Recent highlights in mixed-coordinate oligophosphorus chemistry

Maximilian Donath,† Felix Hennersdorf‡ and Jan J. Weigand*

This review aims to highlight and comprehensively summarize recent developments in the field of mixed-coordinate phosphorus chemistry. Particular attention is focused on the synthetic approaches to compounds containing at least two directly bonded phosphorus atoms in different coordination environments and their unexpected properties that are derived from spectroscopic and crystallographic data. Novel substance classes are discussed in order to supplement previous reviews about mixed-coordinate phosphorus compounds.

Introduction

Phosphorus is an intriguing element with several different bonding modes. The combination of two phosphorus atoms connected to each other multiplies the possibilities to gain compounds with different P–P bonds displaying a great variety of bonding modes. Such compounds have always attracted much attention and a first review in 1965 by Cowley covered the three basic types of substances containing phosphorus–phosphorus single bonds that are derived from classical diphosphanes and their oxidation products.1 In the report of Dillon et al., which appeared in 1995, the field of P–P bonded compounds was re-reviewed.2 A tremendous development was reported and a great variety of combinations of bonding modes including multiple bonds was discussed.3 However, charged and zwitterionic compounds were only considered very briefly. This review is aiming to give an overview of selected main-group compounds containing at least two phosphorus atoms bonded to each other. Those compounds possess different coordination numbers, valence states and/or formal charges. Consciously excluding the wide field of metal-coordinated compounds, this report focuses on certain intriguing examples for most of the substance classes in order to enable recognition of cross relations, recurring trends or properties. To keep the style of an overview, certain known substance classes or specific compounds which have been discussed extensively in the past, will only be commented on briefly. Thus, the more detailed discussions focus on cationic mixed-coordinate phosphorus compounds for which, in the last two decades,
the most rapid development with respect to neutral or anionic compounds was spotted.

Dillon et al. identified 170 hypothetical modes of P–P bonding which exceeds by far the scope of this review. Thus, the P–P bonding of the compounds in this article is classified only by the number of σ-bonds (vide infra). This allows to overcome the problem of categorizing molecules differently due to distinct resonance structures. Secondary consideration of substituent effects often reveals parallels and differences among a class, thus additional subdivisions are made.

The term valency is only used if unambiguous. As an example, the IUPAC definition gives no clear instruction how to correctly entitle the valence state of an RP⁺ cation that can be obtained by either protonation of the parent λ³-phosphane (phosphonium) or by hydride abstraction from the parent λ⁵-phosphate/phosphorane (λ⁵-phosphanylium). The nomenclature of catenated phosphorus compounds following the IUPAC rules is thoroughly described in literature. Crystal structure analysis permits a precise determination of coordination environments and P···P distances allowing a statement on bonding interactions. Appropriate computational calculations often give further insights into the strength of the respective bond. The P–P distance of 2.2 Å in P₄ is often used as a benchmark in order to classify the bonding situation in the title compounds. Although the sum of the van der Waals radii of the P–P bonded framework allows a statement on bonding strength, in cases where a bridging ligand prevents a longer distance. The number of formal charges or extended coordination numbers of the respective phosphorus atoms, but appeared to be of no ultimate proof in certain cases. Table 1 displays selected P–P bonded frameworks with non-symmetrical bonding motifs A–H, J–K and M–O. In contrast to the well-known symmetrical combinations σ²–σ² (diphosphenes) and σ⁴–σ⁴ (diphosphanes), rare examples exhibiting the symmetrical bonding situation I, L and P were included for reasons of completeness. The overall charge of the resulting systems strongly depends on the nature of substituents attached to the P-atoms.

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<th>Table 1</th>
<th>Selected P–P bonded frameworks with non-symmetrical bonding motifs</th>
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<tr>
<td>σ²</td>
<td>A, B, C, D, H, I</td>
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<td>σ³</td>
<td>E, F, J, L, M</td>
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<td>σ⁵</td>
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Δ Rare symmetrical bonding motifs I, L, and P are considered for reasons of completeness. The overall charge of the resulting systems strongly depends on the nature of the substituents attached to the P-atoms.
The discussion in the following section is divided in the combination of the $\sigma$-matrix as depicted in Table 1. Only for the combination of $\sigma^2-\sigma^2$, $\sigma^3-\sigma^3$, $\sigma^4-\sigma^4$, and $\sigma^5-\sigma^5$ a subdivision into classes of related compounds has been included. In general, for compound classes that are derived from related reactions, only one distinct synthetic approach is discussed. Although some of the related compounds have been reviewed in previous articles, we wish to emphasize on certain reactivity patterns, structural features or physico-chemical properties on the base of their connectivity. All drawings of the crystal structures in this contribution were generated from cif-files obtained exclusively from the CSD-Database or Supporting Information provided by the publisher. The ORTEP software was used for illustration.\(^{11}\)

The parent motif of $\sigma^2-\sigma^2$ phosphorus compounds is the well-known diphosphene unit. These compounds are typically intensely orange to red coloured, were first reported by Yoshifujii et al.\(^{12}\) and extensively reviewed elsewhere.\(^{9}\) However, diphosphenes bearing a phosphanido substituent are closely related, but comparable rare and representative examples of the bonding motif A (Table 1) are found in triphosphaallyl derivatives.

**Bonding motif A**

Selected examples of anionic (1\(^{-}\), 2\(^{-}\), 3\(^{-}\), 4\(^{-}\), 5\(^{-}\), and 6\(^{-}\)) derivatives are summarized in Fig. 1. In these compounds the negative charge of the phosphanido moiety experiences resonance stabilization similar to the allyl and pentadienyl systems in carbon chemistry.

The bonding principle in those compounds strongly depends on the substituents of the adjacent phosphorus atoms. Thus, examples 1\(^{-}\), 3\(^{-}\), 4\(^{-}\), 5\(^{-}\), and 6\(^{-}\) are best described by resonance structure I or II, whereas anion 2\(^{-}\) should rather be described by III which resembles a 1,3-dimethylenetriphosphan-2-ide with formal charges on the central phosphorus or on the carbon atoms (Scheme 1). The difference in the electronic structures of these compounds is also reflected in the \(^{31}\)P chemical shifts (Table 2).

The chemical shift of the central, dicoordinate phosphorus atom of ions 1\(^{-}\), 3\(^{-}\), 4\(^{-}\), 5\(^{-}\), and 6\(^{-}\) is typically observed in the region ranging between 500 and 750 ppm significantly low-field shifted compared to the adjacent two phosphorus atoms of which the chemical shift is observed at around 200 ppm (Table 2). Consistent with resonances structure I and II the central di-coordinate phosphorus atom is obviously involved in a normal conjugated allylic system and uses its p-type orbitals for both $\sigma$- and $\pi$-bonding. The s-type electron lone pair of the central phosphorus atom is therefore not available for electrophiles but the adjacent ones are. Thus, the addition of HOTf to a deep green solution of 5[GaCl\(_4\)] instantly yields an orange oil\(^{19}\) and the \(^{31}\)P{\(^1\)H} NMR spectrum reveals resonances of an AMX spin system which is assigned to the cyclo-triphosphanedadium cation 7\(^{2+}\) (Scheme 2).

The protonation of 5\(^{-}\) is reversible and the addition of a base to a solution of 7\(^{2+}\) instantly forms a deep green solution of 5\(^{3+}\). Upon protonation the phosphaallyl anion [\((\text{Bu}_3\text{Si})_2\text{P}^-\)] (3\(^-\)) rearranges quickly to give the related cyclo-triphosphene derivative 8\(^{15}\). The assignment of the resonances of cation 7\(^{2+}\) is achieved by comparison to the \(^{31}\)P NMR parameter of related derivatives 8\(^{15}\) and 9\(^{20}\) (Fig. 2 and Table 3). The chemical shifts of 7\(^{2+}\) are observed in the characteristic range for cyclo-triphosphenes.\(^{21}\) The resonance at highest field is assigned to the hydrogen-substituted P atom consistent with the additional splitting in the \(^{31}\)P NMR spectrum due to the $\bar{J}$(PH) coupling (7\(^{2+}\): $\bar{J}$(PAPX) = 158.8 Hz; compare 9: $\bar{J}$(PAPX) = 137.1 Hz). The substituents on the other two P atoms are in a transoid arrangement. A larger absolute value of the $\bar{J}$(PP) coupling constant between the hydrogen-substituted P atom and the phosphorus atom with the cis-arranged substituent (7\(^{2+}\): $\bar{J}$(PAPM) = 226.6 Hz) contrasts the smaller coupling constant for the trans-arrangement involving the hydrogen-substituted P atom (7\(^{2+}\): $\bar{J}$(PAPX) = 130.4 Hz; compare 8: $\bar{J}$(PAPX) = 141.3 Hz; 9: $\bar{J}$(PAPM) = 144.1 Hz). A similar trend is observed for the $\bar{J}$(PH) coupling constants. Large values indicate a cis-arrangement of the hydrogen atom at P\(_x\) and the lone pair of electrons at the adjacent P atom (7\(^{2+}\): $\bar{J}$(PAPX) = 34.2 Hz; 8: $\bar{J}$(PAPX) = 16.6 Hz), whereas small values indicate a trans-arrangement (7\(^{2+}\): $\bar{J}$(PAPX) = 17.8 Hz; 8: $\bar{J}$(PAPX) = 6.9 Hz).

The fact that the protonation of 1\(^{-}\) leads to the formation of the open-chain phosphanylphosphene Mes*PH–P = P–Mes* instead of a cyclo-triphosphene underlines the great dependence of the substituents on the electronic structure of triphosphaallyl compounds.\(^{11\text{d}}\) A totally different reaction outcome is found upon protonation of anion 2\(^{-}\) which is in agreement with the different resonance stabilization. According to III (Scheme 1) protonation should occur at the central phosphorus or the...
carbon atoms. Thermolysis of $2^-$ in DME in the presence of traces of moisture led to the formation of the rearranged reaction product 10 suggesting the intermediate 11 with a protonated carbon atom (Scheme 3).

