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Recent highlights in mixed-coordinate oligophosphorus chemistry

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

Introduction

Phosphorus is an intriguing element with several different bonding modes. The combination of two phosphorus atoms connected to each other multiplies the possibilities to gain compounds with different P–P bonds displaying a great variety of bonding modes. Such compounds have always attracted much attention and a first review in 1965 by Cowley covered the three basic types of substances containing phosphorus–phosphorus single bonds that are derived from classical diphosphanes and their oxidation products.¹ In the report of Dillon *et al.*, which appeared in 1995, the field of P–P bonded compounds was re-reviewed.

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,

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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 definition³ 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 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 Å⁶ 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. ³¹P NMR chemical shifts and ³¹P–³¹P-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

Table 1 Selected P–P bonded frameworks with non-symmetrical^a bonding motifs^b

	σ^2	σ^3	σ^4	σ^5	
σ^2					
σ^3					
σ^4					
σ^5					
σ^6					

^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.

proof in certain cases.⁸ 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 σ^2 – σ^2 (diphosphenes)⁹ and σ^3 – σ^3 (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 the 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-coordinate 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



Jan J. Weigand

Jan J. Weigand obtained his diploma in chemistry in 2002 and his Dr. rer. nat. in 2005 from the LMU in Munich (Germany). In 2005 he was awarded the Bavarian culture prize and obtained a Lynen Scholarship from the AvH foundation for postdoctoral research at Dalhousie University in Halifax (Canada). He returned to Germany with a Lynen Return Fellowship and started his habilitation at the WWU Münster at the end of 2007 under the supervision

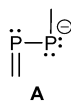
of Prof. Hahn. He was awarded shortly after the Liebig scholarship of the FCI which allowed him to start his independent career in 2008. In April 2010 he became a fellow of the Emmy Noether research program awarded by the DFG and recently obtained the Wöhler research award for young scientists. In 2012, he obtained an ERC starting grant from the European Council. Since 2013 he has been Professor at the TU University Dresden.



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 σ^2 - σ^3 , σ^2 - σ^4 , σ^3 - σ^3 and σ^4 - σ^4 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 All ellipsoids are displayed at 50% probability.

σ^2 - σ^2

The parent motif of σ^2 - σ^2 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.



Bonding motif A

Selected examples of anionic (**1**⁻,¹³ **2**⁻,¹⁴ **3**⁻,¹⁵ **4**⁻ (ref. 16)) and cationic (**5**⁺,¹⁷ **6**⁺ (ref. 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.

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

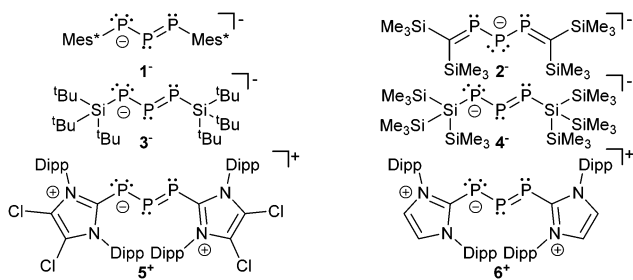
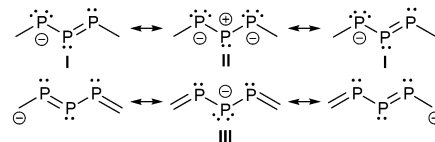


Fig. 1 Selected examples of anionic and cationic derivatives containing the triphosphaallyl and triphosphapentadienyl motif; only one representative resonance structure is shown.



Scheme 1 Resonance structures of triphosphaallyl and triphosphapentadienyl compounds.

The chemical shift of the central, dicoordinate phosphorus atom of ions **1**⁻, **3**⁻, **4**⁻, **5**⁺ and **6**⁺ is typically observed in the region ranging between 500 and 750 ppm significantly low-field shifted compared to the adjacent two phosphorus atoms of which the chemical shift is observed at around 200 ppm (Table 2). Consistent with resonance 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 s-type electron lone pair of the central phosphorus atom is therefore not available for electrophiles but the adjacent ones are. Thus, the addition of HOTf to a deep green solution of 5[GaCl₄] instantly yields an orange oil¹⁹ and the ³¹P{¹H} NMR spectrum reveals resonances of an AMX spin system which is assigned to the *cyclo*-triphosphanediiium cation **7**²⁺ (Scheme 2).

The protonation of **5**⁺ is reversible and the addition of a base to a solution of **7**²⁺ instantly forms a deep green solution of **5**⁺.¹⁹ Upon protonation the phosphaallyl anion [(^tBu₃Si)₂P₃]⁻ (**3**⁻) rearranges quickly to give the related *cyclo*-triphosphane derivative **8**.^{15a} The assignment of the resonances of cation **7**²⁺ is achieved by comparison to the ³¹P NMR parameter of related derivatives **8**^{15a} and **9**²⁰ (Fig. 2 and Table 3). The chemical shifts of **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 ³¹P NMR spectrum due to the ¹J(PH) coupling (**7**²⁺: ¹J(P_AH) = 155.7 Hz; compare **9**: ¹J(P_AH) = 137.1 Hz). The substituents on the other two P atoms are in a *transoid* arrangement. A larger absolute value of the ¹J(PP) coupling constants between the hydrogen-substituted P atom and the phosphorus atom with the *cis*-arranged substituent (**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 (**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 (**7**²⁺: ²J(P_XH) = 34.2 Hz, **8**: ²J(P_XH) = 16.6 Hz), whereas small values indicate a *trans*-arrangement (**7**²⁺: ²J(P_MH) = 17.8 Hz, **8**: ²J(P_MH) = 6.9 Hz).

