Recent highlights in mixed-coordinate oligophosphorus chemistry

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ARTICLE TYPE

Recent highlights in mixed-coordinate oligophosphorus chemistry

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Abstract

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.

-Foto Maximilian Donath-

Maximilian Donath studied at WWU Münster (Germany) with a research stay in Palermo (Italy). He received his diploma degree in 2011 and is currently a Ph. D. student in the Weigand group. After starting his Ph. D. thesis at the WWU Münster supported by a scholarship of the Fonds der Chemischen Industrie (FCI) he continued it at TU Dresden (Germany) since 2013. His research interest is focused on multinuclear NMR spectroscopy, the synthesis of cationic polyphosphorus frameworks and the activation of white phosphorus with p-block compounds.

-Foto Felix Hennersdorf-

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-Foto Jan J. Weigand-

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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 from Dillon and co-workers which appeared in 1995 the field of P−P bonded compounds was re-reviewed. A tremendous development was reported and a great variety of combinations of bonding modes including multiple bonds was discussed.[2] 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[3] gives no clear instruction how to correctly entitle the valence state of an R_4P^+ cation that can be obtained by either protonation of the parent λ^3-phosphane (phosphonium) or

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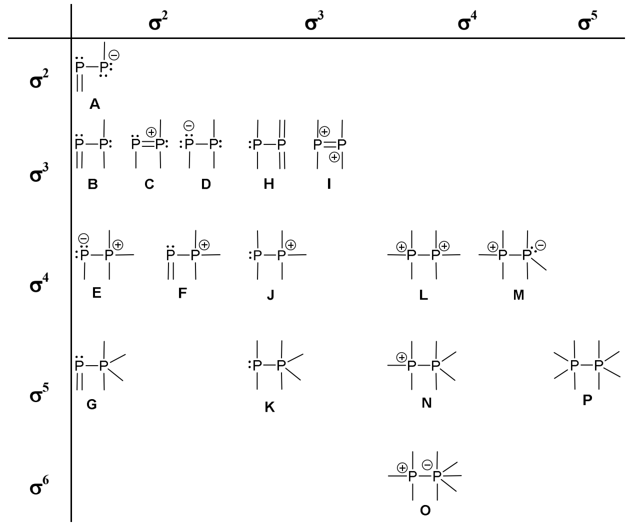
§ Both authors contributed equally.

by hydride abstraction from the parent λ^5-phosphane/phosphorane (λ^5-phosphanylium).[4] The nomenclature of catenated phosphorus compounds following the IUPAC rules is thoroughly described in literature.[5] 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[6] in P_4 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 strongly depends on the oxidation states of the corresponding phosphorus atoms (e.g. 3.6 Å)[7], a value beyond 3 Å is considered as very weak interaction, if not repulsion, in cases where a bridging ligand prevents a longer distance. ^{31}P NMR chemical shifts and ^{31}P-^{31}P-coupling constants are often indicative for a certain bonding situation and coordination numbers of the respective phosphorus atoms, but appeared to be of no ultimate proof in certain cases.[8]

Table 1. Selected P−P bonded frameworks with non-symmetrical[a] bonding motifs.[b]



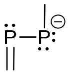
[a] Rare symmetrical bonding motifs **I**, **L** and **P** are considered for reasons of completeness; [b] The overall charge of the resulting systems strongly depends on the nature of substituents attached to the P-atoms.

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)[9] and **σ³–σ³** (diphosphanes)[1] 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. For clarification reasons, a short comment about the σ-notation and the drawing of structures in this review is required. There are several ways to indicate the bonding situation of a P−P bonded system which might seem ambiguous. However, they require certain consideration such as following the octet rule and minimizing the number of formal charges or extended coordination numbers that are exceptions from the octet rule. For most of the depicted systems we decided to draw the simplest Lewis-type structure, which primarily follows the octet rule in combination with formal charges (bonding modes: **A-F**, **I**, **J** and **L**). For a better recognition of lone pairs of electrons they are depicted (as two dots) only where relevant. We are aware that in many cases, these formal drawings do not display the actual electronic structures of the systems but indicate the actual number of bonding partners as denoted with the σ-notation. The number of bonding partners at phosphorus can exceed four in certain cases, thus representing hyper-coordinated bonding situations (bonding modes: **G**, **K**, and **M-P**). As Kilian *et al.* stated: *"Hyper-coordination in phosphorus chemistry is not unusual, penta- and hexa-coordinated compounds are stable when highly electronegative substituents are attached to the phosphorus atom (as e.g. in PF$_5$). On the other hand, hyper-coordination with less electronegative atoms around the central phosphorus is less common and more sophisticated approaches (resonance stabilization, favorable ring size formation) are needed to stabilize such species."*[10]

The discussion in the following section is divided in the combination of the σ-matrix as depicted in **Table 1**. Only for the combination of **σ²–σ³**, **σ²–σ⁴**, **σ³–σ³** and **σ⁴–σ⁴** 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]

σ²-σ²

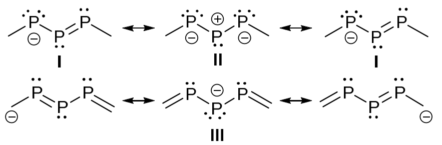
The parent motif of **σ²–σ²** phosphorus compounds is the well-known diphosphene unit. These compounds are typically intensively orange to red coloured, were first reported by Yoshifuji *et al.*[12] and extensively reviewed elsewhere.[9] However, diphosphenes bearing a phosphanido substituent are closely related, but comparable rare and representative examples of the bonding motif **A** (**Table 1**) are found in triphosphaallyl derivatives.



A

Bonding motif A

Selected examples of anionic ($\mathbf{1}^-$,[13] $\mathbf{2}^-$,[14] $\mathbf{3}^-$,[15] $\mathbf{4}^-$ [16]) and cationic ($\mathbf{5}^+$,[17] $\mathbf{6}^+$ [18]) 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.



Sch. 1 Resonance structures of triphosphaallyl and triphosphapentadienyl compounds.

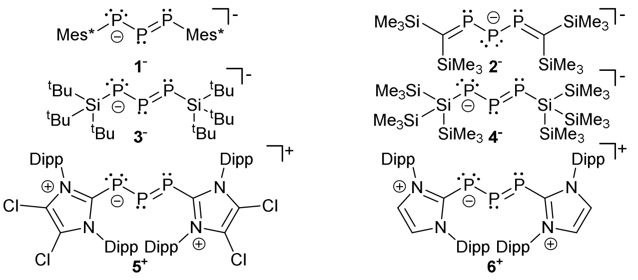


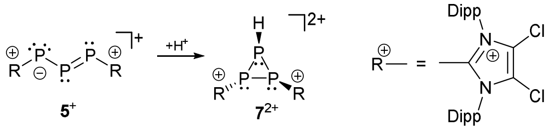
Fig. 1. Selected examples of anionic and cationic derivatives containing the triphosphaallyl and triphosphapentadienyl motif; only one representative resonance structure is shown.

Table 2. Summary of important ^{31}P NMR data and bonding parameters of compounds comprising bonding motif **A**.

	Li[**1**]^{a}	[Li(dme)$_3$][**2**]	[K(thf)$_2$][**3**]	[Li(triaz)$_2$[**4**]	[**5**][GaCl$_4$]	[**6**][Cl]
Ref.	13	14	15c	16b	17	18
Colour	red violet	deep red	purple	violet	green	green
$\delta(^{31}\mathrm{P})_{\mathrm{adjacent}}$ in ppm	208	494.1	232.1	199.8	199.4	190.6
$\delta(^{31}\mathrm{P})_{\mathrm{central}}$ in ppm	548	295.5	730.0	717.2	597.9	591.9
$^{1}J_{\mathrm{PP}}$ in Hz	524	430	552.3	541	508.3	505.9
d(P−P) in Å		2.137(1)	2.072(2)	2.0730(8); 2.0774(8)	2.093(1); 2.091(1)	2.090(1); 2.097(1)
d(P−C/Si) in Å		1.687(3)	2.252(2); 2.260(2)	2.2459(8); 2.2454(9)	1.815(2); 1.814(3)	1.812(1); 1.811(1)
angle P−P−P in °		88.3(1)	105.83(7)	105.52(3)	87.2(4)	92.76(2)

^{a} no structural parameter available

The bonding principle in those compounds strongly depends on the substituents of the adjacent phosphorus atoms. Thus, examples $\mathbf{1}^{-}$, $\mathbf{3}^{-}$, $\mathbf{4}^{-}$, $\mathbf{5}^{+}$ and $\mathbf{6}^{+}$ are best described by resonance structure **I** or **II**, whereas anion $\mathbf{2}^{-}$ 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 (**Sch. 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, di-coordinated phosphorus atom of ions $\mathbf{1}^{-}$, $\mathbf{3}^{-}$, $\mathbf{4}^{-}$, $\mathbf{5}^{+}$ and $\mathbf{6}^{+}$ 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 π- and σ-bonding. The lone s-type electron 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*-triphosphanediium cation $\mathbf{7}^{2+}$ (**Sch. 2**):



Sch. 2. Reversible protonation/deprotonation reaction between $\mathbf{5}^{+}$ and $\mathbf{7}^{2+}$.

The protonation of $\mathbf{5}^{+}$ is reversible and the addition of a base to a solution of $\mathbf{7}^{2+}$ instantly forms a deep green solution of $\mathbf{5}^{+}$.[19] Upon protonation the phosphaallyl anion [(^{t}Bu$_3$Si)$_2$P$_3$]$^{-}$ ($\mathbf{3}^{-}$) rearranges fast to give the related *cyclo*-triphosphane derivative **8**.[15a] The assignment of the resonances of cation $\mathbf{7}^{2+}$ is achieved by comparison to the ^{31}P NMR parameter of related derivatives **8**[15a] and **9**[20] (**Fig. 2**, **Table 3**). The chemical shifts of $\mathbf{7}^{2+}$ are observed in the characteristic range for *cyclo*-triphosphanes.[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 ^{1}J(PH) coupling ($\mathbf{7}^{2+}$: $^{1}J(\mathrm{P_AH}) = 155.7$ Hz; compare **9**: $^{1}J(\mathrm{P_AH}) = 137.1$ Hz). The substituents on the other two P atoms are in a *transoid* arrangement. A larger absolute value of the ^{1}J(PP) coupling constants between the hydrogen-substituted P atom and the phosphorus atom with the *cis*-arranged substituent

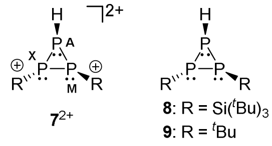


Fig. 2. Substituent arrangement in *cyclo*-triphosphanes $\mathbf{7}^{2+}$, **8** and **9**.

Table 3. ^{31}P{^{1}H} NMR parameters for $\mathbf{7}^{2+}$, **8** and **9**.

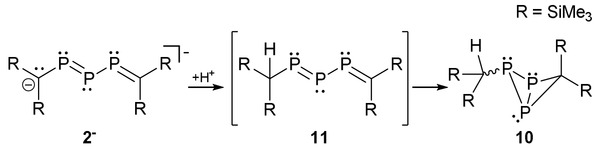
^{31}P	$\mathbf{7}^{2+}$	**8**	**9**
Ref.	19	13a	20
spin system	AMX	AMX	AMX
δ(P$_A$)	−202.3	−260.1	−270.8
δ(P$_M$)	−182.6	−259.5	−149.2
δ(P$_X$)	−156.8	−240.9	−136.3
^{1}J(P$_A$P$_M$)	−158.8	−224.2	−144.1

$^1J(P_AP_X)$	−130.4	−141.3	−226.6
$^1J(P_MP_X)$	−203.0	−188.0	−223.7
$^1J(P_AH)$	155.7	137.1	–[a]
$^2J(P_MH)$	17.8	6.9	–[a]
$^2J(P_XH)$	34.2	16.6	–[a]

[a] coupling constants are not reported.

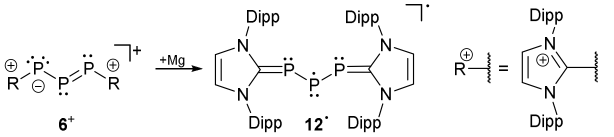
($\mathbf{7}^{2+}$: $^1J(P_AP_M) = -158.8$ Hz; compare **8**: $^1J(P_AP_X) = -224.2$ Hz, **9**: $^1J(P_AP_M) = -226.6$ Hz) contrasts the smaller coupling constant for the *trans*-arrangement involving the hydrogen-substituted P atom ($\mathbf{7}^{2+}$: $^1J(P_AP_X) = -130.4$ Hz; compare **8**: $^1J(P_AP_X) = -141.3$ Hz, **9**: $^1J(P_AP_M) = -144.1$ Hz). A similar trend is observed for ^2J(PH) coupling constants. Large values indicate a *cis*-arrangement of the hydrogen atom at P_A and the lone pair of electrons at the adjacent P atom ($\mathbf{7}^{2+}$: $^2J(P_XH) = 34.2$ Hz, **8**: $^2J(P_XH) = 16.6$ Hz) whereas small values indicate a *trans*-arrangement ($\mathbf{7}^{2+}$: $^2J(P_MH) = 17.8$ Hz, **8**: $^2J(P_MH) = 6.9$ Hz).