The difference in the electronic structure of $2^-$ is evident in the reversed $^{31}{P}$ NMR data. Thus, the more shielded phosphorus atom is now observed at 295.5 ppm and the resonance for the adjacent phosphorus atoms is observed at significantly lower field at 494.1 ppm. The $J(PP)$ coupling constant of 430 Hz is only slightly affected but in accordance with a significant structural change of the $P_3$ bonded system. For triphosphaallyl ions $1^-$, $3^-$, $4^-$, $5^-$ and $6^-$ a significantly shortened P–P bond length (<2.1 Å) is observed indicating partial double-bond character as expected for an allyl system. In comparison, the P–P bond length is significantly elongated (2.137(1) Å) in the case of anion $2^{2-}$. The other bonding parameters display the expected values for those compounds and the large deviations of the P–P–P angle ranging from 87–105° are best explained by the very soft bending potential of the $P_3$-fragment. Unfortunately, for most of the compounds UV/VIS spectroscopic data is not available and only the observed colour in solution is reported (Table 2). The UV/VIS spectrum of the deep-green compound $5[GaCl_4]$ in C$_6$H$_5$F shows two absorption bands of which the strongest band ($I_{max}$) is observed at 696 nm corresponding to an n → π* transition. The second absorption maximum at 443 nm can be assigned to a π → π* transition. The related cation $6^+$, dissolved in THF, shows the corresponding absorption bands at 666 nm and 434 nm, respectively. The reduction of $6^+$ into its corresponding neutral radical species $12$ was achieved by reacting the cation with an excess of magnesium (Scheme 4).

Closely related to these triphosphaallyl systems are the cyclopentadienide related 1,2,3-triphospholides. Although first described already in 1990, the isolation of the non-coordinate parent compound [Pn$_3$C$_3$R$_3$] (Pn = P, As; 13) and its arsa-analogue was achieved only recently by Goicoechea et al. The related cations $6^+$ are obtained from the reaction of heptapnictide trianions [Pn$_7$]$^{3-}$ (Pn = P, As)$^{23}$ or the monoprotonated derivatives [HPn$_7$]$^{2-}$ with alkynes in dimethylformamide in the presence of a cation sequestering ligand like 2,2,2-crypt or 18-crown-6 (Scheme 5).

Noteworthy is that the electronic structures of these “carbon-copy” ligands possess notable differences in comparison to...
Another example related to bonding motif B

Scheme 5 L2,3-Tripinctoaloids 13 formed by the reaction of heptaphosphanides and alkynes.

cyclopentadiene ligands and derivatives thereof. They generally possess greater $\pi$-acceptor character than [Cp] ligands which allows for the stabilization of complexes of electron-rich metal centres. The presence of Lewis basic sites on the phospholide ring allows for multiple coordination modes and the formation of multimetalic molecules and supramolecular systems.25

catena-Tetraphosphene dianions of the general formula [R–P4PPP–R]2– may be described as doubly phosphanido substituted diphosphenes and are therefore related to the triphosphaallyl ions. The supersilyl-bearing (R = 3′Bu3Si) alkali salts26 as well as the terphenyl substituted thallium analogue17 (R = C6H3-2,6-(C6H2-2,6-iPr2)2) were isolated and characterized. The bond lengths compare well to [Li(dime)],22 (Fig. 1). All 31P chemical shifts are shifted to higher field. The alkali salts show highfield shifted resonances at 390–420 and $-$53 to 19 ppm for the inner and outer phosphorus atoms, respectively. The 31P NMR shifts of the thallium complex (285/180 ppm) could not be assigned.

Phosphanyl-substituted diphosphenes such as 14 represent another example related to bonding motif A and were first reported by Romanenko et al.28 The treatment of amino-substituted diphosphene 15 with triflic acid (Scheme 6) eliminates [3′Bu3SiNH]OTf accompanied by the in situ formation of the highly reactive phosphorus-analogue of a diazonium ion 16+$^+$ which, due to its high reactivity, is not stable even at $-$78 °C and forms bicycle[1.1.0]tetraphosphanes besides unidentified products.

In the presence of a tert-phosphate such as PPh3, the adduct 17+$^+$ (R = R' = Ph) is formed with a $\sigma^2$–$\sigma^2$–$\sigma^4$ connectivity of the P$_2$ backbone representing an example of bonding motif F (vide infra). The formation of 17+$^+$ was confirmed by X-ray structure analysis and the obtained P–P bonding parameters of 2.025(1) Å and 2.206(1) Å are in the range of a double and a single bond, respectively. Employing a sec-phosphate such as Bu$_3$PH in the reaction with 16+$^+$, the initially formed cation 17b+$^+$ slowly liberates HOTf to give the first example of a $\sigma^2$–$\sigma^2$–$\sigma^4$ triphosphene 14 as an example of bonding motif B (vide infra).28,29

Scheme 6 Protonation of 15 in the presence of phosphanes leading to $\sigma^2$–$\sigma^2$–$\sigma^4$.27 and $\sigma^2$–$\sigma^2$–$\sigma^4$-compounds 14 formally via 16+$^+$. Scheme simplified for clarity reason.

Recently, Grützmacher et al. reported on the synthesis of three polarized, cationic diphosphenes 18a–c.30 Independently, a fourth derivative was also reported by our group.31 The synthesis of the precursor compound 19a–d, which belongs to bonding motif B, was achieved by two distinctly different synthetic strategies (Scheme 7). The group of Grützmacher followed the approach of DABCO (1,4-diazabicyclo[2.2.2]octane) assisted condensation of the parent phosphinidene carbene adduct 20 with chlorophosphanes to synthesize 19a–c. Our group used the NHC induced [3+2] fragmentation reaction of the P$_5$-cage cation 21a+$^+$ (bonding motif J, vide infra) yielding the triphosphaallyl compound 5+$^+$ as P$_2$-fragment (vide supra) besides the P$_2$-fragment 19d.$^+$. The subsequent chloride abstraction from all four derivatives 19a–d+$^+$ by GaCl leads to the formation of the polarized, cationic diphosphenes 18a–d+$^+$.

The derivatives 18a,c+$^+$ with smaller residues on the phosphonium-type side prevent their isolation but enable dimerization to form dicationic cyclo-tetraphosphanes 22a,c+$^+$ (Scheme 8, left) demonstrating the diphosphanic-type reactivity. In contrast, the electrophilicity of the R-substituted P atom can be demonstrated by treatment of 18d+$^+$ with PMe$_3$, yielding the unique $\sigma^2$–$\sigma^2$–$\sigma^4$ species 23+$^+$ (Scheme 8, right) incorporating both bonding motif B and J (vide infra). The product may be depicted in another resonance structure including a phosphalkene moiety, but a dihedral N–C–P–P angle of 50.5(3)$^+$ suggests a preference of the phosphane structure. This is
supported by quantum chemical calculations indicating a negative charge on the phosphane P atom. The distance between the di- and tetracoordinate phosphorus atom is at 3.478(1) Å slightly below the edge of the sum of the van der Waals radii.

Three bonding motifs can be described connecting a di- and a tricoordinate phosphorus atom of which examples are already reported. They comprise alkylidene diphosphanes or phosphanylpophsaalkenes and related heteroatom-substituted derivatives of the general bonding motif B as well as diphosphen-1-ium C and diphosphan-1-ide D ions.

**Bonding motif B**

As compounds with bonding motif B are known for more than two to three decades and have been reviewed earlier, we only want to comment shortly on selected examples depicted in Fig. 3.

In 1990 Niecke et al. reported on the 1-phosphanyldiaza-phosphene 24 produced by a base-catalysed elimination of Me3SiCl from the corresponding phosphane. The amino group at the nitrogen atom lengthens the P–N double bond, whereas the phosphanyl group at phosphorus itself exerts only negligible changes on the P–N bond. In this example the phosphanyl group acts as a σ-donor and the amino group simultaneously as a σ-acceptor and a π-donor. As a consequence, both substituents at the P–N double bond refer to the case of σ-push pull substitution and enforce enhanced lengthening of the P–N double bond.

Du Mont et al. investigated the reactions of the P-phosphanyl phosphaalkene 25 at its P=C and P-P bonds (Scheme 9). The reactions at the P=C bond with 2,3-dimethylbutadiene or cyclopentadiene lead to the respective [4+2] cycloaddition products 26 and 27 which is a typical reactivity shown by phosphaalkenes. In the case of 27 also the Retro–Diels–Alder reaction could be observed at elevated temperatures. They reported that the main reaction in the oxidation of 25 with chalcogens E (E = S, Se) is the cleavage of the P–P bond to give 28 which is subsequently oxidized to 29.

In the reaction of 25 with trichlorosilytrimethylgermane (Me3GeSiCl3) they observed an unusual P–C bond cleavage accompanied by a double dichlorosilylene (SiCl2) transfer, which represented an important contribution to the chemistry of stable Group 14 carbene analogues. The trichlorosilytrimethylgermane represents a versatile reagent for the transfer of SiCl3 moieties to P-phosphanyl phosphaalkenes under very mild conditions.

**Bonding motif C**

The first phosphanylphosphenium ion 30a+ was obtained as triflate salt by Grützmacher et al. from the reaction of diphosphen 31a (R = 2Bu) with a 35-fold excess of MeOTf in CH2Cl2 as solvent (Scheme 10).