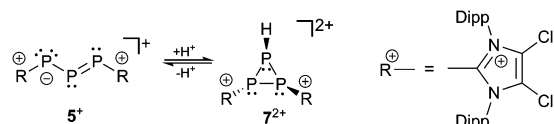
The fact that the protonation of **1**⁻ leads to the formation of the open-chain phosphanyldiphosphene Mes*PH-P = P-Mes* instead of a *cyclo*-triphosphane underlines the great dependence of the substituents on the electronic structure of triphosphaallyl compounds.^{13a} A totally different reaction outcome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



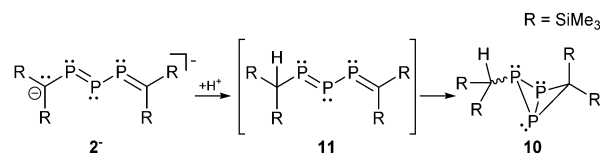
Table 2 Summary of important ^{31}P NMR data and bonding parameters of compounds comprising bonding motif A

	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
$\delta(^{31}\text{P})_{\text{adjacent}}$ in ppm	208	494.1	232.1	199.8	199.4	190.6
$\delta(^{31}\text{P})_{\text{central}}$ in ppm	548	295.5	730.0	717.2	597.9	591.9
$^1J_{\text{PP}}$ in Hz	524	430	552.3	541	508.3	505.9
$d(\text{P-P})$ in Å	2.137(1)	2.072(2)	2.072(2)	2.0730(8); 2.0774(8)	2.093(1); 2.091(1)	2.090(1); 2.097(1)
$d(\text{P-C/Si})$ in Å	1.687(3)	2.252(2); 2.260(2)	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)	105.83(7)	105.52(3)	87.2(4)	92.76(2)

^a No structural parameter available.



Scheme 2 Reversible protonation/deprotonation reaction between 5^+ and 7^{2+} .



Scheme 3 Rearrangement reaction of 2^- upon protonation.

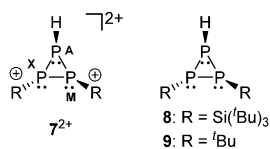


Fig. 2 Substituent arrangement in cyclo-triphosphanes 7^{2+} , **8** and **9**.

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

^{31}P	7^{2+}	8	9
Ref.	19	13a	20
Spin system	AMX	AMX	AMX
$\delta(\text{P}_A)$	-202.3	-260.1	-270.8
$\delta(\text{P}_M)$	-182.6	-259.5	-149.2
$\delta(\text{P}_X)$	-156.8	-240.9	-136.3
$^1J(\text{P}_A\text{P}_M)$	-158.8	-224.2	-144.1
$^1J(\text{P}_A\text{P}_X)$	-130.4	-141.3	-226.6
$^1J(\text{P}_M\text{P}_X)$	-203.0	-188.0	-223.7
$^1J(\text{P}_A\text{H})$	155.7	137.1	— ^a
$^2J(\text{P}_M\text{H})$	17.8	6.9	— ^a
$^2J(\text{P}_X\text{H})$	34.2	16.6	— ^a

^a Coupling constants are not reported.

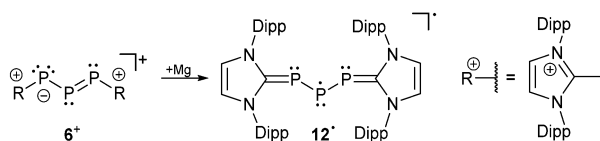
carbon atoms. Thermolysis of 2^- in DME in the presence of traces of moisture led to the formation of the rearranged reaction product **10** suggesting the intermediate **11** with a protonated carbon atom (Scheme 3).¹⁴

The difference in the electronic structure of 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 $^1J(\text{PP})$ coupling constant of 430 Hz is only slightly affected but in accordance with a significant structural change of the P_3 bonded system. For triphosphaallyl ions 1^- , 3^- , 4^- , 5^+ and 6^+ a significantly shortened P-P bond length (<2.1 Å) is observed indicating

partial double-bond character as expected for an allyl system. In comparison, the P-P bond length is significantly elongated (2.137(1) Å) in the case of anion 2^- . 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**[GaCl₄] in $\text{C}_6\text{H}_5\text{F}$ shows two absorption bands of which the strongest band (I_{max}) is observed at 696 nm corresponding to an $n \rightarrow \pi^*$ transition. The second absorption maximum at 443 nm can be assigned to a $\pi \rightarrow \pi^*$ transition. The related cation 6^+ , dissolved in THF, shows the corresponding absorption bands at 666 nm and 434 nm, respectively. The reduction of 6^+ into its corresponding neutral radical species **12** was achieved by reacting the cation with an excess of magnesium (Scheme 4).¹⁸

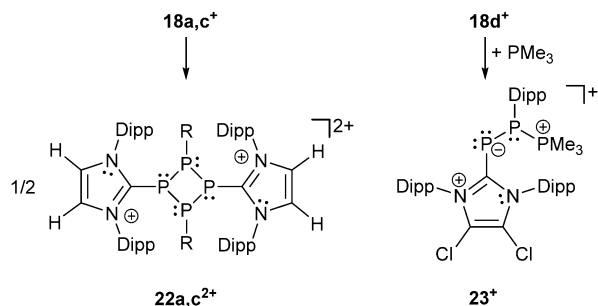
Closely related to these triphosphaallyl systems are the cyclopentadienide related 1,2,3-triphospholides. Although first described already in 1990,²² the isolation of the non-coordinate parent compound $[\text{Pn}_3\text{C}_2\text{R}_2]^-$ (Pn = P, As; **13**⁻) and its arsa-analogue was achieved only recently by Goicoechea *et al.* Anions **13**⁻ are obtained from the reaction of heptapnictide trianions $[\text{Pn}_7]^{3-}$ (Pn = P, As)²³ or the monoprotonated derivatives $[\text{HPn}_7]^{2-}$ with alkynes in dimethylformamide in the presence of a cation sequestering ligand like 2,2,2-crypt or 18-crown-6 (Scheme 5).²⁴

Noteworthy is that the electronic structures of these “carbon-copy” ligands possess notable differences in comparison to



Scheme 4 Reduction of 6^+ to neutral radical species 12^* .



