zwitterionic silylene 39 into P-P bonds of P₄ yielding SiP₄-cage compound 40 and Si₂P₄-cage compound 41

which is obtained by the reaction of P4 with zwitterionic silvlene 39. This compound reacts with a second equivalent of 39 to give the Si₂P₄-cage compound 41 (Scheme 11).¹⁴ 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 P₄ with a low valent Al(I) species (Fig. 2).13

Distinct results were obtained in the investigation of multiple insertions of phosphenium ions into P-P bonds of P₄. In this context, solvent-free mixtures of P4, Ph2PCl and GaCl3 in various stoichiometries and at different temperatures were investigated. A 1:1:1 mixture yields quantitatively the Ph₂P₅⁺cage compound 36f[GaCl₄] after 45 min at 60 °C (Scheme 12).⁵¹

The Ph₄P₆²⁺-cage cation 42²⁺ is observed in a mixture of 1:8:5 stoichiometry (P4:Ph2PCl:GaCl3) as the main product after a reaction time of seven hours at 70 °C. The ³¹P NMR spectrum of 42²⁺ shows a characteristic ABMM'XX' spin system which is in accordance with the insertion of a second Ph₂P⁺phosphenium ion into a P-P bond adjacent to the phosphonium



Scheme 12 Stepwise insertion of Ph₂P⁺-phosphenium ions into P-P bonds of P₄ yielding Ph₄P₆²⁺-cage cation 42²⁺ and Ph₃P₇³⁺-cage compound 43[Ga2Cl7]3

moiety in 36f⁺. Two second-order resonances corresponding to an AA'XX'X"X"' spin system are expected for the isomer of 422+ formed via formal insertion into two opposing P-P bonds of P₄. Such a species is not formed in the melt reaction. The formation of dication 42²⁺ can only be observed if the ratio of Ph₂PCl and GaCl₃ is higher than 0.5. In these mixtures, the dominant gallium species is GaCl₄⁻; hence, the melt can be considered as basic medium. In a more Lewis acidic melt, composed of P₄, Ph₂PCl and GaCl₃ in a 1:3:6 stoichiometry, the tricationic Ph₆P₇³⁺-cage 43³⁺ is formed exclusively. Large single crystals of 43³⁺ as a heptachlorodigallate salt are formed in the respective melt after 12 h at 100 °C. Cation 433+ 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 $P_7^{3-,52}$ several polyphosphanes $R_3P_7^{53}$ and many polyphosphorus-chalcogenides like e.g. P₄S₃.⁵⁴ The ³¹P NMR spectrum of 43³⁺ shows an AA'A"BXX'X" spin system resulting from the C_3 symmetry of the cage. A 2J or 3J 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 43³⁺ is stable only in the presence of excess GaCl₃. This prevents the detrimental presence of chloride anions which decompose 433+ by nucleophilic attack and subsequent degradation via 42²⁺ to 36f⁺. This illustrates that the consecutive insertion of up to three Ph₂P⁺-moieties into P-P bonds of P₄ 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 phosphenium 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.⁵⁶ The diphosphadiazenium ion 45⁺ is generated from 44 upon chloride abstraction with GaCl₃. Solutions of 45⁺ are characterized by a bright red colour and the ³¹P NMR spectrum shows a broad resonance at characteristic low field (δ = 242.3 ppm) indicating the formation of a di-coordinated P moiety. Subsequent addition of P4 to this solution leads to discolouration and quantitative formation of the P5+cage compound **46**[GaCl₄].⁵⁷ 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 A₂MVXZ spin system observed in the ³¹P NMR spectrum of $C_{\rm S}$ -symmetric cation 46⁺. Interestingly, the P₅⁺-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 in situ generation of a phosphenium ion upon addition of three equivalents of GaCl₃ to the reaction mixture. The resulting dicationic intermediate

Dipp Dipp
$$|GaCl_4|$$

CI $+GaCl_3$ CI \oplus

Dipp Dipp $|GaCl_4|$
 $+P_4$

Dipp $|GaCl_4|$

Dipp $|GaCl_4|$
 $+P_4$

Dipp $|Ga_2Cl_7|_2$
 $+P_4$
 $+P_4$

Dipp $|Ga_2Cl_7|_2$
 $+P_4$
 $+3 GaCl_3$
 $+P_4$
 $+2 GaCl_3$
 $+P_4$
 $+3 GaCl_3$
 $+P_4$
 $+3 GaCl_3$
 $+P_4$
 $+2 GaCl_3$
 $+P$

Scheme 13 Stepwise synthesis of N_2P_{10} -cage compound $47[Ga_2Cl_7]_2$ via insertion of phosphenium ions generated in situ by the reaction of diphosphadiazane 44 with $GaCl_3$.