The same reaction with the very electron deficient diphosphene 31b (R = CF3) does not form the related cation 30b+ (R = CF3) even in boiling, neat methyl triflate. However, the methylation succeeds in liquid SO2 with very strong methylation reagents of the type K[CHB11Me5X6] (R = Me, Et, iPr; X = Cl, Br) introduced by Reed et al. (Scheme 10). This class of potent electrophilic “R+” alkylating agents uses the weakly nucleophilic carborane anions [CHB11Me5X6]− (X = Cl, Br) as leaving groups. In this way the Reed group managed to transform alkanes into carbenium ions via hydrate abstraction below room temperature or to methyldene electron deficient phosphorus compounds that are otherwise inert to conventional alkylating agents such as methyl triflate. The mixture of Me[CHB11Me5Br6] and diphosphen 31b (R = CF3) in SO2 was studied by NMR-spectroscopy revealing an AX spin system of 30b+ with chemical shifts at 260 and 279 ppm, typical for the tri- and diaordinate phosphorus atoms,
respectively and significantly upfield shifted compared to diphosphanes that typically display resonances at very low field (e.g. 31a (R = 'Bu); δ = 495 ppm). The large coupling constant of \(^1\)J(PP) = 610 Hz confirms the direct connectivity. Similar values have been obtained for 30a\(^+\). Although 30a[OTf] is extremely sensitive in nonpolar solvents and decomposes readily in solution, they succeeded to obtain crystals suitable for X-ray diffraction. The methylation of 31a (P–P bond length: 2.034(2) Å) does not significantly affect the P–P bond length in cation 30a\(^+\) (2.024(2) Å). Attempts to deprotonate cation 30a\(^+\) with Et\(_2\)NH as a base did not yield the expected ylide but resulted in the formation of the diphosphirane 32 (Scheme 11). The targeted product would have been well comparable to both bis(alkylidene)-phosphoranes and bis(imino)phosphoranes. For those compound classes a thermally sensitive, conrotatory electrocyclic reaction according to the Woodward–Hoffmann rules has been suggested earlier on the base of theoretical and experimental results.\(^{37}\)

**Bonding motif D**

Phosphoranes and bis(phosphanyl)imidophosphoranes that typically display resonances at very low field (e.g. 31a (R = 'Bu); δ = 495 ppm). The large coupling constant of \(^1\)J(PP) = 610 Hz confirms the direct connectivity. Similar values have been obtained for 30a\(^+\). Although 30a[OTf] is extremely sensitive in nonpolar solvents and decomposes readily in solution, they succeeded to obtain crystals suitable for X-ray diffraction. The methylation of 31a (P–P bond length: 2.034(2) Å) does not significantly affect the P–P bond length in cation 30a\(^+\) (2.024(2) Å). Attempts to deprotonate cation 30a\(^+\) with Et\(_2\)NH as a base did not yield the expected ylide but resulted in the formation of the diphosphirane 32 (Scheme 11). The targeted product would have been well comparable to both bis(alkylidene)-phosphoranes and bis(imino)phosphoranes. For those compound classes a thermally sensitive, conrotatory electrocyclic reaction according to the Woodward–Hoffmann rules has been suggested earlier on the base of theoretical and experimental results.\(^{37}\)

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**Selected examples of protonated oligophosphides.**

![Selected examples of protonated oligophosphides.](image)

**Fig. 4**

The degradation and aggregation pathways of white phosphorus in the presence of nucleophiles are of unquestionable complexity. Therefore, the underlying mechanisms, in which the phosphanyl-phosphane motif also plays a key role, continue to attract attention which has led to numerous publications in the last decades. Parts of the interrelations between substituted oligophosphides, their reactivity and the mechanisms of their formation have been investigated employing e.g. bulky silanides and have been discussed elsewhere.\(^{43}\)

Fritz et al. synthesized a series of bis-phosphanyl substituted lithium phosphanides 33a–d by treatment of the parent silyl phosphanes 34a–d with n-butyl lithium (Scheme 12).\(^{44}\) Interestingly, in the solid state, the lithium ion is not coordinated to the negatively charged phosphorus atom itself, but chelated by the two adjacent phosphane moieties instead. Several related acyclic and cyclic anions of the form [P(PR\(_2\))\(_n\)]\(^-\) are known and comprehensively discussed in the review by Macdonald et al.\(^{9}\)

Tetraphosphane-1,4-diides represent another interesting substance class described by bonding motif D. Their solid state structures usually comprise mono- or dimeric ion-contact complexes.\(^{45}\) Fig. 5 depicts the tetraphosphane-1,4-diide [Na(solv)]\(_2\)[34] as representative example, showing the characteristic M\(_2\)P\(_4\) arrangement found in solid state structures of bis(alkali metal)catena-oligophosphane-\(\alpha,\omega\)-diides [M\(_2\)(solv)]\(_2\)[(R,P)]

![Scheme 12](image)

**Scheme 12** Upon treatment with 'BuLi the silylated triphosphanes 34a–d form bis-phosphanyl substituted lithium phosphanides 33a–d.
The sodium ions of \([\text{Na(solv)}]_2\) can be sequestered by 2,2,2-crypt. In solution the product splits into two radical anions \([\text{[35]}}^2\)–, and only one resonance structure of \([\text{[35]}}^2\)– shown.

\[
\begin{align*}
\text{[Na(solv)]}_2 & \rightarrow \text{2 [Na(2,2,2-crypt)]}^+ \\
\text{excess 2,2,2-crypt} & \rightarrow \text{NaOTf}
\end{align*}
\]

Scheme 13 The sodium ions of \([\text{Na(solv)}]_2\) can be sequestered by 2,2,2-crypt. In solution the product splits into two radical anions \([\text{[35]}}^2\)–. Only one resonance structure of \([\text{[35]}}^2\)– shown.

The two bonding motifs E and F describe the connectivity of di- and tetracoordinate phosphorus atoms.

\[
\sigma^2-\sigma^4
\]

Bonding motif E

Bonding motif E comprises a large variety of zwitterionic phosphonophosphanides. They represent the phosphorus analogues of allyldiene-\(\sigma^4\)-phosphoranes or Wittig reagents and are thus called phosphanyldiene-\(\sigma^4\)-phosphoranes or Phospha-Wittig reagents in this context. Compounds of type E have already been known for more than a half century and were first described as the donor stabilized Me3PCF3 adduct (36a) resulting from the reaction of PMe3 and cyclic (PCF3)n (n \(=\) 4, 5; Scheme 14).\(^{47}\) Only very few examples are known (e.g. 36b,c (b: R \(=\) Mes, c: R \(=\) Mes*)) \(^{48}\) and synthetically accessible in their free form (Fig. 6). They are mainly obtained as transition metal-stabilized compounds \(\text{[L}_n\text{M=}\text{P}(\text{R})\text{P}_3]\), which are employed for \(\text{P=}\text{C}\) bond formation alternatively to terminal phosphinidene complexes \(\text{R}–\text{P} = \text{ML}_{16}\) (for reviews see ref. 25b, c and 52a–f; for a recent example of reversible phosphinidene transfer to triarylpshosphate see ref. 52g).

The known free phosphanyldiene-\(\sigma^4\)-phosphoranes have received only little attention so far, due to their high reactivity. Their isolation requires sterically demanding or electron withdrawing substituents at the \(\sigma^2\)-phosphorus moiety in order to stabilize them kinetically and prevent di- or oligomerization.\(^{48,51}\) The \(\text{peri}\)-substituted compound 39 is sterically less encumbered than previous examples. Similar to the BH3 adduct 40, which is obtained from the reaction of 36a with BH3 in Et2O (Scheme 14),

\[
\begin{align*}
\text{[PCF}_3\text{h}]_n & \rightarrow \text{PMe}_3 \\
\text{PMMe}_3 & \rightarrow \text{H}_2\text{BH}_3
\end{align*}
\]

Scheme 14 Dealigomeration of cyclo-phosphanes to phosphanyliden-\(\sigma^4\)-phosphorane 36a and subsequent bis-borane adduct formation.

Fig. 6 Examples of zwitterionic phosphonophosphanides comprising bonding motif E.
the bis-borane adduct 39 2BH₃ was isolated and fully characterized. It has been stated that steric rather than electronic properties are the limiting factor for the accessibility of the second lone-pair of electrons for coordination.¹⁵ A follow-up study on the coordination behaviour of 39 towards several transition metals, as well as on the oxidation products obtained by treatment with chalcogens is described elsewhere.⁵⁴

Phosphanides bearing two adjacent phosphonio moieties are related to carbodiphosphoranes and cover triphosphonium cations and phospha-derivatives of cyclo-phosphazenes as their cyclic congeners. Cyclic triphosphonium cations 41a,b⁺ with 5- or 6-membered rings are typically obtained from the reaction of an appropriate chelating bisphosphane ligand (e.g. a: dppe; b: dppp) and PX₃ (X = Cl, Br, I; Scheme 15).⁹,⁵⁵

Although they were first reported by Fluck, extensive contributions to this field have been made by Schmidpeter, Dillon, Ragogna, Macdonald and others.⁹,⁵⁶ Currently, triphosphonium ions are a topic of great interest as they serve as both, potential two- or four-electron donor ligands in transition metal complexes⁵⁷ and as source of P⁺. Especially the latter allows for the synthesis of fused tricyclic 2-phosphaallylic cations such as 42⁺ which are derived from a convenient one-pot reaction of chelating bis-NHC (R = Me, Br,¹⁰Bu) and [41a]Br (Scheme 16). Calculations confirm that these species are best considered as carbene-ligated P(II) ions.⁵⁸

Cyclic triphosphonium cations are very poor ligands and there are several arguments explaining why there is only a moderate number of metal complexes.⁵⁷ Besides the positive charge lowering the frontier orbital energy, the accompanying anion may interfere in the complex formation. Furthermore, π-backbonding from the central phosphorus atom to the adjacent phosphonio moieties lowers the HOMO energy and therefore restrains coordination. Although metal complexes with cationic triphosphium ions have been detected in solution, their low stability has so far precluded their isolation.⁵⁷a,⁵⁹ Ragogna et al. succeeded to synthesize appropriate ligands by introducing a bridging borate moiety into the backbone to give zwitterionic derivatives 43a,b (a: R = Ph, b: R = Pr). These ligands can undergo coordination to several transition metals as either two- or four-electron bridging donor to give stable and soluble neutral complexes (e.g. [AuCl(43a)], [AuCl₂(µ-43a)], [Co(CO)₃]₂(µ-43a); Fig. 7).⁵⁷b

The bromide salts proved to be suitable precursors for metathesis reactions. Accordingly, formation of phosphorus-rich oligomers by P⁺-transfer is observed when triphosphonium cation 41a⁺ is treated with LiN[P(Ph₂)₂]. The release of dppe accompanies the formation of the known compound 44,⁶⁰ however, in a much better yield.⁶¹ Reacting 41a[Br] with NaN[PiPr₂]₂ gives compound 45 in which two five-membered rings are linked via two phosphorus atoms. The mechanism of formation is unclear for both cases, however, their structural arrangement is confirmed by crystal structure analysis (Scheme 17).