The fact that the protonation of $\mathbf{1}^-$ leads to the formation of the open-chain phosphanyldiphosphene Mes*PH–P=P–Mes* instead of a cyclo-triphosphane underlines the great dependence of the substituents on the electronic structure of triphosphaallyl compounds.[13a] A totally different reaction outcome is found upon protonation of anion $\mathbf{2}^-$ which is in agreement with the different resonance stabilization. According to **III** (**Sch. 1**) protonation should occur at the central phosphorus or the carbon atoms. Thermolysis of $\mathbf{2}^-$ 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 (**Sch. 3**).[14]



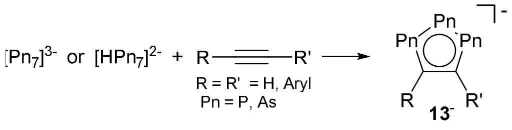
Sch. 3. Rearrangement reaction of $\mathbf{2}^-$ upon protonation.

The difference in the electronic structure of $\mathbf{2}^-$ is also evident in the reversed ^{31}P NMR data. Thus, the more shielded central 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 ^1J(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 $\mathbf{1}^-$, $\mathbf{3}^-$, $\mathbf{4}^-$, $\mathbf{5}^+$ and $\mathbf{6}^+$ 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 $\mathbf{2}^-$. 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_6H_5F 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 $\mathbf{6}^+$ in THF shows the corresponding absorption bands at 666 nm and 434 nm, respectively. The reduction of $\mathbf{6}^+$ into its corresponding neutral radical species **12** was achieved by reacting the cation with an excess of magnesium (**Sch. 4**).[18]



Sch. 4. Reduction of $\mathbf{6}^+$ to neutral radical species $\mathbf{12}^{\bullet}$.

Closely related to these triphosphaallyl systems are the cyclopentadienyl related 1,2,3-triphospholides. Although first described already in 1990,[22] the synthetic access to the isolation of the non-coordinate parent compound $[Pn_3C_2R_2]^-$ (Pn = P, As; $\mathbf{13}^-$) and its arsa-analogue was achieved only recently by Goicoechea *et al*. Anions $\mathbf{13}^-$ 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 (**Sch. 5**).[24]

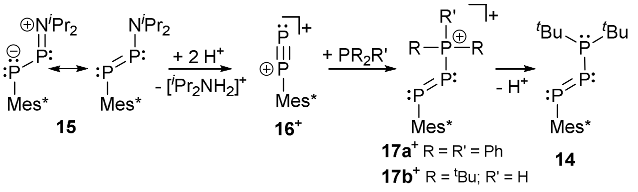


Sch. 5. 1,2,3-Tripnictoolides $\mathbf{13}^-$ formed by the reaction of heptapnictides and alkynes.

Noteworthy is that the electronic structures of these "carbon-copy" ligands possess notable differences in comparison to cyclopentadienyl and derivatized cyclopentadienyl ligands. They generally possess greater π-acceptor character than $[Cp]^-$ ligands which allows for the stabilization of complexes of electron-rich metal centres and the presence of Lewis basic sites on the phospholide ring allows for multiple coordination modes and the formation of multimetallic molecules and supramolecular systems.[25]

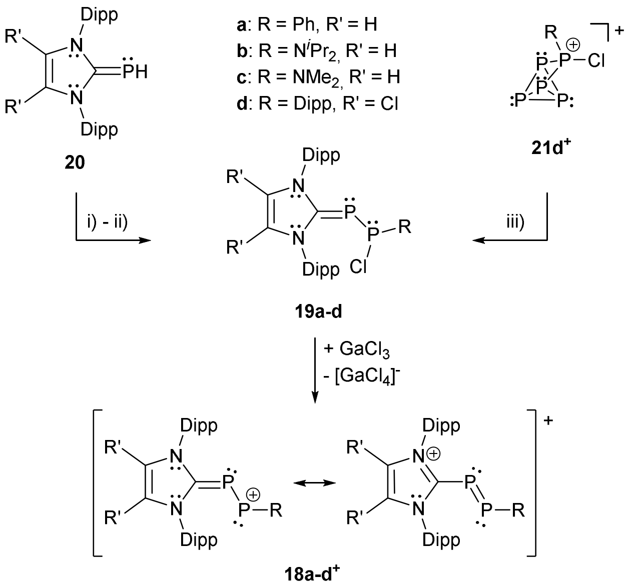
Catena-tetraphosphene dianions of the general formula $[R−PPPP−R]^{2-}$ may be described as doubly phosphanido substituted diphosphenes and are therefore related to the triphosphaallyl ions. The supersilyl–bearing (R = ^{t}Bu$_3$Si) alkali salts[26] as well as the terphenyl substituted thallium analogue[27] (R = C_6H_3-2,6-(C_6H_2-2,6-^{i}Pr$_2$)$_2$) were isolated and characterized. The bond lengths compare well to [Li(dme)$_3$][**2**] (**Fig 1**). All ^{31}P chemical shifts are shifted to higher field. The alkali salts show highfield shifted resonances of 390–420 and −53–19 ppm for inner and outer phosphorus atoms, respectively. The ^{31}P 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 and co-workes.[28] The treatment of amino-substituted diphosphene **15** with triflic acid (**Sch. 6**) eliminates [^{i}Pr$_2$NH$_2$][OTf] accompanied by the *in situ* formation of the highly reactive phosphorus-analogue of a diazonium-ion $\mathbf{16}^+$ which, due to its high reactivity, is not stable even at −78 °C and forms bicyclo[1.1.0]tetraphosphanes besides unidentified products.



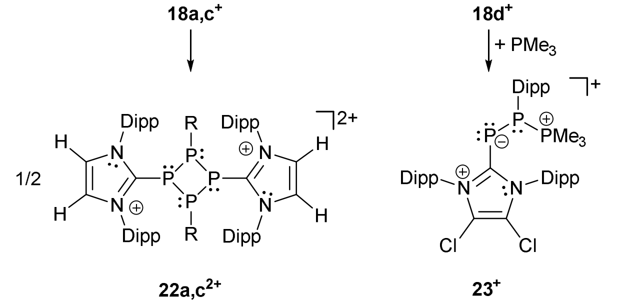
Sch. 6. Protonation of **15** in the presence of phosphanes leading to σ^2-σ^2-σ^4- (**17**$^+$) and σ^2-σ^2-σ^4-compounds (**14**) formally via **16**$^+$. Scheme simplified for clarity reason.

In the presence of a *tert*-phosphane such as PPh_3 the adduct **17a**$^+$ (R = R' = Ph) is formed with a $\boldsymbol{\sigma^2}$–$\boldsymbol{\sigma^2}$–$\boldsymbol{\sigma^4}$ connectivity of the P_3-backbone representing an example of bonding motif **F** (*vide infra*). The formation of **17a**$^+$ 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*-phosphane such as $^tBu_2PH$ in the reaction with **16**$^+$, the initially formed cation **17b**$^+$ slowly liberates HOTf to give the first example of a $\boldsymbol{\sigma^2}$–$\boldsymbol{\sigma^2}$–$\boldsymbol{\sigma^3}$ triphosphene **14** as an example of bonding motif **B** (*vide infra*).[28-29]



Sch. 7. Two different approaches for the synthesis of NHC stabilized chlorodiphosphanes **19a-d** comprising bonding motif **B**. For **19a,b**: i) $+RPCl_2$, +DABCO, −DABCO*HCl; for **19c**: ii) $+PCl(NMe_2)_2$, +DABCO, −DABCO*HCl, $-P(NMe_2)_3$; for **19d**: iii) +3 1,3-bis(2,6-diisopropylphenyl)-4,5-dichloro-imidazole-2-ylidene, -**5**$^+$. Subsequent chloride abstraction yields polarized cationic diphosphenes **18a-d**$^+$. Only two resonance structures that indicate the polarization of **18a-d**$^+$ are shown.

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 **(Sch. 7)**. The group of Grützmacher followed the approach of DABCO (1,4-diaza[2.2.2]bicyclooctane) 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_3-fragment (*vide supra*) besides the P_2-fragment **19d**.[17] The subsequent chloride abstraction from all four derivatives **19a-d** by $GaCl_3$ leads to the formation of the polarized cationic diphosphenes **18a-d**$^+$. The derivatives **18b,d**$^+$ with sterically more demanding substituents could be isolated and structurally characterized. The P–P bond lengths are in the expected range for polarized double bonds (**18b**$^+$: 2.061(1) Å, **18d**$^+$: 2.038(1) Å).

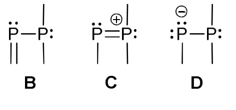


Sch. 8. [2+2] dimerization reaction of diphosphenes **18a,c**$^+$ (left) and PMe_3 attacking the more electrophilic P atom of diphosphene **18d**$^+$ forming $\boldsymbol{\sigma^2}$–$\boldsymbol{\sigma^3}$–$\boldsymbol{\sigma^4}$ compound **23**$^+$ (right).

The derivatives **18a,c**$^+$ with smaller residues on the phosphenium-type side prevent their isolation but enable dimerization to form dicationic *cyclo*-tetraphosphanes **22a,c**$^{2+}$ (**Sch. 8**, left) demonstrating the diphosphene-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 $\boldsymbol{\sigma^2}$–$\boldsymbol{\sigma^3}$–$\boldsymbol{\sigma^4}$ species **23**$^+$ (**Sch. 8**, right) incorporating both bonding motif **B** and **J** (*vide infra*). The product may be depicted in another resonance structure including a phosphaalkene moiety, but a dihedral N–C–P–P angle of 50.5(3)° suggests a preference of the phosphanide structure. This is supported by quantum chemical calculations indicating a negative charge on the phosphanide 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.

$\boldsymbol{\sigma^2}$-$\boldsymbol{\sigma^3}$

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 phosphanylphosphaalkenes 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[32] and have been reviewed earlier[2] we only want to comment shortly on selected examples depicted in **Fig. 3**.

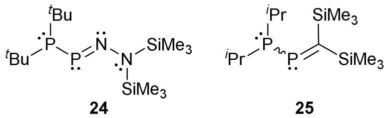
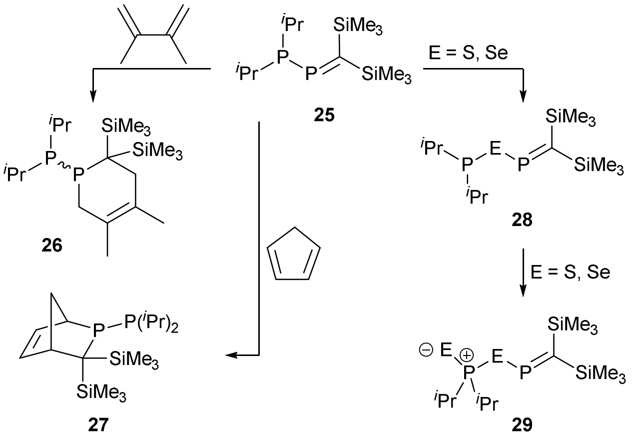


Fig. 3. Selected examples of compounds comprising bonding motif **B**.

In 1990 Niecke *et al.* reported on the 1-phosphanyl-diazaphosphene **24** produced by a base-catalysed elimination of Me_3SiCl from the corresponding phosphane.[33] 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 (**Sch. 9**).[34] 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**.[34a]

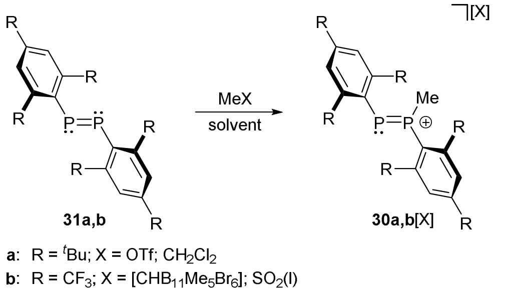


Sch. 9. *P*-phosphanylphosphaalkene **25** undergoing [4+2] cycloaddition reactions at the P=C bond (left) and oxidation of **25** under P–P cleavage (right).

In the reaction of **25** with trichlorosilyltrimethylgermane ($Me_3GeSiCl_3$) they observed an unusual P=C bond cleavage accompanied by a double dichlorosilylene ($SiCl_2$) transfer which represented an important contribution to the chemistry of stable Group 14 carbene analogues. The trichlorosilyltrimethylgermane represents a versatile reagent for the transfer of $SiCl_2$ moieties to *P*-phosphanyl phosphaalkenes under very mild condition.[34b, c]

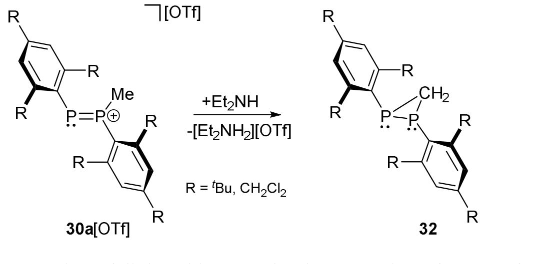
Bonding motif C

The first phosphanylphosphenium ion $\mathbf{30a}^+$ was obtained as triflate salt by Grützmacher and co-workers from the reaction of diphosphene **31a** (R = ^{t}Bu) with a 35-fold excess of MeOTf in CH_2Cl_2 as solvent (**Sch. 10**)[35]:



Sch. 10. Diphosphenes **31a,b** can only be methylated by very strong methylation agents to form diphosphenium cations $\mathbf{30a,b}^+$.