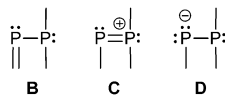


Scheme 8 [2+2] dimerization reaction of diphosphenes **18a,c⁺** (left) and PMe_3 attacking the more electrophilic P atom of diphosphene **18d⁺** forming $\sigma^2\text{-}\sigma^3\text{-}\sigma^4$ compound **23⁺** (right).

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.

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

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 decades³² and have been reviewed earlier² we only want to comment shortly on selected examples depicted in Fig. 3.

In 1990 Niecke *et al.* reported on the 1-phosphanilyldiazaphosphene **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*-phosphanilylphosphaalkene **25** at its P=C and P–P bonds (Scheme 9).³⁴ The reactions at the P=C bond with 2,3-dimethylbutadiene or

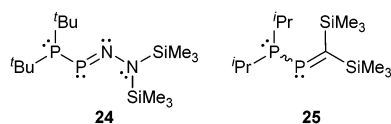
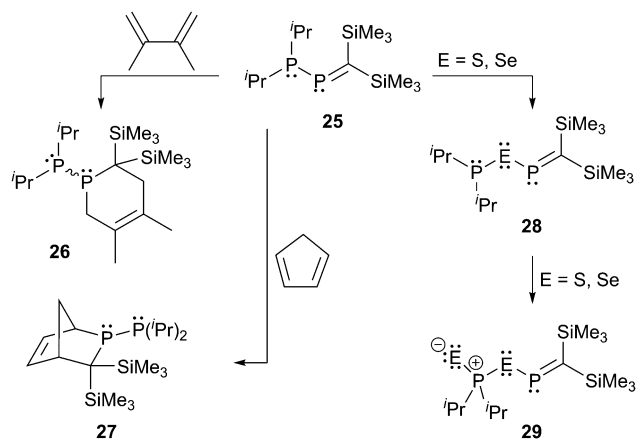


Fig. 3 Selected examples of compounds comprising bonding motif **B**.



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

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}

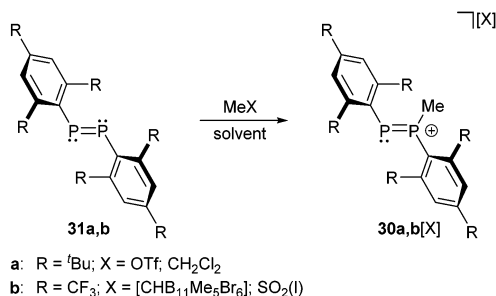
In the reaction of **25** with trichlorosilyltrimethylgermane ($\text{Me}_3\text{GeSiCl}_3$) they observed an unusual P=C bond cleavage accompanied by a double dichlorosilylene (SiCl_2) transfer, which represented an important contribution to the chemistry of stable Group 14 carbene analogues. The trichlorosilyltrimethylgermane represents a versatile reagent for the transfer of SiCl_2 moieties to *P*-phosphanilylphosphaalkenes under very mild conditions.^{34b,c}

Bonding motif C

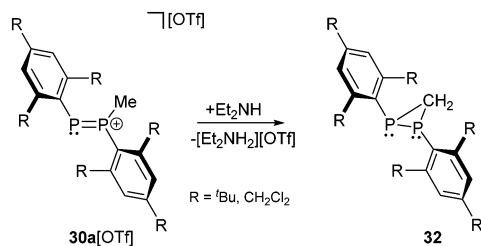
The first phosphanilylphosphenium ion **30a⁺** was obtained as triflate salt by Grützmacher *et al.* from the reaction of diphosphene **31a** (R = ^{*t*}Bu) with a 35-fold excess of MeOTf in CH_2Cl_2 as solvent (Scheme 10).³⁵

The same reaction with the very electron deficient diphosphene **31b** (R = CF_3) does not form the related cation **30b⁺** (R = CF_3) even in boiling, neat methyl triflate. However, the methylation succeeds in liquid $\text{SO}_2(l)$ with very strong methylation reagents of the type $\text{R}[\text{CHB}_{11}\text{Me}_5\text{X}_6]$ (R = Me, Et, ^{*i*}Pr; X = Br) introduced by Reed *et al.* (Scheme 10).³⁶ This class of potent electrophilic “R⁺” alkylating agents uses the weakly nucleophilic carborane anions $[\text{CHB}_{11}\text{Me}_5\text{X}_6]^-$ (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 $\text{Me}[\text{CHB}_{11}\text{Me}_5\text{Br}_6]$ and diphosphene **31b** (R = CF_3) in $\text{SO}_2(l)$ was studied by NMR-spectroscopy revealing an AX spin system of **30b⁺** with chemical shifts at 260 and 279 ppm, typical for the tri- and dicoordinate phosphorus atoms,





Scheme 10 Diphosphenes **31a,b** can only be methylated by very strong methylation agents to form diphosphenium cations **30a,b⁺**.