The readily available Janus-head type diphosphorus compound 46[OTf] (pyr = 3,5-dimethylpyrazolyl) is an attractive precursor for the construction of cationic ring and cage systems.⁴⁸,⁶² The stepwise reaction of 46[OTf] with Cy₂PH gives the two novel cationic polyphosphorus frameworks [Cy₄P₉pyr]⁺ (47⁺) and [Cy₄P₂]⁺ (48⁺) as well as 49[OTf] as one of the isolated side-products (Scheme 18).⁶³ Cations 47⁺ and 48⁺ (Fig. 8) feature di-, tri- and tetracoordinate phosphorus atoms derived from P₁-synthons via a one-pot multiple P–P bond formation and represent the
first examples of a $\sigma^2\sigma^4\pi^1$ bonding motif. In this reaction eight P-P bonds are formed by a combination of substitution and unprecedented base-induced reductive coupling steps to yield unusual cationic polyphosphorus compounds. The synthesis of these cations is an example of the distinct reactivity of phosphorus-centred cations compared to neutral and anionic phosphorus compounds.62

**Bonding motif F**

The main difference between bonding motif E and F is the $\pi$-acceptor ability of the substituent $X$ relative to the phosphonium moiety (Fig. 9). This results in a different bond order or degree of $\pi$-(back)bonding of the dicoordinate phosphorus atom to the two substituents. From our point of view there is a continuous transition of $\pi$-(back)bonding predominantly to the phosphonium moiety (e.g. phosphanyliden-$\sigma^4$-phosphoranes) to equal $\pi$-(back)-bonding to both moieties (e.g. triphosphinen-compounds) (both bonding motif E). In compounds described by bonding motif F the $\pi$-(back)bonding is predominantly to the other substituent $X$ and can mainly be described as genuine double bond.

A typical representative of bonding motif F was synthesized by Niecke et al. already in 1994. The phosphonio-phosphaalkene or triphenylphosphine stabilized methylenediylphosphonium ion 50 as tetrachloroaluminate salt 50(AlCl4) remains unchanged in solution, whereas 50(OTf) decomposes quantitatively into phosphaalkyne 51 under elimination of Me3SiOTf and PPh3 (Scheme 19). A reaction proceeding in the reverse manner has been reported in which the phosphonio-phosphaalkene 52+ is formed by a 1,2-addition reaction of [HPPPh3][OTf] to the bulky adamantyl-substituted phosphaalkyne 53. Further reactions of phosphaalkynes leading to comparable derivatives comprising bonding motif F are described elsewhere.66

The cation 17a+ which also comprises bonding motif F was already discussed in the context of bonding motif B. The regular P-P double (2.025(1) Å) and single bond (2.206(1) Å) of 17a+ allow a clear categorization. A formal substitution of the carbon bonded phosphorus atom by nitrogen leads to the cation 54+ which was described as the triphenylphosphane adduct of an imino-phosphonium or phosphadiazonium ion. This compound is especially intriguing, since a classification of the bonding motif is not straightforward. In fact, on the one hand, 54+ is valence isoelectronic to cations 17a+ and 52+ which, due to a regular P-C or P-P double bond, clearly belong to bonding motif F. On the other hand, the P-N $\pi$-interaction to the Mes*N-moiety as X-substituent exceeds a bond order of two and is therefore much stronger than in examples belonging to bonding motif E or F.

In order to understand the bonding situation in 54+ we first want to discuss the phosphadiazonium ion (Mes*PN)+ which can be described by a set of resonance structures I–III (Scheme 20). Although it was frequently described as a cation with a $\sigma^1$ phosphorus atom (I), this is certainly only the case with a weakly coordinating anion and in the absence of donors. Actually, the bonding environment of the phosphorus atom in Mes*NPX derivatives shows a great flexibility depending on the substituent $X$. This is achieved by a possible rehybridization of the nitrogen atom from sp$^3$ in well-stabilized sp in poorly stabilized (Mes*NPN)+ derivatives. Mes*NPCI is best described as covalent chlorimorphosene (II) with a $\sigma^2$ P atom and a slightly elongated P-Cl single bond (2.142(4) Å). The P-N distance is rather short (1.495(4) Å) and the P-N-C angle (154.8(4)°) is much larger than expected for an sp$^3$-imine, thus indicating a starting transition to an iminosphosphonium ion.67 If X is a weakly coordinating anion such as [AlCl4]$^-$ the P-N distance...
(1.475(8) Å) is only slightly shortened, but the P–N–C angle (177.0(7)°) is widened to almost 180° suggesting sp-hybridization of nitrogen. Additionally, two P–Cl contacts (3.16 and 3.27 Å) shorter than the sum of the van der Waals radii (~3.55 Å)² are observed.⁶⁷ Also the triflate derivative 55[OTf] shows a short P–N bond length (1.467(4) Å) and an almost linear environment at the nitrogen atom (P–N–C: 176.4(3)°). Despite a P–O distance of 1.923(3) Å that is much closer to a P–O single bond (~1.6 Å) than to the sum of the van der Waals radii (~3.3 Å),⁷ the large P–N–C angle reflects an efficient stabilization of the phosphorus atom by the Mes*N-moiety (II).⁶⁸

Returning to compound 54[OTf], which is obtained by addition of PPh₃ to 55[OTf], the crystal structure comprises a central σ³ phosphorus atom which adopts a distorted trigonal pyramidal geometry (Scheme 21 and Fig. 10).⁶⁹ The P–P bond length (2.625 Å) corresponds to a long single bond and the P–O distance to the coordinate triflate anion (2.298 Å) is roughly 0.4 Å longer than in 55[OTf] but still closer to a P–O single bond than to the sum of the van der Waals radii. The P–N bond (1.486(4) Å) is slightly longer and the P–N–C angle (169.5(4)°) more acute compared to 55[OTf]. This may be rationalized by a more effective stabilization of the central phosphorus atom by PPh₃ as additional donor ligand. Therefore, the solid state structure of 54[OTf] might best be described by resonance structures II and III. Interestingly, in solution the P–P bond is obviously not preserved as there was found no evidence of P–P coupling in 54[OTf]. In contrast, the weaker coordinating anion [AlCl₄]⁻ in 54[AlCl₄] effects a stronger fixation of the PPh₃ substituent and allows the observation of two doublets in the ³¹P NMR spectrum (δ(NP) = 87 ppm, δ(PPh₃) = 22 ppm, J[PP] = 340 Hz).⁷⁰

A similar compound, in which the P–P bonds are maintained in solution is obtained by the addition of the bidentate ligand dppe to 55[OTf] yielding 56[OTf] (Scheme 21 and Fig. 11).⁷¹ The triflate anion is liberated and, in this case, non-coordinating, whereas two long P–P bonds are formed to the central σ³ P atom (2.5708(9) Å and 2.5392(9) Å). A low temperature NMR study at −80 °C revealed that the P–P bonds also remain unequal in solution (δ(NP) = 36 ppm, δ(dppe1) = 10.2 ppm, J[PP] = 492 Hz, δ(dppe2) = 10.3 ppm, J[PP] = 419 Hz). The coordination environment at the distorted trigonal pyramidal P atom may be rationalized by the occupied π⁺ and π⁻ orbitals of nitrogen overlapping the σ⁺ orbitals of the P–P bonds, thus elongating them, but shortening the P–N bond (1.489(1) Å) and facilitating an effective sp-hybridization of the nitrogen atom (P–N–C: 179.3(7)°) (Fig. 11, right).

From our point of view 54 and 56 mark the transition zone to phospane stabilized phosphonium or phosphanylphosphonium ions which belong to bonding motif J (vide infra).

**Bonding motif G**

Examples of a dicoordinate phosphorus atom adjacent to a pentacoordinate phosphorus atom are very rare. We believe that up to date only two examples are reported of which one was proven its structural connectivity by X-ray diffraction analysis. In order to stabilize such an unusual bonding situation the dicoordinate phosphorus atom is required to be comparably electron poor. Regitz et al. treated the tetracyclic phosphanyl-phosphaalkene cage compound 57 with o-chloranil. Instead of the expected [4+2] cycloaddition reaction with the P=C double bond, they observed the oxidative addition to the σ⁶ phosphorus atom to give compound 58 (Scheme 22). The phosphaalkene moiety occupies an equatorial position and
the P–P bond length of 2.239(1) Å clearly indicates a regular P–P single bond (Fig. 12). 72

Treatment of silylated phosphaalkene 59 with the chlorobis(catecholato)phosphorane 60 yields another example of a compound (61) which features the rare σ^2–σ^5 bonding motif G. The reaction is accompanied by the formation of two eq. of Me_3SiCl and the product can be obtained in 80% yield after recrystallization (Scheme 23). Characterization of this compound included NMR, IR and elemental analysis.73 Evidence of the structural arrangement was recently supported by a computational study of the same group on the mechanism of formation. They suggest a three step mechanism for the formation of the first experimentally observable intermediate, in which the P–P bond is already established, but the Si–O bond is still intact. The P–C bond is found to be in slightly disfavoured (8.9 kJ mol⁻¹) E-configuration.74

σ^3–σ^4

Apart from diphosphanes, which are the most prominent representatives of σ^3–σ^4 phosphorus compounds, two other possibilities to connect two σ^3 phosphorus atoms can be described by bonding modes H and I.