The same reaction with the very electron deficient diphosphene **31b** (R = CF_3) does not form the related cation $\mathbf{30b}^+$ (R = CF_3) even in boiling neat methyl triflate. However, the methylation succeeds in liquid $SO_{2(l)}$ with very strong methylation reagents of the type $R[CHB_{11}Me_5X_6]$ (R = Me, Et, ^{i}Pr; X = Br) introduced by Reed *et al.* (**Sch. 10**).[36] This class of potent electrophilic "R^+" alkylating agents uses the weakly nucleophilic carborane anions $[CHB_{11}Me_5X_6]^-$ (X =Cl, Br) as leaving groups. In this way the Reed group managed to transform alkanes into carbenium ions *via* hydride abstraction below room temperature or to methylate electron deficient phosphorus compounds that are otherwise inert to conventional alkylating agents such as methyl triflate. The mixture of $Me[CHB_{11}Me_5Br_6]$ and diphosphene **31b** (R = CF_3) in $SO_{2(l)}$ was studied by NMR-spectroscopy revealing an AX spin system of $\mathbf{30b}^+$ with chemical shifts at 260 and 279 ppm typical for the tri- and di-coordinate phosphorus atoms, respectively and significantly upfield shifted compared to diphosphenes that typically display resonances at very low field (e.g. **31a** (R = ^{t}Bu): $\delta = 495$ ppm). The large coupling constant of $^1J(PP) = 610$ Hz confirms the direct connectivity. Similar values have been obtained for $\mathbf{30a}^+$. 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 $\mathbf{30a}^+$ (2.024(2) Å). Attempts to deprotonate cation $\mathbf{30a}^+$ with Et_2NH as a base did not yield the expected ylide but resulted in the formation of the diphosphirane **32** (**Sch. 11**).[35] The targeted product would have been well comparable to both bis(alkylidene)phosphoranes, and bis(imino)phosphoranes. For those compound classes a thermally induced conrotatory electrocyclic reaction according to the Woodward-Hoffmann rules has been suggested earlier on the base of theoretical and experimental results.[37]



Sch. 11. Formation of diphosphirane **32** by deprotonation of **30a**[OTf].

Bonding motif D

Phosphanidophosphanes or diphosphan-1-ide ions belong to the bonding motif **D** and are the anionic congeners in the **σ^2–σ^3** category of P−P bonded phosphorus compounds. Surprisingly little is known about this class of compounds, unless considering phosphorus rich oligo- and polyphosphides. This might be due to their high tendency towards condensation reactions. Baudler *et al.* extensively described the reaction of P_2H_4 in liquid ammonia. They stated that the initial step represents the deprotonation by an amide anion.[38] The resulting $P_2H_3^-$ anion in turn again attacks diphosphane and initiates a cascade of disproportionation and aggregation reactions. Under evolution of PH_3 gas the reaction ultimately leads to the formation of phosphorus rich anions which are only slightly nucleophilic and do not tend to incorporate further diphosphane. Interestingly the formation of a large number of different Zintl type anions such as $[P_7]^{3-}$, $[P_{14}]^{4-}$, $[P_{16}]^{2-}$, $[P_{19}]^{3-}$, $[P_{21}]^{3-}$, $[P_{22}]^{4-}$ and $[P_{26}]^{4-}$ is observed.[23] The reaction of P_2H_4 in ammonia in the presence of solvents such as THF yields hydrogen phosphides of which the selected examples $[H_3P_3]^{2-}$,[39] $[H_8P_7]^-$, $[H_4P_7]^-$, $[H_5P_8]^-$,[40] $[HP_7]^{2-}$[41] and $[H_2P_7]^{-}$[42] are depicted in **Fig. 4**.

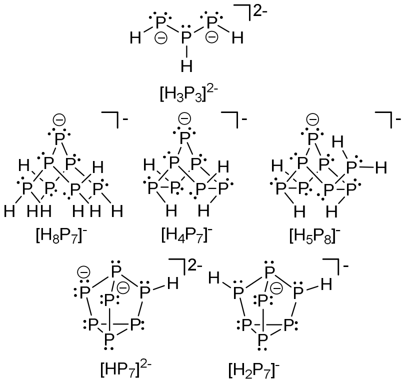
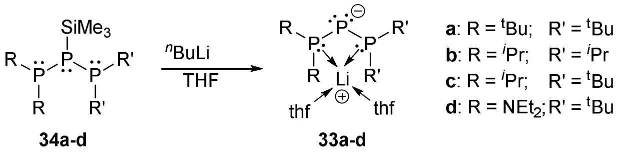


Fig. 4. Selected examples of protonated oligophosphides.

The degradation and aggregation pathways of white phosphorus in the presence of nucleophiles are of unquestionable complexity. Therefore, the underlying mechanisms, in which the phosphanylphosphanide 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]



Sch. 12. Upon treatment with ^{n}BuLi the silylated triphosphanes **34a-d** form bis-phosphanyl substituted lithium phosphanides **33a-d**.

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 (**Sch. 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 $[P(PR_2)_2]^-$ 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 $[Na(solv)_x]_2$[**34**] as representative example showing the characteristic M_2P_2 arrangement found in solid state structures of bis(alkali metal)-*catena*-oligophosphane-α,ω-diides $[M_2(solv)_x(R_nP_n)]$ (M = Li, Na, K; n = 2, 3, 4; R = Ph, Mes, ^{t}Bu; solv = solvent molecule or ligand). The formation of such bicyclobutane-shaped ion triples is found frequently for dianions as a result of a minimized net electrostatic energy. Four attractive Coulombic interactions ($r_{+,-}$) are opposed by only two repulsive ones ($r_{+,+}$ and $r_{-,-}$).

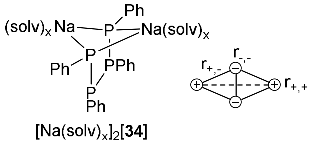
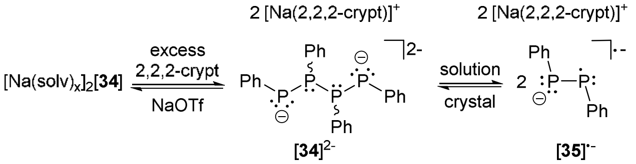


Fig. 5. Schematic view of the tetraphosphane-1,4-diide $[Na(solv)_x]_2$[**34**] showing the characteristic bicyclobutane-shaped M_2P_2 arrangement (left); illustration of point charges and coulombic interactions (right).

The group of Grützmacher reported an unexpected result from the removal of this charge-stabilizing cation anion contacts by the reaction of $[Na(solv)_x]_2$[**34**] with the cation sequestering ligand 2,2,2-crypt (**Sch. 13**).[45c, d] The yellow solution immediately turns to red-orange upon addition of 2,2,2-crypt accompanied by precipitation of a red, quickly crystallizing oil giving red (*meso* diastereomer) and yellow crystals (*rac* diastereomer) of $[Na(2,2,2\text{-crypt})]_2$[**34**].



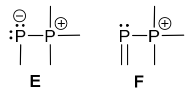
Sch. 13. The sodium ions of $[Na(solv)_x]_2$[**34**] can be sequestrated by 2,2,2-crypt. In solution the product splits into two radical anions [**35**]$^{\bullet-}$. Only one resonance structure of [**35**]$^{\bullet-}$ shown.

As may be expected the P_4-chains in both diastereomers adopt a 1,4-*anti*-conformation due to electrostatic repulsion. Interestingly, the dissolution of the slightly soluble crystals yields an orange solution which contains free diphenyldiphosphene radical anions [**35**]$^{\bullet-}$ resulting from the homolytic cleavage of the central P−P bond in [**34**]$^{2-}$. The radical anions exhibit a strong EPR signal (g = 2.0089) with a triplet splitting (a_{iso}[P] = 115 MHz) resulting from two identical phosphorus nuclei. Further hyperfinecoupling to two non-equivalent ortho-protons (a_{iso}[H] = 8.5 MHz , a_{iso}[H'] = 4.0 MHz) indicates a hindered rotation of the phenyl groups on the EPR time scale along with a certain degree of π-type delocalization. Furthermore, the group of Grützmacher could show a complete reversibility of both reactions. Upon concentration of solutions of [**35**]$^{\bullet-}$ again crystals of $[Na(2,2,2\text{-crypt})]_2$[**34**] are obtained and the addition of $[Na(2,2,2\text{-crypt})]_2$[**34**] to a solution of NaOTf in THF reforms the ion triple $[Na(solv)_x]_2$[**34**]. Since the P−P bond lengths of the unstabilized

$[Ph_4P_4]^{2-}$-chains (central P−P: 2.224(2) Å, terminal P−P: 2.178(1) Å) in crystals of $[Na(2,2,2\text{-crypt})]_2$[*meso*-**34**] refer to normal single bonds they reasoned that the dissociation process into radical anions must originate from the Coulombic repulsion. Similarly, the P−P bond cleavage leading to $[P_2Mes_2]^{\cdot-}$ radical anions was also reported by another group to occur in concentrated THF solutions of the singly protonated species [K(18-crown-6)]$[P_4HMes_4]$. In contrast to solutions of the dianions, $[P_4HMes_4]^{\cdot-}$ was found to undergo redistribution reactions forming complex mixtures of neutral and anionic species.[46]

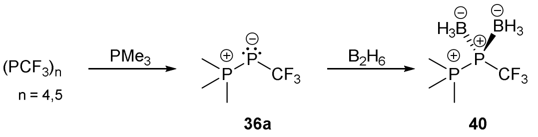
σ^2-σ^4

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



Bonding motif E

Bonding motif **E** comprises a large variety of zwitterionic phosphoniophosphanides. They represent the phosphorus analogues of alkylidene-σ^4-phosphoranes (R_2C^-–P^+R_3) or Wittig reagents and are thus called phosphanylidene-σ^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 Me_3PPCF_3 adduct (**36a**) resulting from the reaction of PMe_3 and cyclic $(PCF_3)_n$ (n = 4, 5; **Sch. 14**).[47] Only very few examples are known (e.g. **36b,c** (b: R = Mes, c: R = Mes*),[48] **37**,[49] **38**[50] and **39**[51]) and synthetically accessible in their free form (**Fig. 6**). They are mainly obtained as transition metal-stabilized compounds (L_nM-P(R)-PR_3) which are employed for P=C bond formation alternatively to terminal phosphinidene complexes R–P=ML_n (For reviews see [25b, 25c, 52a-f]; for a recent example of reversible phosphinidene transfer to triarylphosphine see [52g]).



Sch. 14. Deoligomerization of cyclophosphanes to phosphanylidene-σ^4-phosphorane **36a** and subsequent bis-borane adduct formation.

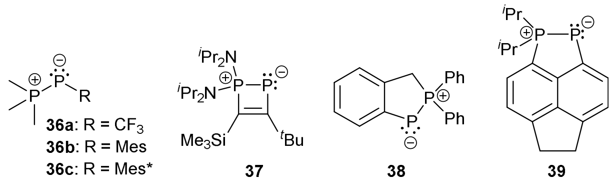
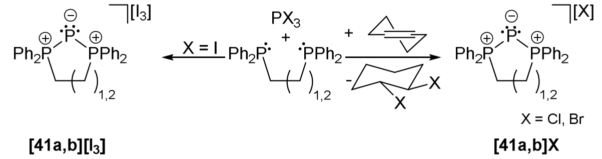


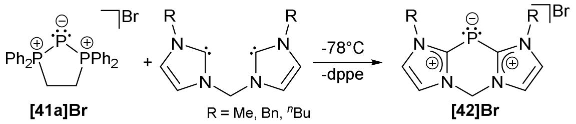
Fig. 6. Examples of zwitterionic phosphoniophosphanides comprising bonding motif **E**.

The known free phosphanylidene-σ^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 σ^2-phosphorus moiety in order to stabilize them kinetically and prevent di- or oligomerization.[48, 53] The *peri*-substituted compound **39** is sterically less encumbered than previous examples. Similar to the BH_3 adduct **40** which is obtained from the reaction of **36a** with B_2H_6 in Et_2O (**Sch. 14**), the bis-borane adduct **39**·2 BH_3 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.[51] 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 triphosphenium cations and phospha-derivatives of *cyclo*-phosphazenes as their cyclic congeners. Cyclic triphosphenium 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 PX_3 (X = Cl, Br, I; **Sch. 15**).[9, 55]



Sch. 15. Synthesis of triphosphenium ions $[\mathbf{41a,b}]^+$ from PX_3 and bidentate phosphanes.



Sch. 16. Transfer of P^+ from $[\mathbf{41a}]^+$ onto bis-NHC to give $[\mathbf{42a}]^+$.