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_2MX_2 spin system which is consistent with two C_{2V} -symmtric P_5^+ -cages bridged by two imido-groups. The dication can be isolated as heptachlorodigallate salt $47[Ga_2Cl_7]_2$ 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_2 -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^{2+} , 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 conditions⁵⁸ similar to acyclic, diamino-phosphenium ion (i- P_2N)₂ P^+ (*vide infra*). This indicates that the strained four-membered ring geometry present in diphosphadiazenium ions is crucial for its reactivity towards P_4 .

Other cyclic, four-membered phosphorus containing heterocycles can be employed in reactions with P₄ as well.⁵⁹ The cyclic chlorophosphane **48**, featuring a SiCl₂-backbone,⁶⁰ reacts with GaCl₃ to give the corresponding Lewis acid–base adduct **49** (Scheme 14).

$$\begin{array}{c} \text{SiMe}_3 \\ \text{Cl} \\ \text{SiMe}_3 \\ \text{Cl} \\ \text{SiMe}_3 \\ \text{SiMe}$$

Scheme 14 Preparation of P_5^+ -cage cation $\mathbf{51}^+$ from P_4 , $GaCl_3$ and chlorophosphane $\mathbf{48}$ (top) and preparation of zwitterionic P_5 -cage compound $\mathbf{53}$ from P_4 and zwitterionic phosphenium ion $\mathbf{52}$.

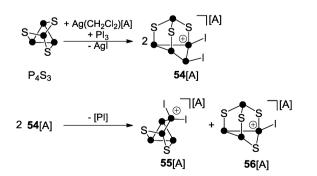
The formation of related phosphenium ion 50⁺ is observed only upon addition of a second equivalent of GaCl3. This can be explained by the suppression of detrimental concentrations of nucleophilic chloride anions through the formation of Ga₂Cl₇⁻.

Cation 50⁺ is not stable in solution and decomposes via Lewis acid mediated Me₃SiCl elimination. However, the insertion reaction with P4 requires only the use of one equivalent of GaCl₃. In 1:1:1 mixtures of 48, GaCl₃ and P₄ the corresponding P₅⁺-cage compound 51[GaCl₄] 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 phosphenium ion 52 features a formally anionic AlCl₂-backbone. 60 It reacts with P₄ in toluene giving the formally neutral P5-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 P4 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 P₄S₃ with in situ generated phosphenium ion PI₂⁺ (Scheme 15). 44b

The phosphenium ion formally inserts into a P-P bond of the basal P₃-ring accompanied by migration of one of the iodosubstituents 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.

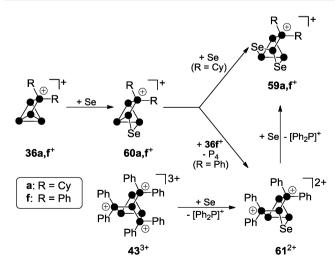


Scheme 15 Reaction of P₄S₃ with in situ generated phosphenium ion PI_2^+ ; A = Al(OC(CF₃)₃)₄.

Scheme 16 Reaction of α -P₄S₃I₂ with Ag(CH₂Cl₂)[A], A = Al(OC(CF₃)₃)₄.

The second protocol is based on halide abstraction from α-P₄S₃I₂ with Ag(CH₂Cl₂)[Al(OC(CF₃)₃)₄] and yields the spirocyclic cage cation 58⁺ (Scheme 16).⁶² The initial step involves the formation of 57^+ via iodide abstraction from α -P₄S₃I₂. Cation 57⁺ subsequently reacts with a second equivalent of α-P₄S₃I₂ and this in association with the formal extrusion of phosphinidene [PI] gives rise to spiro-cyclic 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 R₂P₅⁺-cage compounds 36a[GaCl₄] and 36f[GaCl₄] with elemental grey selenium yield the corresponding polyphosphorus-selenium cages 59a[GaCl₄] and 59f[GaCl₄] (Scheme 17). Both are obtained at elevated temperatures (110–150 °C) following a solvent-free protocol. In some cases,