Bonding motif H

This substance class contains compounds in which a phosphanyl moiety is linked to a σ^4 phosphorane. Predominantly in the early 1990’s phosphanyl-bis(imino)phosphoranes and phosphanyl-bis(alkylidene)phosphoranes have been studied and discussed elsewhere.37 a, b, 75

Bonding motif I

To the best of our knowledge, only once such a dication has been synthesized and characterized.76 Recognizing the relationship to the aforementioned σ^3–σ^4 phosphophosphonium ions (bonding motif C) and the difficulties in accessing them, the necessity to employ a weakly coordinating anion such as [Al(OR)₄]⁻ (R⁺ = C(CF₃)₃) seems obvious. The red dication 62^2⁺ was obtained from the parent diphosphane 63 by two single electron oxidation steps with Ag[Al(OR)₄] via the radical monocation (trip = 2,4,6-trisopropylphenyl; Scheme 24). The ³¹P NMR resonance at 168.8 ppm is shifted to even higher field than that of the related phosphophosphonium ions (30¹). The P–P bond length of 2.021(2) Å and the planar geometry in the crystal structure indicate a regular double bond (Fig. 13).

σ^3–σ^4

Bonding motif J

The category of the σ^3–σ^4 bonding motif J comprises neutral derivatives and a large variety of cations. The group of neutral derivatives (Fig. 14) includes the diphosphane monochalcogenides 64a (E = O, S). Although not many examples have appeared in the literature so far, they are of interest as flame retardants.77 The applicability of the well-known diphosphane monooxides R_2P(O)–PR_2 (64a; E = O)1,2 is somehow restricted by their lability towards moisture and oxygen. The tautom on of these oxides are di(phosphanyl) oxides or anhydrides of phosphinous acids, R_2P–O–PR_2 (64b; E = O) which are in most cases less stable than the corresponding diphosphane monoxides (46a). For compounds with alkoxy- (OR) and aminosubstituents (NR₂) or mixtures of both equilibria between 64a and 64b are observed in certain.
cases depending also on steric demand. However, it has been shown that the introduction of strongly electron-withdrawing substituents such as fluoride, trifluoromethyl- or 2,4-bis(trifluoromethyl)phenyl- groups stabilize the anhydrides of the phosphinous acids. The bis(trifluoromethyl)phosphanyl oxide, is stable with respect to its corresponding phosphate oxide tautomer, however, it degrades readily on contact with air. Hoge et al. succeeded to synthesize and crystallographically characterize the derivative, but also observed small quantities of the isomeric diphenylphosphine monoxide in the reaction, identified by its characteristic resonance in the P NMR spectrum at ppm for the trivalent phosphorus atom (δ = 105.6 ppm). The stability of is improved for the heavier congeners with E = S or Se, however, large scale syntheses of these compounds in high purity are currently not available. Reported syntheses that are not suitable on an industrial scale involve desulfurization of phosphine oxides.89 or comproportionation reactions of the anhydrides of the phosphinous acids.81 The bis(bis(trifluoromethyl)phosphanyl) oxide, is stable with respect to its corresponding phosphate oxide tautomer, however, it degrades readily on contact with air. Hoge et al. succeeded to synthesize and crystallographically characterize the derivative in the reaction, identified by its characteristic resonance in the P NMR spectrum at 39 ppm for the oxygen-bonded phosphorus atom and 2.25 Å in the cyclic dication is indicated by geometry and.86 To the best of our knowledge, synthetic protocols for diphenylphosphines monoselenides (64a; E = Se) and tellurides (64a; E = Te) are unreported. Only very few derivatives (R = Bu, ) of di(phosphanyl) selenides (64b; E = Se) and even fewer tellurides (64b; E = Te) are reported and prepared in a similar manner to the sulfur derivatives or via persistent phosphanyl radicals.87

Iminophosphoranes have found applications in organic synthesis or as ligands in transition metal complexes. However, the chemistry of the related iminodiphenylphosphines of the general structure is only scarcely developed. They are isoelectronic to the diphenylphosphino monochalcogenides and are also tautomers of the more commonly encountered di(phosphanyl)amines with an Ph–NR–PR2 skeleton. Similar to the rearrangement of to a transformation of compounds of type to has been shown to take place upon coordination to transition metals.

The oxidation of cyclo-phosphines with chalcogens leads to the formation of product mixtures, as exemplified in the reaction of with a deficiency of selenium in which one or two [PPh] units of the cyclo-phosphane are formally replaced by Se atoms. The oxidation of with chalcogens showed that the two antipodal CH units of the starting material provide structural braces that allow dichalcogenation to occur without disruption of the six-membered C2P4 ring giving dichalcogenated derivatives such as the 2,5-isomers.

calculation for the 2,5-chalcogenated derivatives (E = S, Se) and the corresponding radical cations and dications predict significant structural changes of the six-membered ring upon oxidation. The formation of a transannular P–P single bond (ca. 2.25 Å) in the cyclic dications is indicated by geometry and consideration of the frontier orbitals. Boron adducts of diphenylphosphines of type comprising bonding motif are very scarce and only very few reports are known. However, borane complexes of cyclo-oligophosphanes are interesting objects of study since their structures give insight into the reactivity of cyclo-oligophosphanes and particularly into the relative nucleophilicity of the coordinated and uncoordinated phosphorus atoms. First reports by Cowley and Pinell on the treatment of cyclo-oligophosphanes with boron trihalides were recently complemented by Hey-Hawkins et al. They investigated the adduct formation of cyclo-oligophosphanes (68a) and (68b) in the reaction with to form complexes (Scheme 25). The latter complex is of particular interest since they
There is a large number of cationic species comprising bonding motif J. Phosphanylphosphonium ions consist of a tricoordinate phosphanyl moiety and a phosphonium centre which is analogous to an ammonium centre and conventionally defined as a tetracoordinate phosphorus center bearing a formal positive charge (ii, Scheme 26). According to another resonance structure, they are also termed phosphane stabilized phosphonium ions (ii). The question whether the $\sigma^3-\sigma^4$ P–P bond possesses rather a covalent or a dative character was theoretically investigated by Pietschnig. Calculations (MP2/6-311G(d)) on a model system ($R = \text{Me}$, $X = \text{Me}$ or $\text{NH}_2$; Scheme 26) revealed that according to Wiberg bond indices (0.867 for $X = \text{Me}$, 0.807 for $X = \text{NH}_2$) the P–P bond in both derivatives are best described as single bonds. However, the heterolytic cleavage was only found to be slightly preferred over the homolytic P–P cleavage in case of the $\pi$-donating amino substituent. As already discussed, the low field shifted to the tetracoordinate phosphorus atom.

Generally independent of the nature of the P–P bond in a wide range of phosphanylphosphonium ions, the $\sigma^4$ P atom represents a good nucleofuge and is therefore easily substituted by stronger Lewis bases. This inherent high reactivity makes cationic species containing polyphosphorus frameworks prominent synthetic targets. Catenated and cyclic polyphosphanylphosphonium salts are most intensely studied within this diverse group of cations. Typically phosphanylphosphonium cations can be accessed from either the reaction of a chlorophosphane with a halide abstracting agent (Abs) (Scheme 27, top), the reaction of a chlorophosphane, a phosphane and a halide abstracting agent (Scheme 27, middle) or by protonation or alklyation of a diphosphane (Scheme 27, bottom).

A library of crystallographic data for several derivatives is available and shows consistent P–P distances that are close to 2.2 Å for most cases. The most important of the many reported catena- and cyclo-phosphorus cations comprising bonding motif J are depicted in Fig. 15. They offer new synthetic approaches, not only for P–P bond formation, but also for other aspects in synthesis. Phosphanylphosphonium cations with two phosphorus atoms typically exhibit two well separated doublets in $\text{^31P}$ NMR spectra with the high field shifted resonance corresponding to the tricoordinate phosphorus atom and the low field shifted to the tetracoordinate phosphorus atom. $J(\text{PP})$ coupling constants are normally observed in the range of 250–450 Hz. In the solid state phosphanylphosphonium cations contain a slightly distorted tetrahedral environment for the tetracoordinate and a pyramidal geometry for the tricoordinate phosphorus atom that is typical of a phosphane. As expected, the distortion can be more intense in more complex and cyclic systems as a result of ring strain or steric demand of the substituents.
The prototypical phosphanyldiphosphonium framework can be decorated with halo-substituents (X = Cl, Br, I) at either the phosphane or the phosphonium centres to yield an array of acyclic and cyclic halo-functionalized cations (Fig. 15). In this context, the preparation of diphosphanes or cyclo-polyphosphanes from the reduction of respective chlorophosphanes can be applied to access catenated cationic polyphosphorus frameworks.105a–d Cation 70+ readily reacts with Lewis bases such as 4-(dimethylamino)pyridine (dmap) and phosphanes (R3P), providing approaches to new open-chain and cyclic phosphorus frameworks (Scheme 28). Upon reaction with R3P (R = Me or Pr) or dmap the three-membered ring is opened to yield the adducts [R3PCy3]+–[P3Cy2]2+ (Scheme 29, top) and release of a diphosphiranium salt [Cy4P4Cl]+ and [OTf] (Scheme 29, bottom), which has a related structure to cation 71a+ and a single diastereomer of 71b+. This ring-opening reactivity of the cation 70+ parallels the reactivity of isologal epoxides with nucleophiles under acidic conditions.