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, triphosphenium ions are a topic of great interest as they serve as both potential two- or four-electron donor ligands in transition metal complexes[57] and as source of P^+. Especially the latter allows for the synthesis of fused tricyclic 2-phosphaallylic cations such as $\mathbf{42}^+$ which are derived from a convenient one-pot reaction of chelating bis-NHC (R = Me, Bn, ^{n}Bu) and [**41a**]Br (**Sch. 16**). Calculations confirm that these species are best considered as carbene-ligated P(I)-ions.[58]

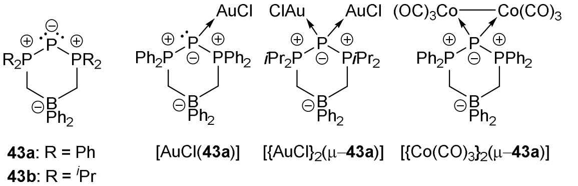
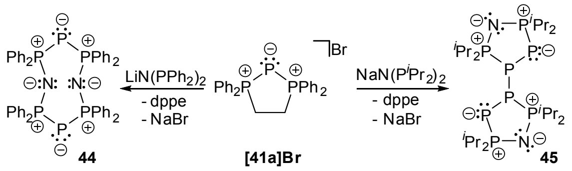
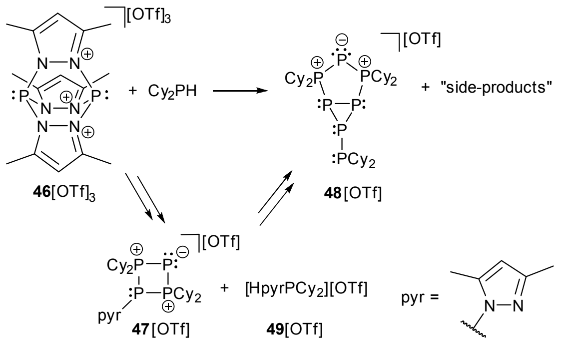


Fig. 7. Zwitterionic triphosphenium derivatives **43a,b** (a: R = Ph, b: R = ^{i}Pr) and selected coordination complexes with AuCl and $[Co(CO)_3]_2$.

Cyclic triphosphenium 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-back-bonding from the central phosphorus atom to the adjacent phosphonio moieties lowers the HOMO energy and therefore restrains coordination. Although metal complexes with cationic triphosphenium 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 = ^{i}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**)], [{AuCl}$_2$(μ-**43a**)], [{Co(CO)$_3$}$_2$ (μ-**43a**)]; **Fig. 7**).[57a] The bromide salts proved to be suitable precursors for metathesis reactions. Accordingly, formation of phosphorus-rich oligomers by P$^+$-transfer is observed when triphosphenium cation **41a**[Br] is treated with LiN(PPh$_2$)$_2$. 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(P^{i}Pr$_2$)$_2$ 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 (**Sch. 17**).



Sch. 17. Formation of phosphorus-rich oligomers **44** and **45** by P$^+$-transfer from **[41a]**$^+$ onto bis(phosphanyl)amides.



Sch. 18. Formation of cyclic (**47**$^+$) and bicyclic (**48**$^+$) cationic polyphosphorus frameworks comprising the triphosphenium motif. Equation is not balanced.

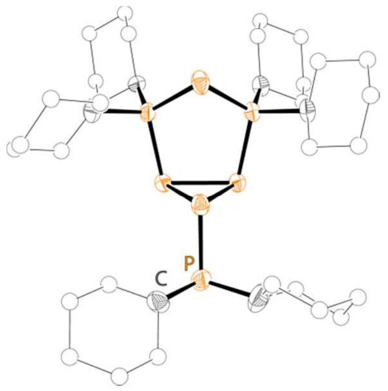


Fig. 8. Molecular structure of cation **48**$^+$ in **48**[OTf]; hydrogen atoms and anion are omitted for clarity, ellipsoids at 50% probability.

The readily available Janus-head type diphosphorus compound **46**[OTf] (pyr = 3,5-dimethylpyrazole) is an attractive precursor for the construction of cationic ring and cage systems.[8b, 62] The stepwise reaction of **46**[OTf] with Cy$_2$PH gives the two novel cationic polyphosphorus frameworks [Cy$_4$P$_4$pyr]$^+$ (**47**$^+$) and [Cy$_6$P$_7$]$^+$ (**48**$^+$) as well as **49**[OTf] as one of the isolated side-products (**Sch. 18**).[63] Cations **47**$^+$ and **48**$^+$ (**Fig. 8**) feature di-, tri- and tetracoordinate phosphorus atoms derived from P$_1$-synthons *via* a one-pot multiple P−P bond formation and represent the first examples of a $\boldsymbol{\sigma^2}$–$\boldsymbol{\sigma^4}$–$\boldsymbol{\sigma^3}$ 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.[62a, b]

Bonding motif F

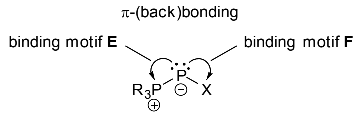
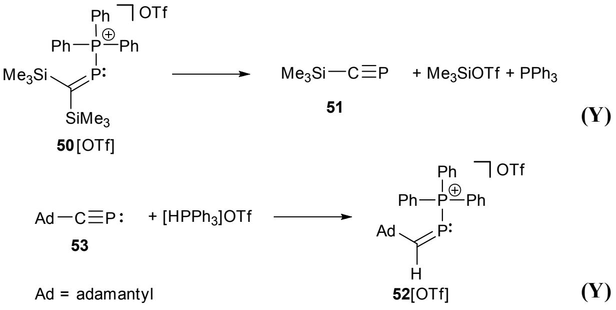


Fig. 9. Illustration of π-(back)bonding in $\boldsymbol{\sigma^2}$-$\boldsymbol{\sigma^4}$ phosphorus compounds.

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

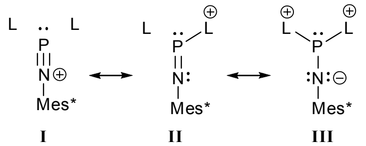


Sch. 19. The phosphonio-phosphaalkene **50**$^+$ decomposes giving phosphaalkyne **51**. In a reverse reaction **53** and triphenylphosphonium triflate form phosphonio-phosphaalkene **52**[OTf].

A typical representative of bonding motif **F** was synthesized by Niecke et al. already in 1994.[64] The phosphonio-phosphaalkene or triphenylphosphane stabilized methylenediylphosphenium ion **50**$^+$ as tetrachloroaluminate salt **50**[AlCl$_4$] remains unchanged in solution, whereas **50**[OTf] decomposes quantitatively into phosphaalkyne **51** under elimination of Me$_3$SiOTf and PPh$_3$

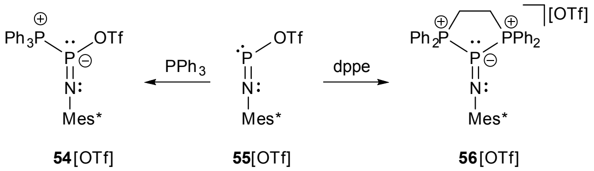
(**Sch. 19**). A reaction proceeding in the reverse manner has been reported in which the phosphonio-phosphaalkene **52**$^+$ is formed by a 1,2-addition reaction of [HPPh$_3$]OTf to the bulky adamantyl-substituted phosphaalkyne **53**.[65] Further reactions of phosphaalkynes leading to comparable derivatives 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**.[28] 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 iminophosphenium 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 π-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**.



Sch. 20. Representative resonance structures **I-III** illustrating the bonding situation in phosphadiazonium ions (Mes*NP)$^+$. L can be a neutral ligand/donor or a counterion.

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** (**Sch. 20**). Although it was frequently described as a cation with a **σ^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*^{2} in well-stabilized to *sp* in poorly stabilized (Mes*NP)$^+$ derivatives. Mes*NPCl is best described as covalent chloroiminophosphane (**II**) with a **σ^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*^{2}-imine thus indicating a starting transition to an iminophosphenium ion.[67] If X is a weakly coordinating anion such as [AlCl$_4$]$^-$ 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)[7] 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) 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]



Sch. 21. Reaction of lewis acidic **55**[OTf] with PPh$_3$ and dppe to yield P−P bonded compounds **54**[OTf] and **56**[OTf].

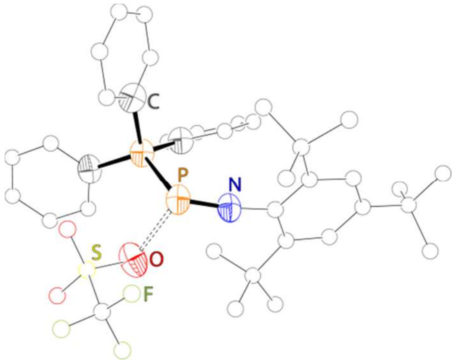


Fig. 10. Molecular structure of **54**[OTf]; Hydrogen atoms omitted for clarity.

Returning to compound **54**[OTf] which is obtained by addition of PPh$_3$ to **55**[OTf], the crystal structure comprises a central **σ^3** phosphorus atom which adopts a distorted trigonal pyramidal geometry (**Sch. 21**, **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 PPh$_3$ 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 [AlCl$_4$]$^-$ in **54**[AlCl$_4$] effects a stronger fixation of the PPh$_3$ substituent and allows the observation of two doublets in the ^{31}P NMR spectrum (δ(NP) = 87 ppm, δ(PPh$_3$) = 22 ppm, ^1J(PP) = 340 Hz).[70]

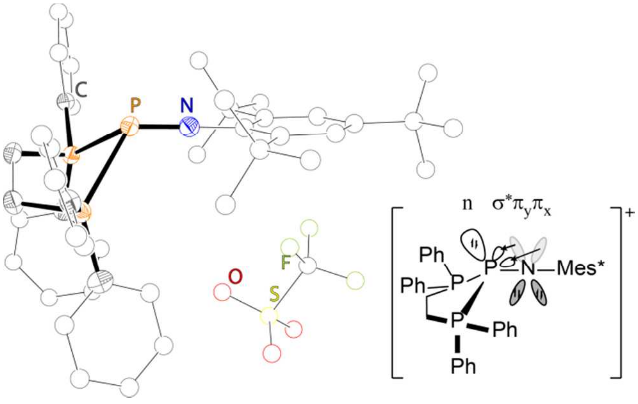
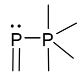


Fig. 11. Molecular structure of **54**[OTf]; Hydrogen atoms omitted for clarity (left); Illustration of negative hyperconjugation in **56**[OTf].

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] (**Sch. 21, 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 **σ^3** 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, ^1J(PP) = 492 Hz, δ(dppe2) = 10.3 ppm, ^1J(PP) = 419 Hz). The coordination environment at the distorted trigonal pyramidal P atom may be rationalized by the occupied π_x- and π_y-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 phosphane stabilized phosphenium or phosphanylphosphonium ions which belong to bonding motif **J** (*vide infra*).

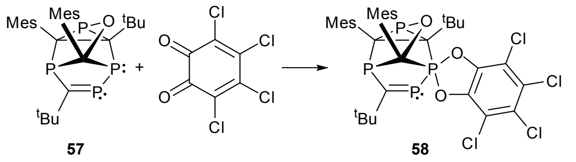
σ^2-σ^5



G

Bonding motif G

Examples of a dicoordinate phosphorus atom adjacent to a pentacoordinate phosphorus atom are very rare. We believe that up to date maybe 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 phosphanylphosphaalkene 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 **σ^3**-phosphorus atom to give compound **58** (**Sch. 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]



Sch. 22. Oxidative addition of *o*-chloranil to phosphanylphosphaalkene **57** yielding a rare example (**58**) comprising bonding motif **G**.

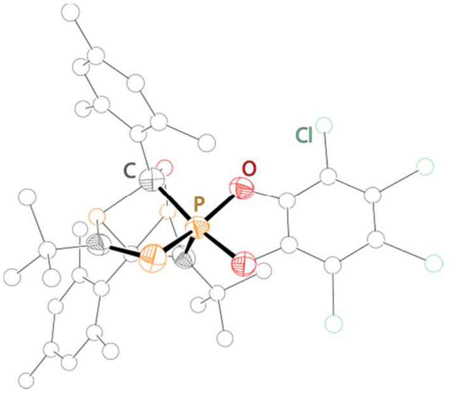
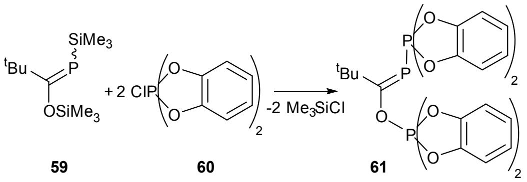


Fig. 12. Molecular structure of compound **58**; hydrogen atoms are omitted for clarity, ellipsoids at 50% probability.

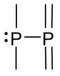
Treatment of silylated phosphaalkene **59** with the chlorobis(catecholato)phosphorane **60** yields another example of a compound (**61**) featuring a **σ^2–σ^5** bonding motif. The reaction is accompanied by the formation of two eq. of Me_3SiCl and the product can be obtained in 80 % yield after recrystallization (**Sch. 23**). Characterization of this compound included NMR, IR and elemental analysis[73] and evidence of the structural arrangement was supported from the same group recently by a computational study 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) *E*-configuration.[74]



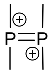
Sch. 23. Condensation of silylated phosphaalkene **59** and chlorophosphorane **60** giving **61** which features the rare **σ^2–σ^5** bonding motif **G**.