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

respectively and significantly upfield shifted compared to diphosphenes that typically display resonances at very low field (*e.g.* **31a** (R = ^tBu): $\delta = 495$ ppm). The large coupling constant of $^1J(\text{PP}) = 610$ Hz confirms the direct connectivity. Similar values have been obtained for **30a⁺**. Although **30a[OTf]** is extremely sensitive in nonpolar solvents and decomposes readily in solution, they succeeded to obtain crystals suitable for X-ray diffraction. The methylation of **31a** (P–P bond length: 2.034(2) Å) does not significantly affect the P–P bond length in cation **30a⁺** (2.024(2) Å). Attempts to deprotonate cation **30a⁺** with Et₂NH as a base did not yield the expected ylide but resulted in the formation of the diphosphirane **32** (Scheme 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

Bonding motif D

Phosphanidophosphanes or diphosphan-1-ide ions belong to the bonding motif **D** and are the anionic congeners in the $\sigma^2-\sigma^3$ 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 P₂H₄ in liquid ammonia. They stated that the initial step represents the deprotonation by an amide anion.³⁸ The resulting P₂H₃[−] anion in turn again attacks diphosphane and initiates a cascade of disproportionation and aggregation reactions. Under evolution of PH₃ gas the reaction ultimately leads to the formation of

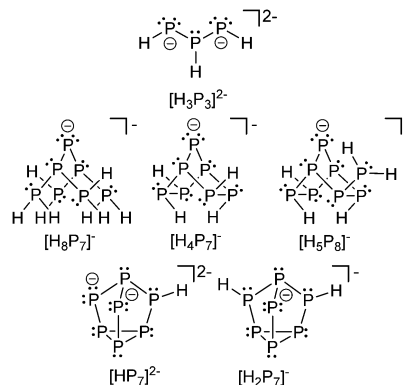


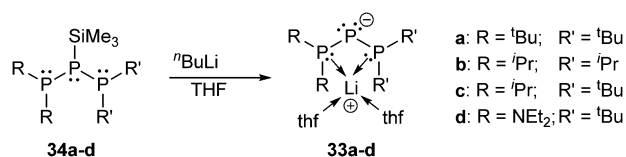
Fig. 4 Selected examples of protonated oligophosphides.

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 [P₇]^{3−}, [P₁₄]^{4−}, [P₁₆]^{2−}, [P₁₉]^{3−}, [P₂₁]^{3−}, [P₂₂]^{4−} and [P₂₆]^{4−} is observed.²³ The reaction of P₂H₄ in ammonia in the presence of solvents such as THF yields hydrogen phosphides of which the selected examples [H₃P₃]^{2−},³⁹ [H₈P₇][−], [H₄P₇][−], [H₅P₈][−],⁴⁰ [HP₇]^{2−} (ref. 41) and [H₂P₇][−] (ref. 42) are depicted in Fig. 4.

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

Fritz *et al.* synthesized a series of bis-phosphanyl substituted lithium phosphanides **33a–d** by treatment of the parent silyl phosphanes **34a–d** with *n*-butyl lithium (Scheme 12).⁴⁴ Interestingly, in the solid state, the lithium ion is not coordinated to the negatively charged phosphorus atom itself, but chelated by the two adjacent phosphane moieties instead. Several related acyclic and cyclic anions of the form [P(PR₂)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(solvent)_x]₂[**34**] as representative example, showing the characteristic M₂P₂ arrangement found in solid state structures of bis(alkali metal)-catena-oligophosphane- α,ω -diides [M₂(solvent)_x(R_nP_n)]



Scheme 12 Upon treatment with ⁿBuLi the silylated triphosphanes **34a–d** form bis-phosphanyl substituted lithium phosphanides **33a–d**.



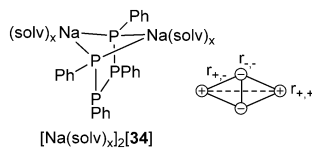
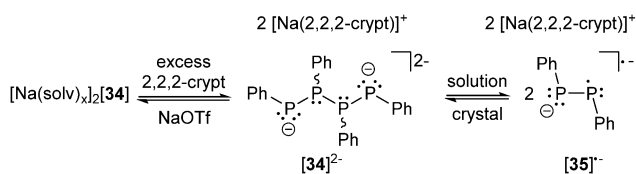


Fig. 5 Schematic view of the tetraphosphane-1,4-diide $[\text{Na}(\text{solvent})_x]_2[\mathbf{34}]$ showing the characteristic bicyclobutane-shaped M_2P_2 arrangement (left); illustration of point charges and coulombic interactions (right).

($\text{M} = \text{Li}, \text{Na}, \text{K}$; $n = 2, 3, 4$; $\text{R} = \text{Ph}, \text{Mes}, \text{}^t\text{Bu}$; $\text{solvent} = \text{solvent molecule or ligand}$). 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 $r_{-,-}$).

The group of Grützmacher reported an unexpected result from the removal of this charge-stabilizing cation-anion contacts by the reaction of $[\text{Na}(\text{solvent})_x]_2[\mathbf{34}]$ with the cation sequestering ligand 2,2,2-crypt (Scheme 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 $[\text{Na}(2,2,2\text{-crypt})]_2[\mathbf{34}]$.