Related to this chemistry is the chlorination of a cyctotetraphosphane 75 by PCl3 in the presence of the Lewis acid GaCl3, which provides a stepwise approach to salts of the first acyclic and cyclic halo-functionalized cations (Fig. 15). Reactions of the dication 762+ with dmpe effect a dissociation of the cyclic framework resulting in the formation of the cationic cyclodimerization of a phosphaalkene 81 (bottom). The most stable cation according to quantum chemical calculations indicating the HOMO of P4 and a π*-type LUMO at [NO]+ as the interacting frontier orbitals.111 The reaction of [P4NO]–cage compound 84[A] with...
The 1:1 mixtures of RPCl2 and a Lewis acid ECl3 (E = Al, Ga) in THF are the best candidates for a large range of distinct alkyl- and aryl-substituted phosphenium ions [RPCl]+, which formally insert into P–P bonds of P4. The 1:1 mixtures of RPCl2 and a Lewis acid ECl3 (E = Al, Ga) in THF are synthesized using a solvent free melt reaction, whereas alkyl-substituted derivatives [87d–k][GaCl4] are formed in Cs2H2F solution. These compounds can be prepared on a multi-gram scale in good to excellent yields and are fully characterized with an emphasis on 31P NMR spectroscopy in solution and single crystal structure determination. By addition of more eq. of GaCl3, the melt approach can be extended to dication [Ph4P6]+ (88)[X]; [X] = [GaCl4] and trication [Ph5P5]+ (89)[X]; [X] = [GaCl4] via the consecutive insertion of up to three [Ph2P]− fragments into the P–P bonds of the P4 tetrahedron. This approach has been extended to highly functionalized cation 90+[X] = [AlCl4] and the zwitterionic P5−cage 91, which are formed by the insertion of the corresponding phosphenium cations that are derived from four-membered phosphorus–nitrogen–metal heterocycles. Similarly, the reaction of P4 with the cyclo-diphosphadiazidane [DippNPCI]2 (Dipp = 2,6-disopropylphenyl) and GaCl3 in fluorene yields compound 92[GaCl4]. The addition of an excess of GaCl3 and a second eq. of P4 to a solution of 92[GaCl4] afforded the dicaticonic species 932+ as [GaCl4]− salts.

Also cationic polyphosphorus–chalcogen cages are rarely described in the literature. Until recently only two synthetic procedures were reported for their preparation. In the first approach P4S3 reacts with in situ generated [PL3]+–phosphenium ions yielding cation 94+ which disproportionates to cations 95+ and 96+ (Fig. 17). The second approach is based on halide abstraction from α-P2S5I3 using Krossing’s silver salt Ag[AlOC(CF3)3]4 giving the spiro-cyclic cage cation 97+. The formation of cation 98+ is observed in the protonation reaction of cyclic P–E-heterocycles (MesPSe)4 or reaction of P4Se4 with MesPCl2 in the presence of AlCl3 as Lewis acid. Reacting P3E3 with Mes2CCl2 in the presence of AlCl3 the formation of cations 99+ [E = S, Se] is observed. The cations are only formed in small amounts but their connectivity was confirmed by extensive NMR investigation and X-ray analysis of suitable single crystals. Basal alkylation of P3E3 is observed in the reaction with secondary alkylhalides (sec-RX) to give cations of the type 100+ [E = S, Se].

Another approach to generate cationic chalcogen–phosphorus cages (E = S, Se) is based on cationic polyphosphorus cages as...
starting materials. 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. Chalcogenation reactions of \([\text{R}_2\text{P}]^+\)-cage compounds \(87\text{c},\text{f}[\text{GaCl}_4]\) with elemental grey selenium yield the corresponding polyphosphorus-chalcogen cages \(102\text{[GaCl}_4]\) \((E = \text{Se}, R = \text{Cy}, \text{Ph}; \text{Fig. 17})\). Both cations are formed upon insertion of two selenium atoms into two P–P bonds adjacent to the phosphonium moieties in \(87\text{c},\text{f}\). Their structural motif resembles that of nortricyclane, with a basal \(P_3\) ring, the tetra-coordinate \(P\) atom and the selenium atoms occupying the bridging positions, and one \(P\) atom defining the apex of the cage. This class of compound features interesting \(^{31}\text{P}\) and \(^{77}\text{Se}\) NMR characteristics. They reveal an \(\text{AM}_2\text{OX}\) spin system for the isotopologues without a \(^{77}\text{Se}\) nucleus. These resonances are superimposed by the \(C_1\)-symmetric isotopologues featuring one \(^{77}\text{Se}\) atom in one of the bridging positions. This gives rise to an \(\text{AMNOXZ}\) spin system which is strongly influenced by higher order effects. However, in the case of \(102\text{e, i}\) \((R = \text{Cy})\), both spin systems were successfully simulated allowing for the exact determination of chemical shifts and coupling constants. A series of experiments employing variable temperatures, reaction times and stoichiometries gave meaningful insights into the mechanism of the chalcogenation. These experiments indicate that the insertion of \(\text{Se}\) atoms into P–P bonds of \(87\text{c, f}\) proceeds in a stepwise manner via the intermediates \(101\text{e, i}\). The targeted preparation of \(103\text{e}\) \((E = \text{S}, \text{Se})\) was obtained by reacting an \(\text{AM}_2\text{OX}\) salt with grey selenium \((E = \text{Se})\). Another synthetic approach for the preparation of \(103\text{e}\) \((E = \text{S}, \text{Se})\) is the targeted substitution of one \([\text{Ph}_2\text{P}]^+\)-moiety in the tricaticonic cage \(89\text{f}\). This was achieved by reacting \(89\text{f}\) with grey selenium or sulfur under solvent-free conditions. Dication \(103\text{f}\) was comprehensively characterized by X-ray crystallography as well as \(^{31}\text{P}\) and \(^{77}\text{Se}\) NMR spectroscopy \((E = \text{Se})\). The polyphosphorus cation \(89\text{f}\) and cationic polyphosphorus–chalcogen cages \(103\text{f}\) and \(102\text{f}\) are formally derived by stepwise isolobal exchange of \([E]\) atoms by \([\text{Ph}_2\text{P}]^+\) units in the bridging positions of the nortricyclane type structure of \(P_3\text{E}_2\) derivatives \((E = \text{S}, \text{Se})\).

Despite the fairly large number of binary group 15/16 element cations that have been reported, an example involving phosphorus in combination with a group 16 element has not been synthesized and characterized until very recently. Although cation \([P_3\text{Se}_4]^+\) \((104\text{f})\) does not belong to bonding motif \(J\) it complements the series of polyphosphorus–selenium cages. Three distinct synthetic routes for salts of the nortricyclane type cation \(104\text{f}\) were independently discovered. Cation \(104\text{f}\) is obtained as metallate salt \(104\text{[MX}_4]\) \((M = \text{Al, Ga}; X = \text{Cl, Br})\), either via a melt approach from elemental red or white phosphorus, grey selenium and selenium tetrachloride in the Lewis-acidic ionic liquid BMIMCl/AlCl\(_3\) \((M = \text{Al}; X = \text{Cl, Br}, \text{Scheme 32, top})\) or an arylation reaction of \(P_3\text{Se}_3\) with pentamethylbromobenzene \((\text{Me}_5\text{C}_6\text{Br})\) in the presence of \(\text{AlCl}_3\) in CH\(_2\text{Cl}_2\) \((M = \text{Al}; X = \text{Cl, Br}, \text{Scheme 32, middle})\) or the addition of \((\text{Me}_5\text{Si})_2\text{Se}\) to a solution of \(\text{PX}_3\) and \(\text{MX}_2\) in CH\(_2\text{Cl}_2\) at ambient temperature \((M = \text{Al, Ga}; X = \text{Cl, Br}, \text{Scheme 32, bottom})\). The materials have been structurally characterized by single-crystal X-ray diffraction, Raman, in solution and solid state NMR and quantum chemical calculations. Remarkably, the tricoordinate \(\text{Se}\) atom in the basal plane of the adamantane-like \(P_3\text{Se}_4^+\) cation presents a \(J(\text{Se}^{131}\text{P})\) coupling constant near zero Hz, in agreement with results from quantum chemical calculations. The dynamic disordering phenomena suggested by the results from X-ray crystallography were further investigated by detailed solid state NMR spectroscopy. These studies indicate an interesting dynamic heterogeneity phenomenon, where one of the two cations in the asymmetric unit shows slow reorientation dynamics on the NMR timescale, while the other one can be considered rigid.