σ^3-σ^3

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



H



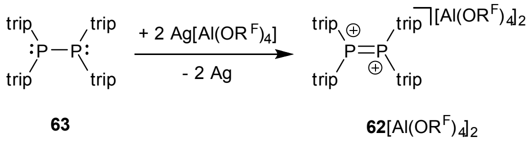
I

Bonding motif H

This substance class contains compounds in which a phosphanyl moiety is linked to a σ^3-phosphorane. Predominantly in the early 1990’s phosphanyl-bis(imino)phosphoranes and phosphanyl-bis(alkylidene)phosphoranes have been studied and discussed elsewhere.[37a, 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^2–σ^3** phosphanylphosphenium ions (bonding motif **C**) and the difficulties in accessing them, the necessity to employ a weakly coordinating anion such as $[Al(OR^F)_4]^-$ ($R^F = C(CF_3)_3$) seems obvious. The red dication **62**$^{2+}$ was obtained after two single electron oxidation steps with $Ag[Al(OR^F)_4]$ from the parent diphosphane **63** *via* the radical monocation (trip = 2,4,6-triisopropylphenyl; **Sch. 24**). The ^{31}P NMR resonance at 168.8 ppm is shifted to even higher field than that of the related phosphanylphosphenium ions (**30**$^+$). 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**).



Sch. 24. Oxidation of very bulky diphosphane **63** with silver salt of a very weakly coordinating anion yielding **62**$^{2+}$, the only reported example of a diphosphenium dication.

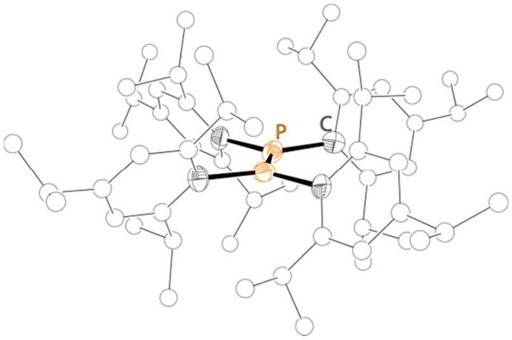
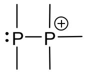


Fig. 13. Molecular structure of the diphosphenium dication **62**$^{2+}$; hydrogen atoms are omitted for clarity, ellipsoids at 50% probability.

σ^3-σ^4



J

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

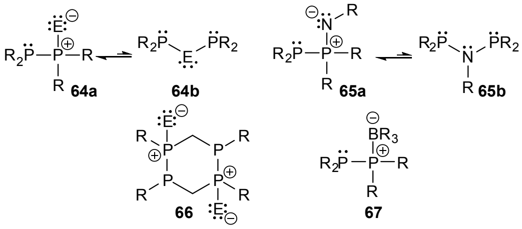
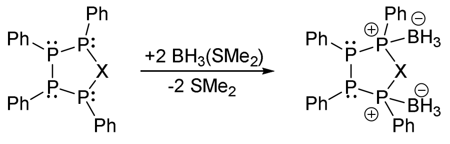


Fig.14. Selected examples of neutral derivatives **46-49** comprising bonding motif **J**.

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 tautomer 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 (NR_2) or mixtures of both equilibria between **64a** and **64b** are observed in certain cases depending also on steric demand.[78] However, it has been shown that the introduction of strongly electron-withdrawing substitutents such as fluoride,[79] trifluoromethyl- (CF_3)[80] or 2,4-bis(trifluoromethyl)phenyl- ($2,4-(CF_3)_2C_6H_3$) groups stabilize the anhydrides of the phosphinous acids.[81] The bis(bis(trifluoromethyl)phosphanyl) oxide, $(CF_3)_2P–O–P(CF_3)_2$, is stable with respect to its corresponding phosphane oxide tautomer, however, it deflagrates readily on contact with air. Hoge *et al.* succeeded to synthesize and crystallographically characterize the $(2,4-(CF_3)_2C_6H_3)_2P–O–P(2,4-(CF_3)_2C_6H_3)_2$ derivative (δ = 105.6 ppm, ^{31}P NMR in $CDCl_3$) but also observed small quantities of the isomeric diphosphane monoxide $(2,4-(CF_3)_2C_6H_3)_2P(O)–P(2,4-(CF_3)_2C_6H_3)_2$ in the reaction, identified by its characteristic resonance in the ^{31}P NMR at 39 ppm for the oxygen-bonded phosphorus atom and −32.5 ppm for the trivalent phosphorus atom (^1J(PP) = 247 Hz).[81] The stability of **64a** is significantly 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 diphosphane disulfides,[82] oxidation reactions of diphosphanes with elemental sulfur,[83] or comproportionation reactions of diphosphanes and diphosphane disulfides.[83a, 84] The reaction of sodium thiophosphinites with R_2PCl has also been applied for the formation of compounds of type **64a**.[85] All these approaches are either not very selective, low-yielding or require harsh condition. Recently, Morris *et al.* presented a convenient approach for the preparation of derivatives of **64a** (R = Ph, Cy; E = S) by reacting R_2PCl with Li_2S. In a subsequent isomerization reaction the rarely reported di(phosphanyl) sulfides (**64b**; E = S) were obtained and used as ligands in ruthenium coordination complexes.[86] To the best of our knowledge, synthetic protocols for diphosphane monoselenides (**64a**; E = Se) and -tellurides (**64a**; E = Te) are unreported. Only very few derivatives (R = ^{t}Bu, R_2N) 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[88] have found applications in organic synthesis[89] or as ligands in transition metal complexes.[90] However, the chemistry of the related iminodiphosphanes of the general structure **65a** is only scarcely developed (**Fig. 14**).[91] They are isolectronic to the diphosphane monochalcogenides **64a** and are also tautomers of the more commonly encountered di(phosphanyl)amines **65b** with an $R_2P–NR–PR_2$ skeleton.[92] Similar to the rearrangement of **64a** to **64b**, a transformation of compounds of type **65a** to **65b** has been shown to take place upon coordination to transition metals.[93]

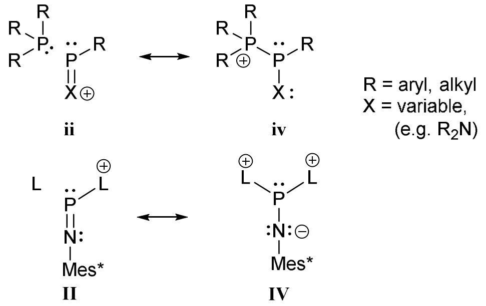
Research directed towards the oxidation of cyclophosphanes with chalcogens[94] leads to the formation of product mixtures, as exemplified in the reaction of $(PPh)_5$ with a deficiency of selenium in which one or two [PPh] units of the cyclophosphane are formally replaced by Se atoms.[95] The oxidation of *cyclo*-1,4-$(CH_2)_2(P^tBu)_4$ with chalcogens showed that the two antipodal CH_2 units of the starting material provide structural braces that allow dichalcogenation to occur without disruption of the six-membered C_2P_4 ring giving dichalcogenated derivatives such as the 2,5-isomers **66** (**Fig. 14**, R = ^{t}Bu; E = S, Se).[96] Density functional theory (DFT) calculations for the 2,5-chalcogenated derivatives **66** (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 A°) in the cyclic dications is indicated by geometry and consideration of the frontier orbitals.[97] Boron adducts of diphosphanes of type **67** comprising bonding motif **J** are very scarce and only very few reports are known.[98] However, borane complexes of cyclooligophosphanes 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 *cyclo*-$(PR)_n$ (R = Et, ^{n}Pr, ^{n}Bu, Ph)[99] with boron trihalides were recently complemented by the group of Hey-Hawkins. They investigated the adduct formation of *cyclo*-oligophosphanes *cyclo*-$(PPh)_5$ (**68a**) and *cyclo*-$(P_4Ph_4CH_2)$ (**68b**) in the reaction with $BH_3(SMe_2)$ to form complexes **69a,b** (**Sch. 25**). The latter complex **69b** is of particular interest since they reasoned that the coordination of the borane facilitates the formation of the respective tetraphosphacyclopentanide anion.[100] In their findings they concluded that the complexes **69a,b** are readily formed from the 1:2 reaction of **68a,b** with BH_3. The formation of adducts with a higher ratio of BH_3 per molecule appears to be disfavoured. The position of the BH_3 moieties in the *cyclo*-phosphane rings indicates a comparable high nucleophilicity of the respective P atoms in both cases. In solution, derivative **68a** forms a mixture of two diastereomers which are related to each other by inversion of the tricoordinate P atoms, while a complex mixture of isomers is observed for **68b**.



68a: X = PPh
68b: X = CH$_2$
69a: X = PPh
69b: X = CH$_2$

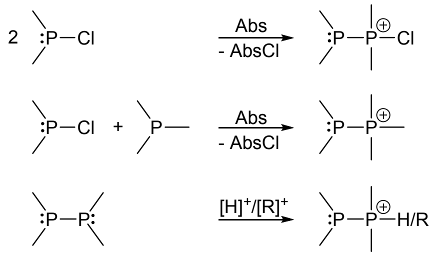
Sch. 25. Formation of bis(borane) adducts of cyclophosphanes.

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 (**iv**, **Sch. 26**). According to another resonance structure they are also termed phosphane stabilized phosphenium ions (**ii**). The question whether the σ^3–σ^4 P–P bond possesses rather a covalent or a dative character was theoretically investigated by Pietschnig.[101] Calculations (MP2/6-311G(d)) on a model system (R = Me, X = Me or NH_2; Fig Y) revealed that according to Wiberg bond indices (0.867 for X = Me, 0.807 for X = 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 π-donating amino substituent. As already discussed in the context of phosphadiazonium ions (bonding motif **F**, **Sch. 20**) an efficient π-stabilization diminishes the necessity for stabilization by additional substituents/donors and may thus lead to a lower coordination number at the P atom. It is therefore not surprising that, to the best of our knowledge, no examples of isolated σ^2 phosphenium ions without a π-donating substituent have been reported.



Sch. 26. Resonance structures describing a phosphane stabilized phosphenium ion (**ii**) and a phosphanylphosphonium ion (**iv**). Resonance structures **II** and **IV** from **Sch. 20** are illustrated for reasons of comparison.

Basically independent of the nature of the P–P bond in a wide range of phosphanylphosphonium ions, the σ^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.[102] Catenated and cyclic polyphosphanylphosphonium salts are most intensely studied within this diverse group of cations.[103] Typically phosphanylphosphonium cations can be accessed from either the reaction of a chlorophosphane with a halide abstracting agent (Abs) (**Sch. 27**, top), the reaction of a chlorophosphane, a phosphane and a halide abstracting agent (**Sch. 27**, middle) or by protonation or alkylation of a diphosphane (**Sch. 27**, bottom).



Sch. 27. Synthesis of phosphanylphosphonium ion by P–P bond formation in the presence of a halide abstracting agent (top, middle) or protonation/alkylation of diphosphanes (bottom).

A library of crystallographic data for several derivatives[104] 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**.[102c, 105] They offer new synthetic approaches, not only for P−P bond formation, but also for other aspects in synthesis.[106] Phosphanylphosphonium cations with two phosphorus atoms typically exhibit two well separated doublets in ^{31}P NMR spectra with the high field shifted resonance corresponding to the tricoordinate phosphorus atom and the low field shifted to the tetracoordinate phosphorus atom. ^1J(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.

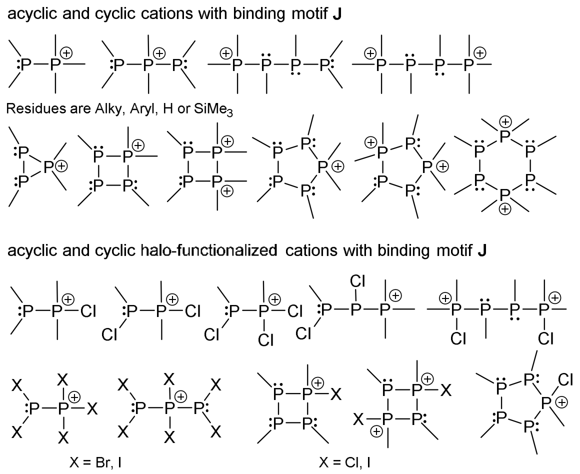
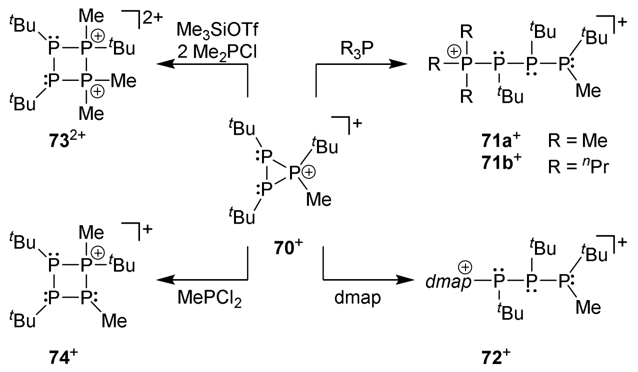
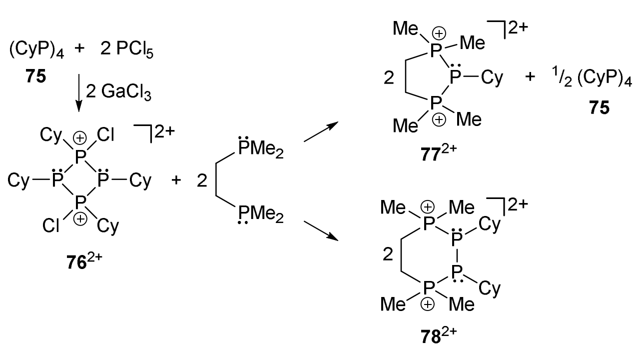


Fig. 15. Selected examples of acyclic and cyclic phosphanylphosphonium cations comprising bonding motif **J**.