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 $[\mathbf{35}]^{\bullet-}$ resulting from the homolytic cleavage of the central P–P bond in $[\mathbf{34}]^{2-}$. The radical anions exhibit a strong EPR signal ($g = 2.0089$) with a triplet splitting ($a_{\text{iso}}[\text{P}] = 115 \text{ MHz}$) resulting from two identical phosphorus nuclei. Further hyperfine-coupling to two non-equivalent *ortho*-protons ($a_{\text{iso}}[\text{H}] = 8.5 \text{ MHz}$, $a_{\text{iso}}[\text{H}'] = 4.0 \text{ MHz}$) 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 $[\mathbf{35}]^{\bullet-}$ again crystals of $[\text{Na}(2,2,2\text{-crypt})]_2[\mathbf{34}]$ are obtained and the addition of $[\text{Na}(2,2,2\text{-crypt})]_2[\mathbf{34}]$ to a solution of NaOTf in THF reforms the ion triple $[\text{Na}(\text{solvent})_x]_2[\mathbf{34}]$. Since the P–P bond lengths of the unstabilized $[\text{Ph}_4\text{P}_4]^{2-}$ -chains (central P–P: 2.224(2) Å, terminal P–P: 2.178(1) Å) in crystals of $[\text{Na}(2,2,2\text{-crypt})]_2[\textit{meso}\text{-}\mathbf{34}]$ 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 $[\text{P}_2\text{Mes}_2]^{\bullet-}$ radical anions, was also reported by another group to occur in concentrated THF solutions

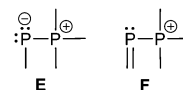


Scheme 13 The sodium ions of $[\text{Na}(\text{solvent})_x]_2[\mathbf{34}]$ can be sequestered by 2,2,2-crypt. In solution the product splits into two radical anions $[\mathbf{35}]^{\bullet-}$. Only one resonance structure of $[\mathbf{35}]^{\bullet-}$ shown.

of the singly protonated species $[\text{K}(18\text{-crown-6})][\text{P}_4\text{HMe}_4]$. In contrast to solutions of the dianions, $[\text{P}_4\text{HMe}_4]^{\bullet-}$ was found to undergo redistribution reactions forming complex mixtures of neutral and anionic species.⁴⁶

$\sigma^2\text{-}\sigma^4$

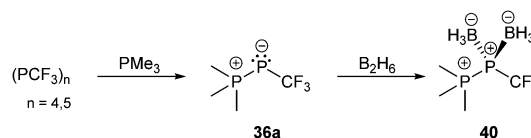
The two bonding motifs **E** and **F** describe the connectivity of di- and tetracoordinate phosphorus atoms.



Bonding motif E

Bonding motif **E** comprises a large variety of zwitterionic phosphoniophosphanides. They represent the phosphorus analogues of alkylidene- σ^4 -phosphoranes ($\text{R}_2\text{C}^--\text{P}^+\text{R}_3$) 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 $(\text{PCF}_3)_n$ ($n = 4, 5$; Scheme 14).⁴⁷ Only very few examples are known (e.g. **36b,c** ($\text{b}: \text{R} = \text{Mes}$, $\text{c}: \text{R} = \text{Mes}^*$),^{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 ($\text{L}_n\text{M-P}(\text{R})\text{-PR}_3$), which are employed for P=C bond formation alternatively to terminal phosphinidene complexes $\text{R-P} = \text{ML}_n$ (for reviews see ref. 25b, c and 52a-f; for a recent example of reversible phosphinidene transfer to triarylphosphane see ref. 52g).

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 (Scheme 14),



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

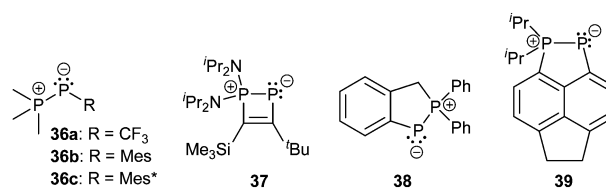


Fig. 6 Examples of zwitterionic phosphoniophosphanides comprising bonding motif **E**.



the bis-borane adduct **39**·2BH₃ was isolated and fully characterized. It has been stated that steric rather than electronic properties are the limiting factor for the accessibility of the second lone-pair of electrons for coordination.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 phospho-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 PX₃ (X = Cl, Br, I; Scheme 15).^{9,55}

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

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-backbonding 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 = ⁱPr). These ligands can undergo coordination to several transition metals as either two- or four-electron bridging donor to give stable and

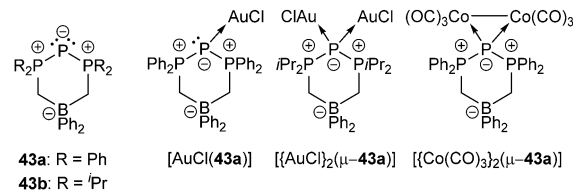
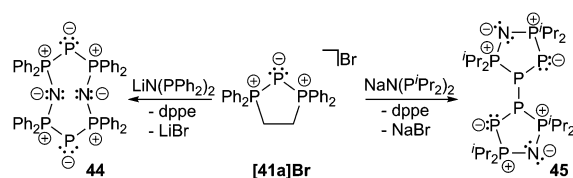


Fig. 7 Zwitterionic triphosphenium derivatives **43a,b** (a: R = Ph, b: R = ⁱPr) and selected coordination complexes with AuCl and [Co(CO)₃]₂.

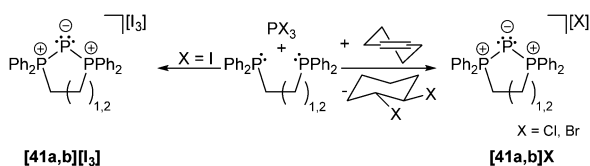
soluble neutral complexes (*e.g.* [AuCl(**43a**)], [(AuCl)₂(μ-**43a**)], [Co(CO)₃]₂(μ-**43a**); Fig. 7).^{57a}

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**⁺ is treated with LiN(PPh₂)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(PⁱPr)₂ gives compound **45** in which two five-membered rings are linked *via* two phosphorus atoms. The mechanism of formation is unclear for both cases, however, their structural arrangement is confirmed by crystal structure analysis (Scheme 17).