The symmetrical butterfly-shaped \(P_6\text{e-diaction} 105\text{a}^2+\) is obtained by substitution of the AsPh\(_3\) moieties of \(106\text{a}^+\) by PPh\(_3\) (Scheme 33). The experimental and iteratively fitted \(^{31}\text{P}[^1\text{H}]\) NMR spectrum reveals an \(A_2\text{MX}^2\) spin system \((\text{Fig. 18})\). The large \(^{31}\text{P}–^{31}\text{P}\) coupling constants observed in \(105\text{a}^2+\) \((J(\text{MX}^0) = 339 \text{ Hz}, J(\text{MM}^0) = -139 \text{ Hz} \text{ and } J(\text{XX}^0) = 39 \text{ Hz})\) indicate a substantial degree of trough space coupling between the \(\text{cis}-\text{orientated free-lone pairs located at each “butterfly-wing”}\). Bertrand et al. reported on the \(P_3\text{N}\) cage compound \(107\) obtained from the insertion reaction of a room temperature stable phosphinynitrene \(108\) into one edge of a \(P_4\) tetrahedron (Scheme 34). The zwiterionic cage compound \(107\) reveals an \(A_2\text{CMX}\) spin system with \(^{31}\text{P}\) chemical shifts in the expected range of intermediate bonding.

\[
\begin{align*}
2 \text{P}_{\text{red}} + \text{Se}_{\text{gray}} + \text{SeCl}_4 + \text{AlCl}_3 \\
\text{P}_3\text{Se}_3 + \text{Me}_3\text{C}_6\text{Br} + \text{Se}_{\text{gray}} + \text{AlCl}_3 \\
(\text{Me}_5\text{Si})_2\text{Se} + 3 \text{PX}_3 + \text{MX}_2
\end{align*}
\]

Scheme 32 Three different approaches for the synthesis of the first binary phosphorus chalcogen cation \(P_3\text{Se}_4^+ (104\text{f})\) as metallate salt.

\[
\begin{align*}
\text{Ph}_3\text{As} + 2 + 2 \text{PPh}_3 + \text{AsPh}_3 \\
\text{Ph}_3\text{As} + 2 \text{P}_{\text{red}} + 2 \text{Ph}_3\text{P}
\end{align*}
\]

Scheme 33 AsPh\(_3\) can be substituted by PPh\(_3\) in the bicyclic compound \(106\text{a}^2+\) to give the analogous dicationic polyphosphorus framework \(105\text{a}^2+\).
for endo,endo-bicyclo[1.1.0]tetraphosphane derivatives but for one exception ($\delta(P_A) = -255.2$, $\delta(P_C) = -154.4$, $\delta(P_M) = 57.6$, $\delta(P_X) = 68.2$ ppm). The $P_M$ atom adjacent to the nitrogen atom is significantly shifted to lower field with respect to the related $P_C$ atom which is connected with the $P_X$ phosphonium atom. This peculiar bonding environment of a $P$ atom incorporated into the rigid bicyclo[1.1.0]tetraphosphane framework is also reflected by the $P$–$P$ bond lengths found in the crystal structure of 107. The distances between $P_A$ and $P_M$ (2.288(3) and 2.275(3) Å) are significantly longer than those between $P_A$ and $P_C$ (2.217(2) and 2.194(3) Å). This finding may be reasoned by the negative hyperconjugation of the nitrogen lone-pairs into the $s^*(P_X)$–(N–$P_X$ 1.575(5) Å) as well as into the $s^*(P_M)$-orbitals (N–$P_M$ 1.614(4) Å) therefore loosening the $P_A$–$P_M$ bonds.

The class of $\sigma^3$–$\sigma^5$ diphosphorus compounds comprises basically only phosphanylphosphoranes (bonding motif K), as no example of the combination of a $\sigma^3$-$\sigma^5$ phosphorus atom adjacent to a $\sigma^5$ phosphorane has been reported.

**Bonding motif K**

As this class of compounds was reviewed earlier, we refrain from a repetition and only want to discuss two particular examples instead.

Compound 109 was obtained by reduction of the corresponding phosphate oxide 110 (bonding motif N) with chloroform (Scheme 35). The $^{31}$P NMR spectrum displays a complex A,B coupling pattern with the $\sigma^5$ phosphorus resonance (A-part) high field shifted with respect to the $\sigma^3$ phosphorus resonance (B-part) (81 MHz, CDCl$_3$, $\delta(P_A) = -28.2$, $\delta(P_B) = 40.9$ ppm, $^3J(PP) = 341.3$ Hz). The crystal structure of 109 (Fig. 19) comprises a central $\sigma^3$ phosphorus atom bearing three $\sigma^5$ phosphoranyl moieties. The $P$–$P$ bonds are in the expected range of single bonds (2.244 Å) and occupy the equatorial positions of the trigonal bipyramidal coordinate $\sigma^5$ phosphorus atom. Since normal phosphate oxides (e.g. $\text{Ph}_3$PO or $\text{nBu}_3$PO) are not reduced to the corresponding phosphanes by chloroform, the reduction of 110 to 109 is quite remarkable though the mechanism is unknown. The authors ascribe the unusual reactivity to the three $P$–$P$ bonded phosphoranyl substituents. Decreased $\pi$-backbonding of the oxygen lone pairs into $P$ based $\sigma^*$-orbitals would render the oxygen atom more nucleophilic and susceptible for the attack of a weak electrophile like chloroform.

As the urea-bridged phosphoniophosphoranide 111 (bonding motif M) and the phosphanyl phosphorane 112 (bonding motif K) have been reviewed earlier, we only want to mention one interesting aspect which points out how closely related the two bonding motifs K ($\sigma^3$–$\sigma^5$) and M ($\sigma^5$–$\sigma^5$) are. When 111 is treated with sodium fluoride in acetonitrile solution the fluoride does not simply substitute the chloride moiety at the same $P$ atom. Both coordination environments are altered as fluoride is binding to the amino-substituted phosphonium $P$ atom (Scheme 36). Thus, the $\sigma^3$–$\sigma^5$ diphosphorus compound 112...
is obtained with the fluoro-substituent and phosphanyl moiety located in axial positions. This transformation also involves an elongation of the P–P bond length from 2.195 Å in 111 to 2.267 Å in 112. While the initial apical P–Cl bond length (2.816 Å) is much longer compared to literature known examples (~2.3 Å) and comparable to the [PCl3]– anion, the P–F distance (1.628 Å) is only slightly longer than those observed in PF5 (1.577(5) Å).

The two bonding motifs L and M describe the connectivity of two tetracoordinate phosphorus atoms that can be linked either as two phosphonium units giving a dication (L) or as the formally neutral phosphoniophosphoranide (M).

**Bonding motif L**

The fundamentally important parent or benchmark P–P bonded diphosphonium unit is present in a few structurally characterized compounds that involve bulky amino substituents (113–115) unsymmetrically substituted alkyl-derivatives (1142) or a polymeric framework (115, 116) (vide infra). Hexaalkyldiphosphonium triiodide salts were speculated as the products of reactions of red phosphorus with alkyl iodides or from trialkylphosphines with iodine, and [Me3PMe3][PF6]2 (96, R = R′ = Me) has first been assigned on the basis of elemental analysis data and IR spectroscopy.

Polyphosphine adducts of electrophilic antimony, thallium, copper, or iron acceptors are known to spontaneously eliminate diphosphonium dications [R2P(PR3)2]1+ and dialkylation of diphosphines, reductive elimination processes or methylation of P–P phosphanylphosphonium cations are versatile synthetic approaches to fundamentally important prototypical examples of diphosphonium dications (Fig. 20) that define the origin of a potentially extensive and diverse catena-phosphorus chemistry, paralleling catena-carbon chemistry. The quantitative nature of the reactions bodes well for the development of polyphosphonium chemistry. Very recently diphosphonium dications were shown to activate B–H, Si–H, C–H and H–H bonds while being part of a frustrated Lewis pair.

**Bonding motif M**

Phosphoniophosphoranides may in principal be obtained as Lewis adducts of two phosphines with one acting as a donor and the other one as an acceptor. The resulting mixed-coordinate P–P compounds display a phosphonium P atom with a tetrahedral and phosphoranide P atom with a disphenoidal geometry.

Reports of such intermolecular Lewis adducts between simple phosphines go back to the 1950’s. The lack of structural proof lasted for almost a half century due to the low stability of this bonding motif in solution. Müller et al. obtained the phosphoniophosphoranide 118 as crystalline solid by slow diffusion of PMe3 into a solution of PBr3 in toluene (Fig. 21). Compound 118 shows a great susceptibility towards decomposition reactions. Keeping the solid below ~40 °C without solvent allows storage over several days. In contrast, the decomposition of 118 in solution is markedly accelerated making an immediate NMR measurement at low temperatures necessary. In comparison to the resonances of free PMe3 (δ = −61.9 ppm in C6D6) and PBr3 (228.5 ppm in CD2Cl2) the resonance of the donating PMe3 unit (Pdon) is shifted to lower field, whereas that of the accepting PBr3 unit (Pacc) is shifted to significantly higher field (δ(Pdon) = 29.5 ppm, δ(Pacc) = 78.5 ppm, J(PP) = 450.3 Hz). The crystal structure of 118 (Fig. 22) shows the typical disphenoidal geometry of the phosphoranide P atom with the phosphonio and one bromo substituent occupying the two equatorial positions. While these bond lengths (P–P 2.264(2) Å, P–Br 2.250(2) Å) correspond to single bonds the two axially bonded bromo substituents display elongated P–Br distances (P–Bracc 2.424(2) and 2.677(2) Å). The most distal bromine atom forms a bridge (3.327 Å; dashed bonds) about an inversion centre towards another PBr3 unit resulting in two edge-sharing distorted square pyramids. Although the distances between two monomeric units of 118 are closer to the sum of the van der Waals radii (3.74 Å) than to a classical single bond, the formation of dimeric structures in the solid state was also observed for other derivatives.

A more elaborate example of a phosphoniophosphoranide (119) features an electron accepting PCl2- and an electron donating 1Pr,P-moiety connected by the rigid acenaphthene backbone (Fig. 21). Compound 119 represents the first phosoniophosphoranide which is stable at room temperature although it tends to decompose under reductive coupling in the presence of nucleophiles. The molecular structure reveals a covalent P–P single bond (2.257(2) Å) with the phosphonio
substituent in the equatorial and the chlorine atoms in the axial positions. The resonances of solution \(^{31}\)P NMR spectra (\(\text{PCl}_2\ 68.8\) and \(\text{PiPr}_2\ 40.4\) ppm) and the observation of a \(^1N\) leads to bonding motif fore we do not consider them as a separate bonding motif.