Scheme 17 Stepwise insertion of selenium atoms into P-P bonds of **36a,f**⁺ and stepwise substitution of [Ph₂P]⁺-moieties in **43**³⁺ by selenium atoms giving the nortricyclane-type polyphosphorus-chalcogen cage cations 59a,f⁺ and 61²⁺

59f⁺ 61²⁺ 43³⁺

Fig. 12 Nortricyclane type molecular structures of the related, polyphosphorus cations **59f**⁺, **61**²⁺ and **43**³⁺.

the addition of one equivalent of $GaCl_3$ 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 $36a_1f^{\dagger}$.

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 C_S-symmetric isotopomer without a ⁷⁷Se nucleus. These resonances are superimposed by the C_1 -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**, \mathbf{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 61²⁺ 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 phosphenium ion Ph₂P⁺, 19,50 this transfer is faster than the insertion of the second selenium atom. Subsequently, one of the [Ph₂P]⁺-moieties of **61**²⁺ is substituted by a selenium atom giving rise to 59f⁺. The formally liberated Ph₂P⁺-phosphenium ion is not stable and reacts with a GaCl₄ anion to give the Lewis acid-base adduct 37 (Ph2PCl-GaCl3). This is in accordance with the observation of only 50% conversion and the quantitative formation of P₄ and 37 or the respective oxidation product Ph₂P(Se)Cl-GaCl₃ in the case of reactions involving **36f**⁺ as a starting material. The targeted preparation of **61**²⁺ as GaCl₄ salt is achieved by utilizing a 2:1 stoichiometry of 36f⁺ and grey selenium. Another synthetic approach for the preparation of 61²⁺ is the targeted substitution of one [Ph₂P]⁺-moiety in

the tricationic cage 43³⁺. This is achieved by reacting 43³⁺ with grey selenium under solvent-free conditions (Scheme 17). Dication 61²⁺ 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 P_7^{3+} -cage 43^{3+} with elemental α -S₈. ⁴⁹ The polyphosphorus cation 43³⁺ and cationic polyphosphorus-chalcogen cages 61²⁺ 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 P₄Se₃. 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 43³⁺, 61²⁺ and 59f⁺, the related sulfur-containing cages 62a⁺ and 63²⁺, and P₄Ch₃ (Ch = Se, S)⁶³ on the number of chalcogen atoms in the corresponding molecules. The stepwise exchange of tetracoordinated P atoms in 433+ 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.63 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. 64 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.65 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.

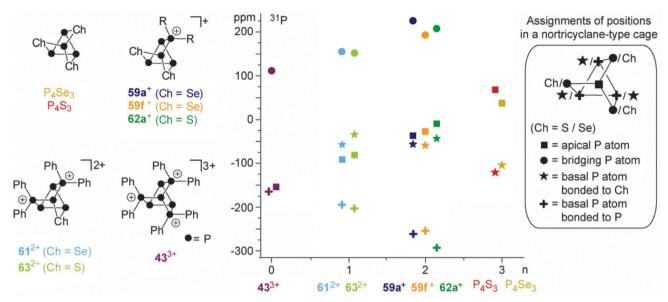


Fig. 13 Family of cationic polyphosphorus-chalcogen cages formally derived from stepwise isolobal exchange of [Ch] by $[R_2P]^+$ units in P_4Ch_3 (Ch = Se, S, left), their ³¹P NMR shifts *versus* the number of chalcogen atoms (n, middle) and the assignment of P or Ch atoms to the positions of a nortricyclane-type cage (right).

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-triphosphirene 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 (Scheme 18). Bertrand and co-workers reacted P_4 with carbenes L^1 and L^3 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 L5.66 This reaction is accompanied by the formation of 67 as a side product. This P_2 -species is formed by the formal [2+2] fragmentation of P_4 by carbene L⁵. A [3+1]-fragmentation of the P₄ tetrahedron was achieved using the sterically less demanding carbene L6 in a reaction with P₄ in a 3:1 stoichiometry. ⁶⁶ The P₁-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 P_3 moiety was indicated in the ^{31}P NMR spectrum of the respective reaction mixture. 66