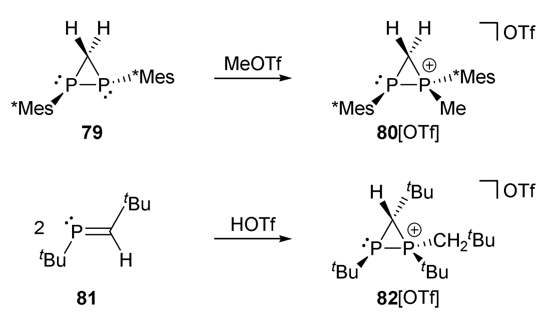
Sch. 28. Diverse reactivity of cation **52**$^+$ in the reaction with a series of nucleophiles such as Me_2PCl, $MePCl_2$, R_3P and dmap (4-(dimethylamino)pyridine).

The prototypical phosphanylphosphonium 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 polyphopshorus frameworks.[105d, e] Cation **70**$^+$ readily reacts with Lewis bases such as 4-(dimethylamino)pyridine (dmap) and phosphanes (R_3P), providing approaches to new open-chain and cyclic phosphorus frameworks (**Sch. 28**). Upon reaction with R_3P (R = Me or ^{n}Pr) or dmap the three-membered ring is opened to yield the adducts [R_3P–P^{t}Bu–P^{t}Bu–P(Me)^{t}Bu][OTf] (R = Me (**71a**$^+$), ^{n}Pr (**71b**$^+$)) and [(dmap)–P^{t}Bu–P^{t}Bu–P(Me)^{t}Bu][OTf] (**72**$^+$). The complicated ^{31}P{^{1}H} NMR spectra of the three compounds were simulated, evidencing the presence of two diastereomeric forms of **71a**$^+$, and a single diastereomer of **71b**$^+$. This ring-opening reactivity of the cation **70**$^+$ parallels the reactivity of isolobal epoxides with nucleophiles under acidic conditions. The reaction with Me_2PCl and Me_3SiOTf resulted in the unexpected formation of dication **73**$^{2+}$, which is postulated to result from two consecutive ring-opening and ring-closing steps. In contrast, employing $MePCl_2$ in the reaction, cation **74**$^+$ is formed from a formal insertion of a “MeP” moiety into the cationic phosphorus framework of **70**$^+$.[107]



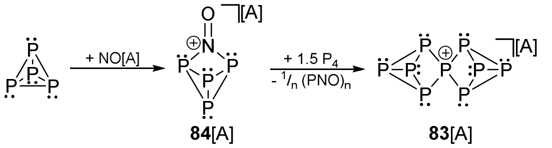
Sch. 29. Synthesis of cyclo-phosphanylchlorophosphonium cation **76**$^{2+}$ (left) and release of [PCy]$^{2+}$ (top right) or [P_2Cy_2]$^{2+}$ fragments (bottom right).

Related to this chemistry is the chlorination of *cyclo*-tetraphosphane **75** by PCl_5 in the presence of the Lewis acid $GaCl_3$ which provides a stepwise approach to salts of the first *cyclo*-phosphanylchlorophosphonium cations [Cy_4P_4Cl]$^+$ and [$Cy_4P_4Cl_2$]$^{2+}$ (**76**$^{2+}$, (**Sch. 29**).[106,108] Reactions of the dication **76**$^{2+}$ with dmpe effect a dissociation of the cyclic framework resulting in the formation of the cyclic cations **77**$^{2+}$ and **78**$^{2+}$ with an extended ring size. The new cations represent phosphane complexes that are formed from **76**$^{2+}$ which dissociates formally via a retro [2+2] or [1+1+1’+1’] process releasing cationic [PCy]$^{2+}$ and [P_2Cy_2]$^{2+}$ fragments, demonstrating the partially coordinative nature of the **σ^3–σ^4** P−P bonds in *cyclo*-phosphanylhalophosphonium cations.[106]



Sch. 30. Synthesis of diphosphiranium cations **80**$^+$ by methylation of diphosphirane **79** (top) and **82**$^+$ by acid-induced dimerization of phospha-alkene **81** (bottom).

The methylation of the diphosphirane **79** with MeOTf allows the formation of the *P*-methylated diphosphiranium salt **80**[OTf] (**Sch. 30**, top) which has a related structure to cation **70**$^+$. This cation is only stable at low temperature in the presence of excess MeOTf.[109] Following another approach, a diphosphiranium salt is obtained *via* the cationic cyclodimerization of a phosphaalkene **81** upon addition of HOTf (**Sch. 30**, bottom). In contrast to **80**[OTf] the diphosphiranium triflate **82**[OTf] showed sufficient stability in solution to be isolated and crystallographically characterized. The P−P bond length of 2.1637(5) Å corresponds to a slightly shortened single bond and the strain in the P_2C ring is reflected by the small internal ring angles ($\boldsymbol{\sigma^3}$-P: 52.69(4)°, $\boldsymbol{\sigma^4}$-P: 55.82(5)°, C: 71.49(5)°).[110]



Sch. 31. Synthesis of the first homoleptic polyphosphorus cation **83**$^+$ from P_4 and **84**$^+$.

The investigation of homoleptic polyphosphorus cations was limited to mass spectroscopy[111] and quantum chemical calculation[112] in the gas phase for decades. In general, P_n^+ cations that feature an even number n of P atoms are paramagnetic. They are less stable than the respective diamagnetic P_n^+ cations composed of an odd number of P atoms. A detailed discussion on polyphosphorus cations has been published.[43a, 113] The most stable cation according to quantum chemical calculations is the P_9^+-cage **83**$^+$, which is composed of two C_{2v}-symmetric P_5-cages fused by a common phosphonium moiety.[112b] Krossing *et al.* investigated the oxidation of P_4 with [NO][A] (A = $Al(OC(CF_3)_3)_4^-$) which yields $[P_4NO]^+$-cage compound **84**[A] (**Sch. 31**) via insertion of the nitrosonium cation into a P–P bond.[114] A two-step mechanism was suggested on the basis of quantum chemical calculations indicating the HOMO of P_4 and a π*-type LUMO at $[NO]^+$ as the interacting frontier orbitals.[114] The reaction of $[P_4NO]^+$-cage compound **84**[A] with additional 1.5 eq. of P_4 yields the P_9^+-cage compound **83**[A] (**Sch. 31**).[115] They suggest that cation **83**$^+$ forms via extrusion of $^1/_n$ $(PNO)_n$ and intermediary formation of a P_3^+-species. The ^{31}P NMR spectrum of cation **83**$^+$ shows a characteristic $A_2A_2'BC_2C_2'$ spin system and confirms a D_{2d} symmetric Zintl-type structure. Despite the electron precise Lewis formula of eight neutral, tricoordinate and one cationic, tetracoordinate P atom the charge is almost evenly distributed over all nine atoms according to quantum chemical calculations.[115]

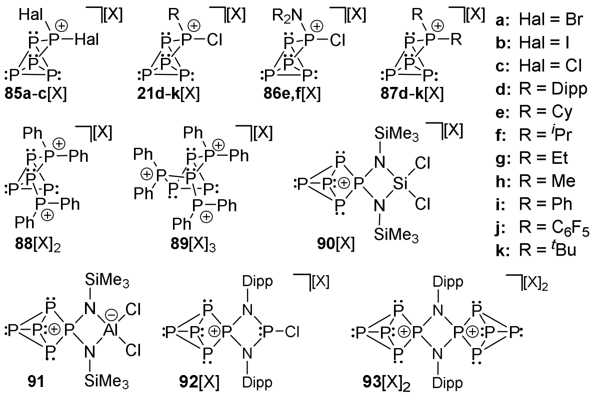


Fig. 16. Selected cationic cage compounds comprising bonding motif **J**.

The same group also reported on the first cationic polyphosphorus cages featuring halogen substituents. They obtained the salts of cage cations **85a,b**$^+$ from the reaction of the silver salt $[Ag(CH_2Cl_2)][X]$ (X = $Al(OC(CF_3)_3)_4$) with $PHal_3$ and P_4 (Hal = Br, I; **Fig. 16.**).[116,104d] Utilizing PCl_3, the formation of the respective cation **85c**$^+$ was only observed in trace amounts.[117] This reaction suffered from decomposition of the weakly coordinating anion $Al(OC(CF_3)_3)_4^-$. The structural motif of the $[P_5Hal_2]^+$-cage is unprecedented and was not observed previously as part of the many known polyphosphides and organo-polyphosphanes. The 1:1 mixtures of $RPCl_2$ and a Lewis acid ECl_3 (E = Al, Ga) in fluorobenzene are potent sources of reactive equivalents of phosphenium ions $[RPCl]^+$, which formally insert into P−P bonds of P_4.[118] Dissolution of P_4 in these mixtures yields white to yellowish precipitates of the corresponding $[RP_5Cl]^+$-cage salts for a large range of distinct alkyl- and aryl-substituents R (**21d-k**$[GaCl_4]$; **Fig. 16**; [X] = $[GaCl_4]$). This approach can also be extended to R_2N-subsituted derivatives **86e,f**$[GaCl_4]$.[119] The cationic $[R_2P_5]^+$-cage compounds **87d-k**$\boldsymbol{[GaCl_4]}$ are synthesized *via* the stoichiometric reaction of R_2PCl, $GaCl_3$, and P_4. The reaction conditions depend on the substituent R. Alkyl-substituted derivatives (**87d-h**$[GaCl_4]$) are best synthesized using a solvent free melt reaction, whereas aryl-substituted derivatives (**87i-k**$[GaCl_4]$) are formed in C_6H_5F solution (**Fig. 16**; [X] = $[GaCl_4]$). All compounds can be prepared on a multi-gram scale in good to excellent yields and are fully characterized with an emphasis on ^{31}P NMR spectroscopy in solution and single crystal structure determination. By addition of more eq. of $GaCl_3$, the melt approach can be extended to dication $[Ph_4P_6]^{2+}$ (**88**$[X]_2$; [X] = $[GaCl_4]$) and trication $[Ph_6P_7]^{3+}$ (**89**$[X]_3$; [X] = $[Ga_2Cl_7]$) *via* the consecutive insertion of up to three $[Ph_2P]^+$ fragments into the P−P bonds of the P_4 tetrahedron.[120] This approach has been extended to highly functionalized cation **90**$^+$ ([X] = $[AlCl_4]$) and the zwitterionic P_5-cage **91**, which are formed by the insertion of the corresponding phosphenium cations that are derived from four-membered phosphorus-nitrogen-metal heterocycles.[121] Similarly, the reaction of P_4 with the *cyclo*-diphosphadiazane $[DippNPCl]_2$ (Dipp = 2,6-disopropylphenyl) and $GaCl_3$ in fluorobenzene yielded compound **92**$[GaCl_4]$. The addition of an excess of $GaCl_3$ and a second eq. of P_4 to a solution of **92**$[GaCl_4]$ afforded the dicationic species **93**$^{2+}$ as $[Ga_2Cl_7]^-$ salt.[122]

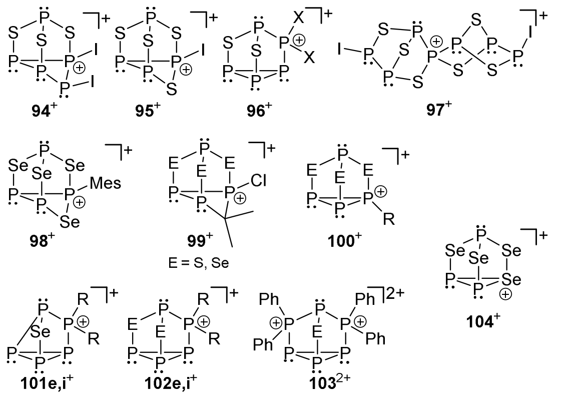
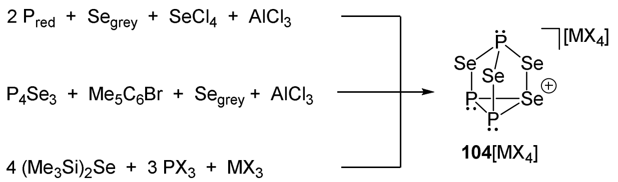


Fig. 17. Selected cationic polyphosphorus-chalcogen cages **94**$^+$-**103**$^{2+}$ (E = S, Se) comprising bonding motif **J**; $^{a)}$ cation **104**$^+$ has been included since it represents the first binary SeP-cation and is related to the other cations.