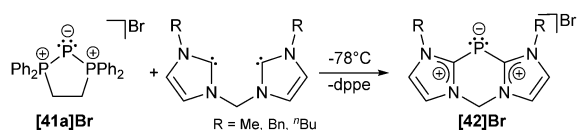
The readily available Janus-head type diphosphorus compound **46**[OTf] (pyr = 3,5-dimethylpyrazolyl) is an attractive precursor for the construction of cationic ring and cage systems.^{6b,62} The stepwise reaction of **46**[OTf] with Cy₂PH gives the two novel cationic polyphosphorus frameworks [Cy₄P₄pyr]⁺ (**47**⁺) and [Cy₆P₇]⁺ (**48**⁺) as well as **49**[OTf] as one of the isolated side-products (Scheme 18).⁶³ Cations **47**⁺ and **48**⁺ (Fig. 8) feature di-, tri- and tetracoordinate phosphorus atoms derived from P₁-synthons *via* a one-pot multiple P–P bond formation and represent the



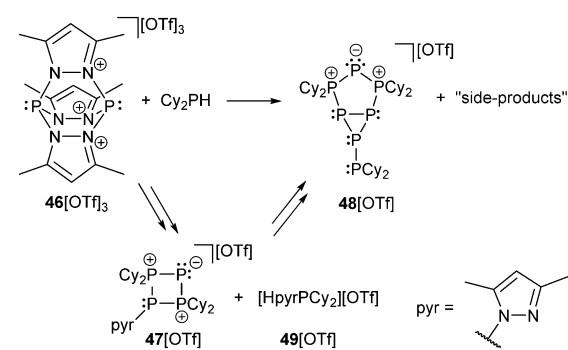
Scheme 17 Formation of phosphorus-rich oligomers **44** and **45** by P⁺-transfer from [41a]⁺ onto bis(phosphanyl)amides.



Scheme 15 Synthesis of triphosphenium ions [41a,b]⁺ from PX₃ and bidentate phosphanes.



Scheme 16 Transfer of P⁺ from [41a]⁺ onto bis-NHC to give [42a]⁺.



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



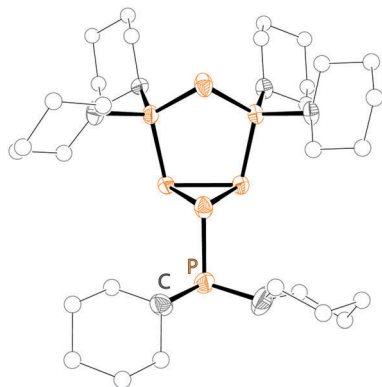


Fig. 8 Molecular structure of cation 48^+ in $48[\text{OTf}]$; hydrogen atoms and anion are omitted for clarity.

first examples of a $\sigma^2-\sigma^4-\sigma^3$ 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

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- σ^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.

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 $50[\text{AlCl}_4]$ remains unchanged in solution, whereas $50[\text{OTf}]$ decomposes quantitatively into phosphalkyne **51** under elimination of Me_3SiOTf and PPh_3 (Scheme 19). A reaction proceeding in the reverse manner has been reported in which the phosphonio-phosphaalkene 52^+ is formed by a 1,2-addition reaction of $[\text{HPPH}_3][\text{OTf}]$ to the bulky adamantyl-substituted phosphalkyne **53**.⁶⁵ Further reactions of phosphalkynes leading to comparable derivatives comprising bonding motif F are described elsewhere.⁶⁶

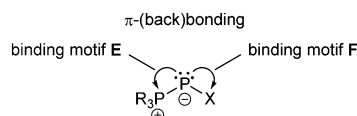
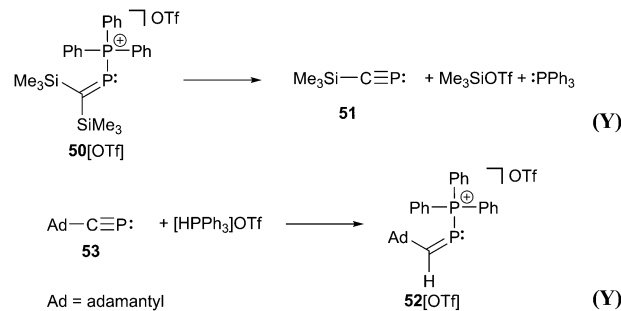


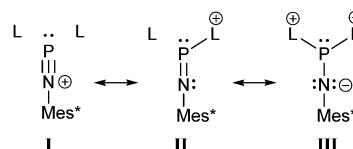
Fig. 9 Illustration of π -(back)bonding in $\sigma^2-\sigma^4$ phosphorus compounds.



Scheme 19 The phosphonio-phosphaalkene 50^+ decomposes giving phosphalkyne **51**. In a reverse reaction **53** and triphenylphosphonium triflate form phosphonio-phosphaalkene $52[\text{OTf}]$.

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.

In order to understand the bonding situation in 54^+ we first want to discuss the phosphadiazonium ion $(\text{Mes}^*\text{PN})^+$ which can be described by a set of resonance structures I–III (Scheme 20). Although it was frequently described as a cation with a 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 $(\text{Mes}^*\text{NP})^+$ 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 $[\text{AlCl}_4]^-$ the P–N distance

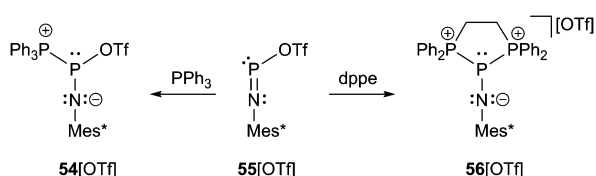


Scheme 20 Representative resonance structures I–III illustrating the bonding situation in phosphadiazonium ions $(\text{Mes}^*\text{NP})^+$. L can be a neutral ligand/donor or a counterion.