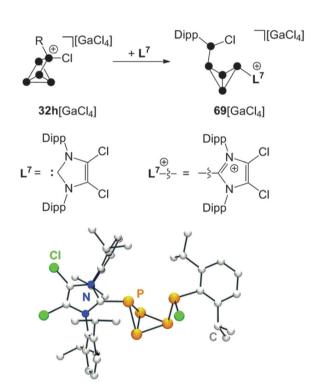
A combination of phosphenium ion and carbene mediated P₄ activation constitutes a novel, potentially versatile approach for the preparation of cationic polyphosphorus cages. This strategy allows for the preparation of polyphosphorus cations

featuring imidazoliumyl-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. The reaction of P5+ cage compound 32h[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 imidazoliumylgroup in an exo-position and a phosphanyl-group in an endoposition. This is reminiscent of the intermediate 31 observed in the formation of RP₅Cl⁺-cages. Cation **69**⁺ features an ACEMX 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 ³/(PP) coupling constant of 244.6 Hz in the ³¹P NMR spectrum.

The reaction of $32h[GaCl_4]$ with carbene L^7 in a 1:3 stoichiometry proceeds *via* a quantitative [3+2]-fragmentation of the P_5^+ -cage (Scheme 20).⁶⁷

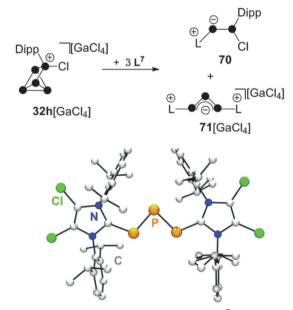
The P_2 fragment was identified as the neutral P_2 species 70 featuring an inversely-polarized⁶⁸ phosphaalkene moiety. The di-coordinated P atom bears a phosphanyl-substituent which originates from the tetra-coordinated P atom of starting material $32h^+$. The P_3 fragment was identified as $GaCl_4^-$ 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

Scheme 18 Carbene-induced transformation and fragmentation reactions of P₄.



Scheme 19 Reaction of 32h[GaCl₄] with carbene L⁷ in a 1:1 stoichiometry (top) and molecular structure of cation 69⁺ (bottom)

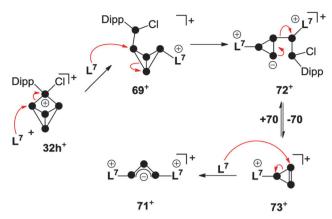
to the classical π -system of the C₃-allyl anion. Thus, 71^+ features a local triphosphaallylanion moiety substituted with imidazoliumylgroups. The mechanism of the [3+2] fragmentation is explained by the reaction sequence in Scheme 21 on the basis of experimental evidence and quantum chemical calculations.⁶⁷ The reaction of 32h⁺ with the first equivalent of L⁷ yields the experimentally verified species 69⁺. The nucleophilic attack of



Scheme 20 Reaction of 32h[GaCl₄] with carbene L⁷ in a 1:3 stoichiometry (top) and molecular structure of cation **71**⁺ (bottom)

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 RP₅Cl⁺-cages (Fig. 7) and is in accordance with the observed reversibility of phosphenium ion insertion into P-P bonds of P_4 (vide infra). The nucleophilic attack of a second carbene L⁷ occurs at the endosubstituted 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



Scheme 21 Reaction sequence for the carbene-induced [3+2]-fragmentation of P_5^+ -cage 32 h^+ .

eliminates the P_2 fragment 70. This yields the elusive triphosphirene derivative 73^+ which is related to the key intermediate C (Fig. 1) of carbene-induced P_4 activation. The nucleophilic attack of a third carbene L^7 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 P_4 and the multitude of carbenes available render this approach suitable for the preparation of a plethora of interesting polyphosphorus compounds.

Abbreviations

- 4 4 ()	A accelia allest amaina a combana
aAAC	Acyclic alkyl amino carbene

Ab Ambiphile

Ch Chalcogen atom (Se or S)

El Electrophile

Et Ethyl

cAAC Cyclic alkyl amino carbene

Cy Cyclo-hexyl

Dipp 2,6-Di-iso-propylphenyl FIA Fluoride ion affinity

HOMO Highest occupied molecular orbital

i-Pr Iso-propyl

LUMO Lowest unoccupied molecular orbital

Me Methyl

Mes* 2,4,6-Tri-*tert*-butylphenyl NHC N-Heterocyclic carbene

Nu Nucleophile

OTf Triflate, trifluoromethylsulfonate

t-Bu *tert*-Butyl

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