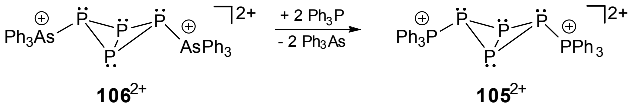
Also cationic polyphosphorus-chalcogen cages are rarely described in the literature. Until recently only two synthetic procedures were reported for their preparation. In the first approach P_4S_3 reacts with *in-situ* generated $[PI_2]^+$-phosphenium ions yielding cation **94**$^+$ which disproportionates to cations **95**$^+$ and **96**$^+$ (**Fig. 17**).[123] The second approach is based on halide abstraction from α-$P_4S_3I_2$ using Krossing's silver salt $Ag[Al(OC(CF_3)_3)_4]$ giving the spiro-cyclic cage cation **97**$^+$.[124] The formation of cations **98**$^+$ is observed in the protonation reaction of cyclic P−E-heterocycles $(MesPSe)_4$ or reaction of P_3Se_4 with $MesPCl_2$ in the presence of $AlCl_3$ as Lewis acid.[125] Reacting P_4E_3 with Me_2CCl_2 in the presence of $AlCl_3$ 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.[126] Basal alkylation of P_4E_3 is observed in the reaction with secondary alkyhalides (*sec*-RX) to give cations of the type **100**$^+$ (E = S, Se).[126]

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 derivates which are all conveniently obtained in one step procedures from white phosphorus.[127] Chalcogenation reactions of $[R_2P_5]^+$-cage compounds **87e,i**$[GaCl_4]$ with elemental grey selenium yield the corresponding polyphosphorus-chalcogen cages **102**$[GaCl_4]$ (E = Se, R = Cy, Ph; **Fig. 17**). Both cations are formed upon insertion of two selenium atoms into two P−P bonds adjacent to the phosphonium moieties in **87e,i**$^+$. Their structural motif resembles that of nortricyclane, with a basal P_3-ring, the tetracoordinate 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}P and ^{77}Se NMR characteristics. They reveal an AM_2OX spin system for the C_s-symmetric isotopomer without a ^{77}Se nucleus. These resonances are superimposed by the C_1-symmetric isotopomer featuring one ^{77}Se atom in one of the bridging positions. This gives rise to an AMNOXZ spin system which is strongly influenced by higher order effects. However, in the case of **102e**$^+$ (R = Cy), both spin systems 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 **87e,i**$^+$ proceeds in a stepwise manner *via* the intermediates **101e,i**$^+$.[127] The targeted preparation of **103**$^+$ as $[GaCl_4]^-$ salt was achieved by utilizing a 2:1 stoichiometry of **48**$^+$ and grey selenium (E =Se). Another synthetic approach for the preparation of **103**$^+$ (E = S, Se) is the targeted substitution of one $[Ph_2P]^+$-moiety in the tricationic cage **89**$^{3+}$. This was achieved by reacting **89**$^{3+}$ with grey selenium or sulfur under solvent-free conditions.[127] Dication **103**$^{2+}$ was comprehensively characterized by X-ray crystallography as well as ^{31}P and ^{77}Se NMR spectroscopy (E = Se). The polyphosphorus cation **89**$^{3+}$ and cationic polyphosphorus-chalcogen cages **103**$^{2+}$ and **102i**$^+$ are formally derived by stepwise isolobal exchange of [E] atoms by $[Ph_2P]^+$ units in the bridging positions of the nortricyclane type structure of P_4E_3 derivatives (E = S, Se).



Sch. 32. Three different approaches for the synthesis of the first binary phosphorus chalcogen cation $P_3Se_4^+$ (**104**$^+$) as metallate salt.

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 $[P_3Se_4]^+$ (**104**$^+$) 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**$^+$ were independently discovered. Cation **104**$^+$ is obtained as metallate salt **104**$[MX_4]$ (M = Al, Ga; X = 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 = Al; X = Cl, **Sch. 32**, top) or an arylation reaction of P_4Se_3 with pentamethylbromobenzene (Me_5C_6Br) in the presence of $AlCl_3$ in CH_2X_2 (M = Al; X = Cl, Br, **Sch. 32**, middle) or the addition of $(Me_3Si)_2Se$ to a solution of PX_3 and MX_3 in CH_2X_2 at ambient temperature (M = Al, Ga; X = Cl, Br, **Sch. 32**, bottom).[128] 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 Se atom in the basal plane of the adamantane-like $P_3Se_4^+$ cation presents a $^1J(^{31}P^{77}Se)$ 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.[128]



Sch. 33. AsPh$_3$ can be substituted by PPh$_3$ in the bicyclic compound **106**$^{2+}$ to give the analogous dicationic polyphosphorus framework **105**$^{2+}$.

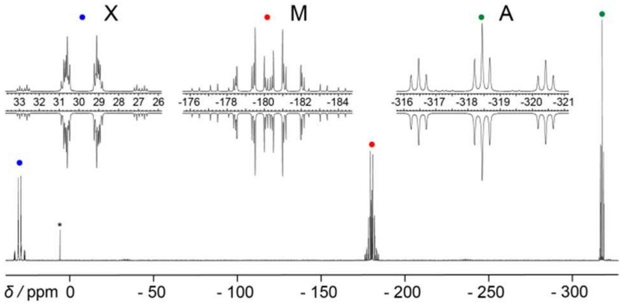
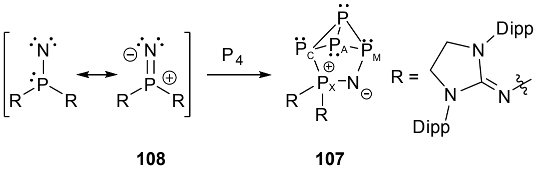


Fig. 18. ^{31}P{^{1}H} NMR spectrum of the butterfly-shaped diaction **105**$^{2+}$ (upwards) and simulation (downwards). This figure has been reproduced from Angewandte Chemistry with permission from John Wiley and Sons[129]

The symmetrical butterfly-shaped P$_6$-diaction **105**$^{2+}$ is obtained by substitution of the AsPh$_3$ moieties of **106**$^{2+}$ by PPh$_3$ (**Sch. 33**). The experimental and iteratively fitted ^{31}P{^{1}H} NMR spectrum reveals an A$_2$MM'XX' spin system (**Fig. 18**). The large ^{31}P–^{31}P coupling constants observed in **105**$^{2+}$ (^{2}J(MM') = 339 Hz, ^{3}J(MX') = −139 Hz and ^{4}J(XX') = 39 Hz) indicate a substantial degree of trough space coupling between the *cis*-orientated free-lone pairs located at each "butterfly-wing".[129]

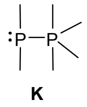


Sch. 34. Insertion of a phosphanylnitrene **108** into one edge of the P$_4$ tetrahedron giving **107**.

Bertrand *et al.* reported on the P$_5$N cage compound **107** obtained from the insertion reaction of a room temperature stable phosphanylnitrene[130] **108** into one edge of a P$_4$ tetrahedron (**Sch. 34**). The zwitterionic cage compound **107** reveals an A$_2$CMX spin system with ^{31}P chemical shifts in the expected ranges for *endo,endo*-bicyclo[1.1.0]tetraphosphane derivatives but for one exception (δ(P$_A$) = −255.2, δ(P$_C$) = −154.4, δ(P$_M$) = 57.6, δ(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 σ*(P$_X$)- (N-P$_X$ 1.575(5) Å) as well as into the σ*(P$_M$)-orbitals (N-P$_M$ 1.614(4) Å) therefore loosening the P$_A$–P$_M$ bonds.

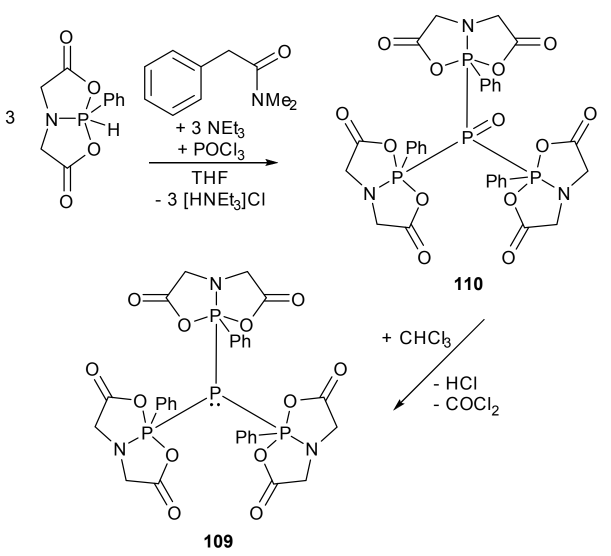
σ^3-σ^5

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



Bonding motif K

As this class of compounds was reviewed earlier,[2] we refrain from a repetition and only want to discuss two particular examples instead.



Sch. 35. Synthesis of **110** and reduction with CHCl$_3$ to triphosphoranyl-phosphane **109**.

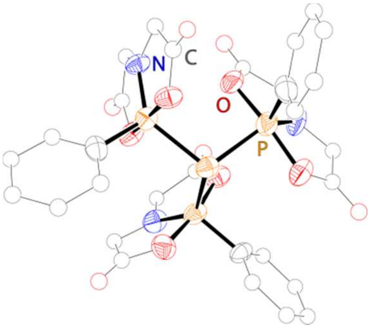
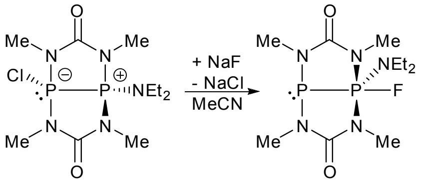


Fig. 19. Molecular structure of triphosphoranyl phosphane **109**; Hydrogen atoms omitted for clarity.

Compound **109** was obtained by reduction of the corresponding phosphane oxide **110** (bonding motif **N**) with chloroform (**Sch. 35**).[131] The ^{31}P NMR spectrum displays a complex A$_3$B coupling pattern with the **σ^5** phosphorus resonance (A-part) high field shifted with respect to the **σ^3** phosphorus resonance (B-part) (81 MHz, CDCl$_3$, δ(P$_A$) = −28.2, δ(P$_B$) = 40.9 ppm, ^{1}J(PP) = 341.3 Hz). The crystal structure of **109** (**Fig. 19**) comprises a central **σ^3** phosphorus atom bearing three **σ^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 σ^5 phosphorus atom. Since normal phosphane oxides (e.g. Ph_3PO or ^{n}Bu$_3$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 π–backbonding of the oxygen lone pairs into P based σ^*-orbitals would render the oxygen atom more nucleophilic and susceptible for the attack of a weak electrophile like chloroform.[132]



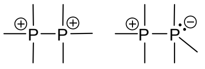
111 **112**

Sch. 36. Transformation of **111** (bonding motif **M**) into **112** (bonding motif **K**) by halide exchange.

As the urea-bridged phosphoniophosphoranide **111** (bonding motif **M**) and the phosphanyl phosphorane **112** (bonding motif **K**) have been reviewed earlier,[133] we only want to mention one interesting aspect which points out how closely related the two bonding motifs **K** (σ^3–σ^5) and **M** (σ^4–σ^4) 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 (**Sch. 36**).[133] Thus, the σ^3–σ^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**.[134] While the initial apical P-Cl bond length (2.816 Å) is much longer compared to literature known examples (~2.3 Å)[135] and comparable to the $[PCl_4]^-$ anion,[136] the P−F distance (1.628 Å) is only slightly longer than those observed in PF_5 (1.577(5) Å).[137]

σ^4-σ^4

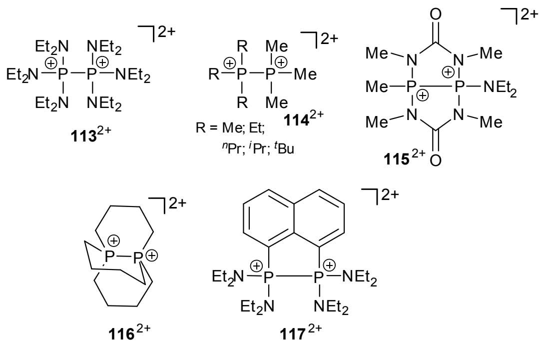
The two bonding motifs **L** and **M** describe the connectivity of two tetracoordinate phosphorus atoms that can be linked either as two phosphonium units giving a dication (**L**) or as the formally neutral phosphoniophosphoranide (**M**).



L **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**$^{2+}$)[138], unsymmetrically substituted alkyl-derivatives (**114**$^{2+}$)[139] or a polycyclic framework (**115**$^{2+}$,[140] **116**$^{2+}$ (*vide infra*),[141] **117**$^{2+}$ (*vide infra*)[142]; **Fig. 20**). Hexaalkyldiphosphonium triiodide salts were speculated as the products of reactions of red phosphorus with alkyl iodides or from trialkylphosphanes with iodine,[143] and $[Me_3PPMe_3][PF_6]_2$ (**96**$^{2+}$, R = R' = Me) has first been assigned on the basis of elemental analysis data and IR spectroscopy.[144]



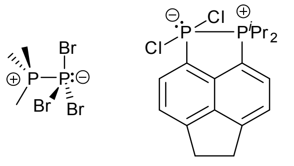
113^{2+} **114**$^{2+}$ **115**$^{2+}$ **116**$^{2+}$ **117**$^{2+}$

Fig. 20. Selected examples of diphosphonium dications comprising bonding motif **L**.