(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) Å that is much closer to a P–O single bond (~1.6 Å) than to the sum of the van der Waals radii (~3.3 Å),⁷ the large P–N–C angle reflects an efficient stabilization of the phosphorus atom by the Mes*N-moiety (**II**).⁶⁸

Returning to compound 54[OTf], which is obtained by addition of PPh₃ to 55[OTf], the crystal structure comprises a central σ³ phosphorus atom which adopts a distorted trigonal pyramidal geometry (Scheme 21 and Fig. 10).⁶⁹ The P–P bond length (2.625 Å) corresponds to a long single bond and the P–O distance to the coordinate triflate anion (2.298 Å) is roughly 0.4 Å longer than in 55[OTf] but still closer to a P–O single bond than to the sum of the van der Waals radii. The P–N bond (1.486(4) Å) is slightly longer and the P–N–C angle (169.5(4)°) more acute compared to 55[OTf]. This may be rationalized by a more effective stabilization of the central phosphorus atom by PPh₃ as additional donor ligand. Therefore, the solid state structure of 54[OTf] might best be described by resonance structures **II** and **III**. Interestingly, in solution the P–P bond is obviously not preserved as there was found no evidence of P–P coupling in 54[OTf]. In contrast, the weaker coordinating anion [AlCl₄][−] in 54[AlCl₄] effects a stronger fixation of the PPh₃ substituent and allows the observation of two doublets in the ³¹P NMR spectrum (δ(NP) = 87 ppm, δ(PPh₃) = 22 ppm, ¹J(PP) = 340 Hz).⁷⁰



Scheme 21 Reaction of Lewis acidic 55[OTf] with PPh₃ and dppe to yield P–P bonded compounds 54[OTf] and 56[OTf].

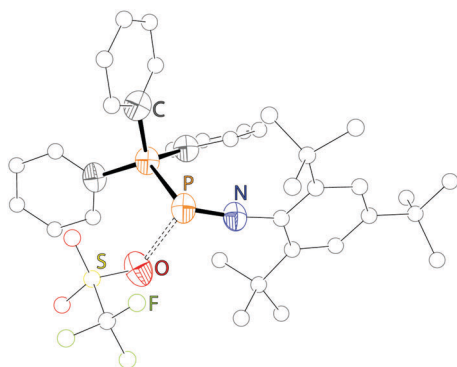


Fig. 10 Molecular structure of 54[OTf]; hydrogen atoms are omitted for clarity.

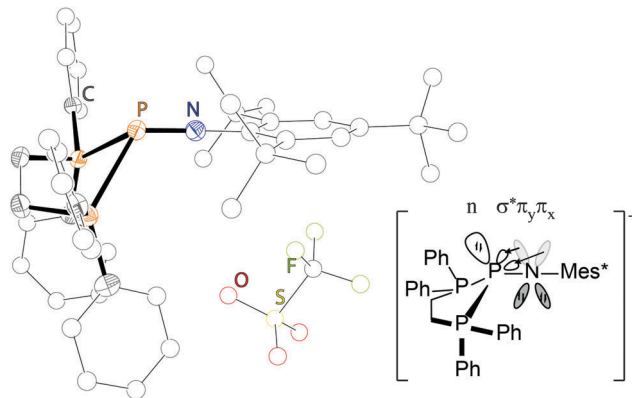
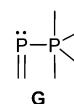


Fig. 11 Molecular structure of 56[OTf]; hydrogen atoms are omitted for clarity (left); illustration of negative hyperconjugation in 56[OTf].

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] (Scheme 21 and Fig. 11).⁷¹ The triflate anion is liberated and, in this case, non-coordinating, whereas two long P–P bonds are formed to the central σ³ P atom (2.5708(9) Å and 2.5392(9) Å). A low temperature NMR study at −80 °C revealed that the P–P bonds also remain unequal in solution (δ(NP) = 36 ppm, δ(dppe1) = 10.2 ppm, 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 phosphonium or phosphanylphosphonium ions which belong to bonding motif J (*vide infra*).

σ²–σ⁵



Bonding motif G

Examples of a dicoordinate phosphorus atom adjacent to a pentacoordinate phosphorus atom are very rare. We believe that up to date only two examples are reported of which one was proven its structural connectivity by X-ray diffraction analysis. In order to stabilize such an unusual bonding situation the dicoordinate phosphorus atom is required to be comparably electron poor. Regitz *et al.* treated the tetracyclic 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 σ³ phosphorus atom to give compound 58 (Scheme 22). The phosphalkene moiety occupies an equatorial position and



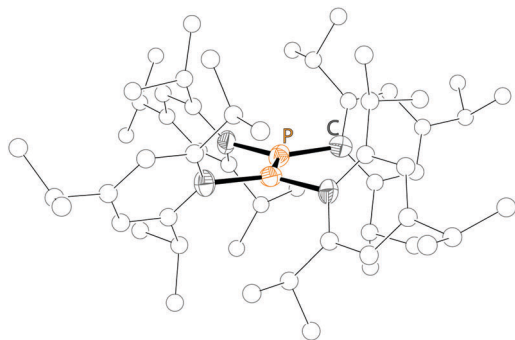


Fig. 13 Molecular structure of the diphosphenium dication 62^{2+} ; hydrogen atoms are omitted for clarity.