The reaction of the anthracene derived triphosphane\(^{10}\) 120 with \(\text{P}_4\text{I}_4\) in the presence of LiCl and chlorinated solvents leads to the formation of the diphosphoniophosphorane 121 as a result of a formal two electron oxidation and substitution process (Scheme 37).

The reaction of the chalcogenation of \(\text{As}\) already mentioned in the discussion of the phosphonio-

The reaction of the anthracene derived triphosphane\(^{10}\) 120 with \(\text{P}_4\text{I}_4\) in the presence of LiCl and chlorinated solvents leads to the formation of the diphosphoniophosphorane 121 as a result of a formal two electron oxidation and substitution process (Scheme 37).

The rather long P–P bond lengths are unequal in the solid state (2.382(5) and 2.528(5) Å). In contrast, the solution\(^{31}\)PN M R spectra (diphenylphosphanyl)naphthalene (Scheme 39, left) and methylation (Scheme 39, right) of 1,8-bis-trialkylphosphanes. The phosphoniophosphorane was calculated to be 24 kJ mol\(^{-1}\) more stable.\(^{153}\)

Schmutzler et al. reinvestigated the single protonation (Scheme 39, left) and methylation (Scheme 39, right) of 1,8-bis-(diphenylphosphanyl)napthalene 125 and reported the crystal structure of the cations 126\(^+\) and 127\(^+\) as triflate salts.\(^{126}\) Unexpectedly, the reaction with the electrophiles showed a pronounced increase in the P–P bond distances (126\(^+\): 3.211 Å; 127\(^+\): 3.265 Å) in contrast to the expected attractive interaction as observed for

As already mentioned in the discussion of the phosphoniophosphorane 118, the solid state structures of some phosphoniophosphoranides (bonding motif M) comprise bridged dimeric structures. From a geometrical point of view they may be considered as \(\sigma^4\)–\(\sigma^5\) motif although interatomic distances suggest not more than attractive interactions.\(^{133,134,149}\) Therefore we do not consider them as a separate bonding motif.

The connection of a phosphonio and a phosphorane moiety leads to bonding motif N.

### Bonding motif N

Alder et al. showed that the addition of nucleophiles to tricyclic propellane-type diphosphonium dications (bonding motif L) of different ring sizes gives phosphoniophosphoranes. Although some aspects of this work have already been summarized elsewhere,\(^{150}\) the different extent of transannular P–P bonding with respect to the applied nucleophiles and ring sizes is worthy to be mentioned here.\(^{151}\) Crystal structure analyses are available for the benzyl-, hydroxo- and hydrido-substituted derivatives indicating a different degree of pyramidalization of the \(\sigma^5\) phosphorane moiety. Different P–P-distances in the range from 2.514 to 2.813 Å are observed.

There seems to be no obvious correlation between P–P distances and coupling constants in such systems. Deprotonation of the doubly protonated bis(phosphonium)dication 123\(^{2+}\) initially gives the monoprotonated bicyclic cation out,out-124\(^+\) which undergoes in,out-inversion of the free lone pair (Scheme 38).\(^{152}\) While out,out-124\(^+\) shows broad signals in the \(^{31}\)PNMR spectra, in,out-124\(^+\) shows two doublets with a \(^1J(PP)\) coupling constant of 253 Hz. The energy barrier of inversion in 124\(^+\) was determined to be only 70 kJ mol\(^{-1}\), an extraordinary low value for trialkylphosphanes. The phosphoniophosphorane was calculated to be 24 kJ mol\(^{-1}\) more stable.\(^{153}\)
the Alder systems (vide supra). Very recently, Stephan et al. synthesized the phosphoniofluorophosphorane as perfluorinated borate salt \( \text{[B(C}_6\text{F}_5)_4] \) by fluorination of \( \text{125} \) and subsequent fluoride ion abstraction from the difluorophosphorane \( \text{129} \) (Scheme 39, bottom).\(^{154}\) Both, the fluoride and the phosphonio moiety occupy apical positions with elongated P–P (2.530(1) Å) and P–F distance (1.637(2) Å) which can be explained by a 3c4e-bonding interaction.

Kilian et al. reported on the isomeric diphosphonium dications \( \text{meso-130}^{2+} \) and \( \text{rac-130}^{2+} \) that are formed by two consecutive methylation steps of the diphosphacenaphthene \( \text{131} \) via a phosphanylphosphonium intermediate \( \text{132}^+ \) (Scheme 40, top). The formation of the respective diastereomer strongly depends on the methylation agent used. An interesting interconversion process of both stereoisomers is facilitated by the presence of fluoride ions which was supported by quantum chemical calculations and \(^{31}\text{P}-\text{EXSY} \) NMR investigations indicating that the inversion occurs via phosphoniphosphorane intermediates \( \text{133a,b}^+ \).\(^{155}\)

These contrary results finally lead to the question which electronic conditions must be fulfilled for \( \sigma^5-\sigma^5 \) phosphonio-phosphoranes to be stable towards dissociation to phosphanes and phosphonium cations and whether they can exist unless restrained by a bridging ligand forcing them to close contact. Besides charged phosphoniophosphoranes, phosphane oxides\(^{131,156}\) (see also \( \text{110} \)) and sulfides\(^{133,157}\) adjacent to the \( \sigma^5 \) phosphorane unit exhibit similar bonding motifs. Although they have been discussed earlier,\(^2\) we like to point out that they are sometimes surprisingly stable and some of them have been also structurally characterized. They feature the tetracoordinate phosphorus atom in an equatorial position. This is in sharp contrast to the aforementioned phosphoniophosphoranes, as the few which could be isolated so far, feature the tetracoordinate phosphorus in an apical position.\(^{158}\) These inherent differences might be explained by the fact that the Lewis adduct formation occurs between a cationic phosphonium ion and in one case a neutral phosphane and in the other case an anionic \( \sigma^5-\sigma^5 \) phosphate (phosphinite, \( \text{R}_2\text{PO}^- \) or phosphinothioite, \( \text{R}_2\text{PS}^- \)). In addition to an expectable coulombic attraction, the significantly enhanced donor strength of the latter ones should lead to a considerably stronger interaction between both phosphorus atoms in a \( \sigma^5-\sigma^5 \) environment.

**\( \sigma^4-\sigma^6 \)**

The only phosphorus moiety bonded to a hexacoordinate phosphate forming stable products that have been observed so far is the phosphonium moiety. Phosphoniophosphates are described by bonding motif \( \text{O} \).

**Bonding motif \( \text{O} \)**

Only few reports on phosphoniophosphates have appeared in the literature. At first, adducts of \( \text{PF}_5 \) and alkylphosphanes were studied by NMR spectroscopy.\(^{159}\)

The first isolated and structurally characterized \( \sigma^4-\sigma^6 \) P–P compound \( \text{134} \) from an electron deficient trifluoroo-\( \lambda^3 \)-dioxophospholane was published by Röschenthaler et al.\(^{160}\) The molecular structure displays a tetrahedral phosphonio moiety bonded to an octahedral \( \sigma^6 \)-phosphate. The P–P bond length (2.234(5) Å) lies well in the expected range for a single bond. Other examples comprising bonding motif \( \text{O} \) (Fig. 23) display comparable bond lengths with those of \( \text{135} \)\(^{161}\) and \( \text{136} \)\(^{133}\) being in the upper and lower range of typical P–P single bonds, respectively. Although nearly all structurally characterized examples contain bridging ligands, prearranging a close contact of the phosphorus atoms, we would like to point out that in diphosphate \( \text{137} \),\(^{162}\)
a relaxed $\sigma^*\sigma^*$ phosphanylporphorane without P–P-bond and a C–C–P angle of 120° at the $sp^2$-hybridized carbon atoms would imply a much higher distance between the two P atoms. Therefore, the distance of 2.296(2) Å clearly indicates a strong attractive interaction between both phosphorus atoms. In the oxidation product 136 of the phosphoniophosphorane 111 (bonding motif M) by $o$-chloranil, the hexacoordinate phosphorus comprises a regular octahedral environment and a bond length of 2.165 Å to the phosphonium moiety. The tetracoordinate phosphorus atom is in a heavily distorted tetrahedral environment due to the urea ligand forcing the two P–P–N angles to be rather small at 97°.135 The structures of the cation 138+ (ref. 163) and the unsymmetrically chlorinated diphosphaacenaphthene 135 exhibit P–P distances of 2.202(1) and 2.338(2) Å, respectively. The latter was suggested to undergo a tautomerization via a not isolatable diphosphorane intermediate ($\sigma^*\sigma^*$) similar to the equilibrium between molecular PCl$_3$ and its ionic form [PCl$_4$][PCl$_6$].164 The optimized geometry of the calculated diphosphorane intermediate shows an axial-apical connection of the phosphorus moieties.

$$\sigma^*-\sigma^*$$

**Fig. 24** Compound 139 comprising the very rare example of bonding motif P.

**Bonding motif P**

Bonding motif P is very rare and the very few known examples are already included in previous reviews.2 One of the two structurally characterized examples shows a $P_{eq}-P_{eq}$ (2.264(1) Å)$^{165}$ and the other one a $P_{as}-P_{as}$ (2.253(1) Å)$^{166}$ connection of both phosphorus moieties. However, compound 139 is of particular interest (Fig. 24), as both phosphorus atoms are in a different pentacoordinate environment which allows for the observation of a large $J/(PP)$ coupling constant of 749.6 Hz. Although no crystal structure is available, it was proposed that the P–P bond is in equatorial position for both pentacoordinate moieties which can also explain the large $J/(PP)$ value observed.$^{167}$

**Abbreviations**

18-crown-6 1,4,7,10,13,16-Hexaoxacyclooctadecane
2,2,2-crypt 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane
Ad Adamantyl

**References**