Polyphosphane adducts of electrophilic antimony,[145] thallium, copper,[144] or iron[146] acceptors are known to spontaneously eliminate diphosphonium cations $[R_3PPR_3]^{2+}$. Dialkylation of diphosphines, reductive elimation 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 diphosphoniumdications were shown to activate B–H, Si–H, C–H and H–H bonds while being part of a frustrated Lewis pair.[147]

Bonding motif M

Phosphoniophosphoranides may in principal be obtained as Lewis adducts of two phosphanes 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.



118 **119**

Fig. 21. Selected examples of compounds comprising bonding motif **M**.

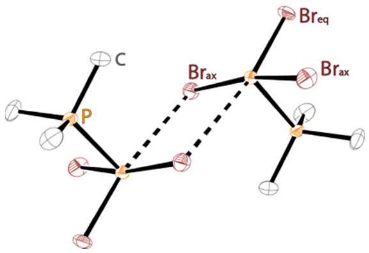
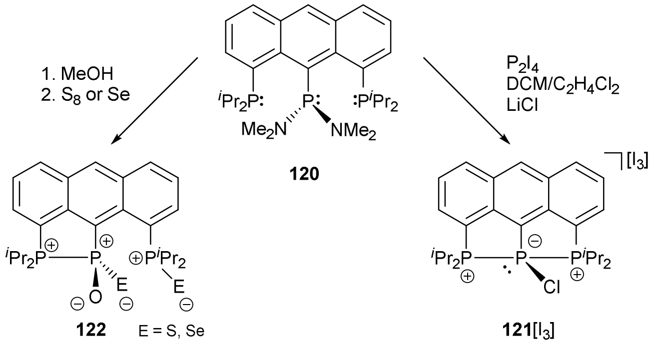


Fig. 22. Molecular structure of **118** displaying two phosphoniophosphoranide units forming a dimeric bridge; Hydrogen atoms omitted for clarity.

Reports of such intermolecular Lewis adducts between simple phosphanes go back to the 1950's.[148] 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 PMe_3 into a solution of PBr_3 in toluene (**Fig. 21**).[149] 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 PMe_3 ($\delta = -61.9$ ppm in C_6D_6) and PBr_3 (228.5 ppm in CD_2Cl_2) the resonance of the donating PMe_3 unit (P_{don}) is shifted to lower field whereas that of the accepting PBr_3 unit (P_{acc}) is shifted to significantly higher field ($\delta(P_{don}) = 29.5$ ppm, $\delta(P_{acc}) = 78.5$ ppm, $^1J(PP) = 450.3$ 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, $P–Br_{eq}$ 2.250(2) Å) correspond to single bonds the two axially bonded bromine substituents display elongated P–Br distances ($P–Br_{ax}$: 2.424(2) and 2.677(2) Å). The most distant bromine atom forms a bridge (3.327(2) Å; dashed bonds) about an inversion centre towards another PBr_3 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)[7] than to a classical single bond, the formation of dimeric structures in the solid state was also observed for other derivatives.[133-134]

A more elaborate example of a phosphoniophosphoranide (**119**) features an electron accepting PCl_2- and an electron donating $^iPr_2P$-moiety connected by the rigid acenaphthene backbone (**Fig. 21**). Compound **119** represents the first phosphoniophosphoranide 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 (PCl_2 68.8 and P^iPr_2 40.4 ppm) and the observation of a $^1J(PP)$ coupling constant of 363 Hz are consistent with the retention of the P–P bond upon redissolution.[135d]



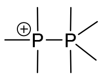
Sch. 37. Reactions of **120** giving **122** (bonding motif **L**) and diphosphoniophosphoranide **121** (bonding motif **M**).

The reaction of the antracene derived triphosphane[10] **120** with P_2I_4 in the presence of LiCl and chlorinated solvents leads to the formation of the diphosphoniophosphoranide **121** as a result of a formal two electron oxidation and substitution process (**Sch. 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}P NMR spectrum shows only two sharp signals at 193 K. A dynamic NMR investigation did not indicate a bond switching process (bell–clapper rearrangement). The chalcogenation of **120** after methanolysis leads to the formation of compound **122** (E = S, Se) which represents an unprecedented neutral example of bonding motif **L** (*vide supra*).

σ^4-σ^5

As already mentioned in the discussion of the phosphoniophosphoranide **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 σ^4–σ^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.

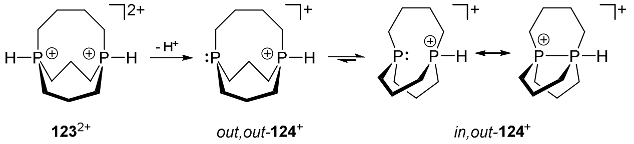
The connection of a phosphonio and a phosphorane moiety leads to bonding motif **N**.



N

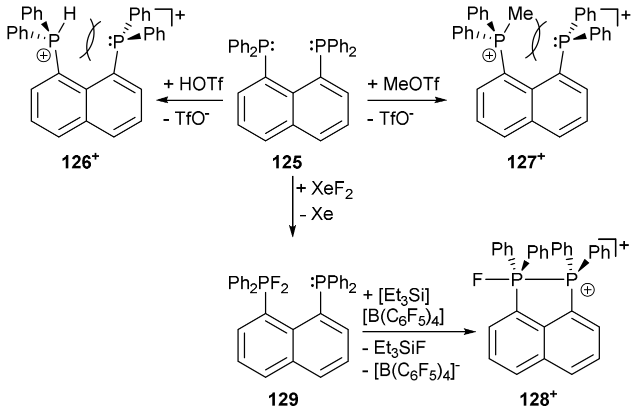
Bonding motif N

Alder *et al.* showed that the addition of nucleophiles to tricyclic propellane-type diphosphoniumdications (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 σ^5-phosphorane moiety. Different P–P-distances in the range from 2.514 to 2.813 Å are observed.



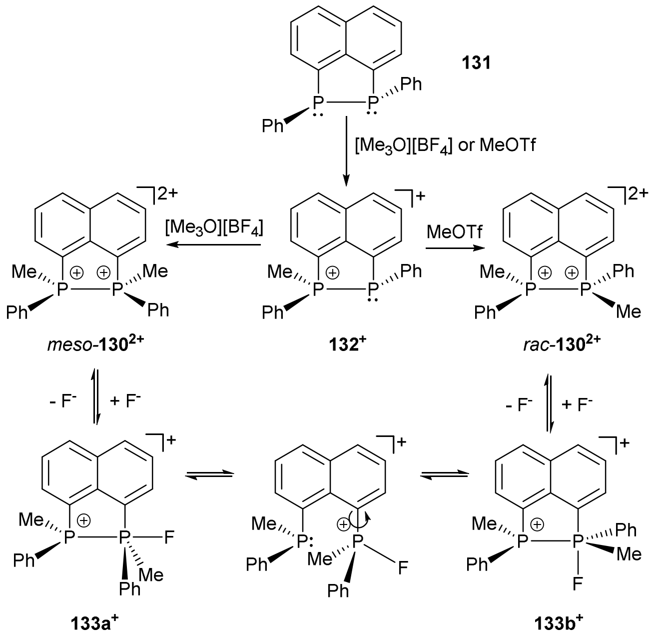
Sch. 38. Deprotonation of 123^{2+} leading to *out,out*-124^+ followed by inversion of P(III) giving *in,out*-124^+ which exhibits transannular P–P bonding.

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 (**Sch. 38**).[152] While *out,out*-124^+ shows broad signals in the ^{31}P NMR 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, an extraordinary low value for trialkylphosphanes. The phosphoniophosphorane was calculated to be 24 kJ/mol more stable.[153]



Sch. 39. Derivatization of **125** to compounds with (**128**$^+$) and without intramolecular P–P bonding (**126**$^+$, **127**$^+$).

Schmutzler *et al.* reinvestigated the single protonation (**Sch. 39**, left) and methylation (**Sch. 39**, right) of 1,8-bis(diphenylphosphanyl)naphthalene **125** and reported the crystal structure of the cations **126**$^+$ and **127**$^+$ as triflate salts.[8a] 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 the Alder systems (*vide supra*). Very recently, Stephan *et al.* synthesized the phosphoniofluorophosphorane as perfluorinated borate salt **128**[B(C_6F_5)$_4$] by fluorination of **125** and subsequent fluoride-ion abstraction from the difluorophosphorane **129** (**Sch. 39**, bottom).[154] Both the fluorine 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.



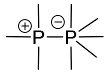
Sch. 40. Single and double methylation of 1,8-naphthalene bridged diphosphane **131** to *meso*- or *rac*-**130**$^{2+}$ (top) and interconversion in the presence of fluoride ions (bottom).

Kilian *et al.* reported on the isomeric diphosphoniumdications *meso*-**130**$^{2+}$ and *rac*-**130**$^{2+}$ that are formed by two consecutive methylation steps of the diphosphaacenaphthene **131** *via* a phosphanylphosphonium intermediate **132**$^+$ (**Sch. 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}P-EXSY NMR investigations indicating that the inversion occurs via phosphoniophosphorane intermediates **133a,b**$^+$.[155]

These contrary results finally lead to the question which electronic conditions must be fulfilled for **σ^4-σ^5** phosphoniophosphoranes 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 **110**) and sulfides[133, 157] adjacent to the **σ^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 **σ^3–λ^3** phosphane (phosphinite, R_2PO^- or phosphinothioite, R_2PS^-). 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 **σ^4–σ^5** environment.

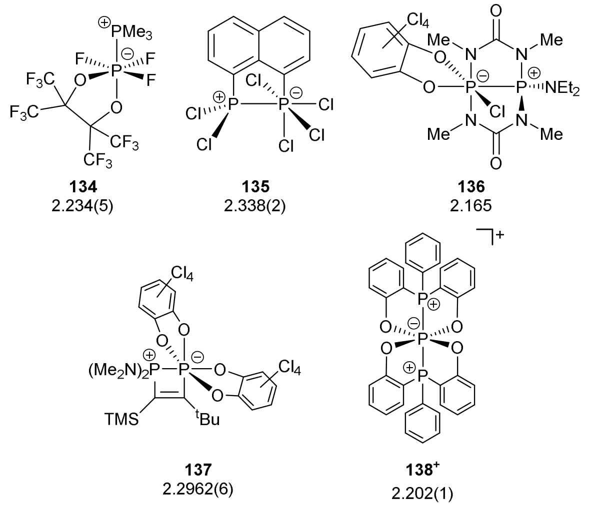
σ^4-σ^6

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 **O**.


O

Bonding motif O

Only few reports on phosphoniophosphates have appeared in the literature. At first, adducts of PF_5 and alkylphosphanes were studied by NMR spectroscopy.[159]

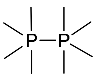


134 2.234(5) **135** 2.338(2) **136** 2.165 **137** 2.2962(6) **138⁺** 2.202(1)

Fig. 23. Selected derivatives comprising bonding motif **O** with respective P–P bond lengths in Å.

The first isolated and structurally characterized **σ^4–σ^6** P–P compound **134** from an electron deficient trifluoro-λ^5-dioxo-phospholane was published by Röschenthaler *et al.*[160] The molecular structure displays a tetrahedral phosphonio moiety bonded to an octahedral **σ^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 **O** (**Fig. 23**) display comparable bond lengths with those of **135**[161] and **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 diphosphete **137**,[162] a relaxed **σ^3–σ^5** phosphanylphosphorane 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 2.2962(6) Å clearly indicates a strong attractive interaction between both phosphorus atoms. In the oxidation product **136** of the phosphoniophosphoranide **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 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°.[133] The structures of the cation **138**$^{+}$[163] and the unsymmetrically chlorinated diphospha-acenaphthene **135**[161] 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 isolable diphosphorane intermediate (**σ^5–σ^5**) similar to the equilibrium between molecular PCl_5 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.

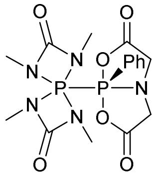
σ^5-σ^5



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_{ax}–P_{ax} (2.255(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 ^1J(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 ^1J(PP) value observed.[167]



139

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

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
Abs	halide abstracting agent
Bu	butyl
Cp	cyclopentadienide
Cy	cyclohexyl
DABCO	1,4-diaza[2.2.2]bicyclooctane
Dipp	2,6-diisopropylphenyl
dmpe	1,2-bis(dimethylphosphanyl)ethane
dppe	1,2-bis(diphenylphosphanyl)ethane
dppp	1,3-bis(diphenylphosphanyl)propane
Et	ethyl
eq.	equivalent(s)
i	iso
Me	methyl
Mes	2,4,6-trimethylphenyl
Mes*	2,4,6-tri(*tert*-butyl)phenyl
n	normal/unbranched
NHC	*N*-heterocyclic carbene
OTf	triflate/trifluoromethanesulfonate
Pr	propyl
Ph	phenyl
pyr	3,5-dimethylpyrazole
t	tert
triaz	1,3,5-trimethylhexahydro-1,3,5-triazine
trip	2,4,6-triisopropylphenyl
vide infra	see below
vide supra	see above

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TOC

This review aims to highlight and comprehensively summarize recent developments in the field of P–P bonded compounds with different bonding modes of the phosphorus atoms.