cases depending also on steric demand.⁷⁸ However, it has been shown that the introduction of strongly electron-withdrawing substituents such as fluoride,⁷⁹ trifluoromethyl- (CF_3)⁸⁰ or 2,4-bis(trifluoromethyl)phenyl- ($2,4\text{-(CF}_3)_2\text{C}_6\text{H}_3$) groups stabilize the anhydrides of the phosphinous acids.⁸¹ The bis(bis(trifluoromethyl)phosphanyl) oxide, $(\text{CF}_3)_2\text{P-O-P}(\text{CF}_3)_2$, 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 $2,4\text{-(CF}_3)_2\text{C}_6\text{H}_3)_2\text{P-O-P}(\text{CF}_3)_2$ derivative ($\delta = 105.6$ ppm, ^{31}P NMR in CDCl_3) but also observed small quantities of the isomeric diphospane monoxide $2,4\text{-(CF}_3)_2\text{C}_6\text{H}_3)_2\text{P(O)-P}(\text{CF}_3)_2$ in the reaction, identified by its characteristic resonance in the ^{31}P NMR spectrum at 39 ppm for the oxygen-bonded phosphorus atom and -32.5 ppm for the trivalent phosphorus atom ($^1J(\text{PP}) = 247$ Hz).⁸¹ The stability of **64a** is significantly improved for the heavier congeners with $\text{E} = \text{S}$ 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 diphospane disulfides,⁸² oxidation reactions of diphosphanes with elemental sulfur,⁸³ or comproportionation reactions of diphosphanes and diphospane 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 conditions. Recently, Morris *et al.* presented a convenient approach for the preparation of derivatives of **64a** ($\text{R} = \text{Ph, Cy}$; $\text{E} = \text{S}$) by reacting R_2PCL with Li_2S . In a subsequent isomerization reaction the rarely reported di(phosphanyl) sulfides

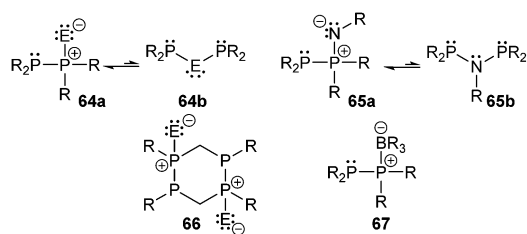
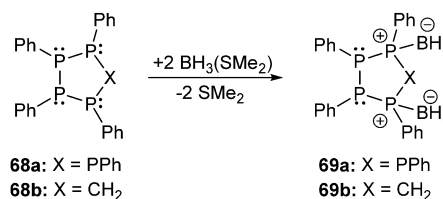


Fig. 14 Selected examples of neutral derivatives **46–49** comprising bonding motif **J**.

(**64b**; $\text{E} = \text{S}$) were obtained and used as ligands in ruthenium coordination complexes.⁸⁶ To the best of our knowledge, synthetic protocols for diphospane monoselenides (**64a**; $\text{E} = \text{Se}$) and -tellurides (**64a**; $\text{E} = \text{Te}$) are unreported. Only very few derivatives ($\text{R} = \text{}^t\text{Bu, R}_2\text{N}$) of di(phosphanyl) selenides (**64b**; $\text{E} = \text{Se}$) and even fewer tellurides (**64b**; $\text{E} = \text{Te}$) are reported and prepared in a similar manner to the sulfur derivatives or *via* persistent phosphanyl radicals.⁸⁷

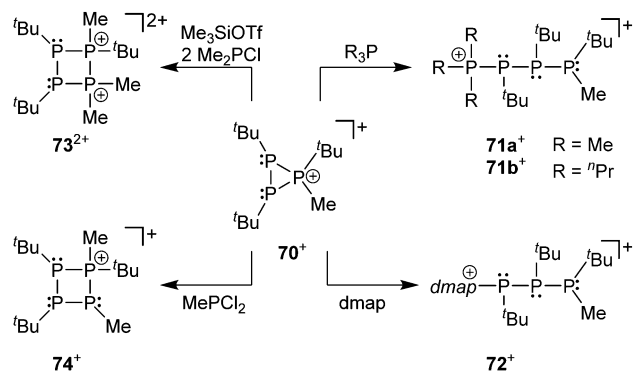
Iminophosphoranes⁸⁸ have found applications in organic synthesis⁸⁹ or as ligands in transition metal complexes.⁹⁰ However, the chemistry of the related iminodiphosphanes of the general structure **65a** is only scarcely developed (Fig. 14).⁹¹ They are isoelectronic to the diphospane monochalcogenides **64a** and are also tautomers of the more commonly encountered di(phosphanyl)amines **65b** with an $\text{R}_2\text{P-NR-PR}_2$ 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

The oxidation of *cyclo*-phosphanes with chalcogens⁹⁴ leads to the formation of product mixtures, as exemplified in the reaction of $(\text{PPh})_5$ with a deficiency of selenium in which one or two $[\text{PPh}]$ units of the *cyclo*-phosphane are formally replaced by Se atoms.⁹⁵ The oxidation of *cyclo*-1,4- $(\text{CH}_2)_2(\text{P}^t\text{Bu})_4$ 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, $\text{R} = \text{}^t\text{Bu}$; $\text{E} = \text{S, Se}$).⁹⁶ Density functional theory (DFT) calculations for the 2,5-chalcogenated derivatives **66** ($\text{E} = \text{S, Se}$) and the corresponding radical cations and dications predict significant structural changes of the six-membered ring upon oxidation. The formation of a transannular P-P single bond (*ca.* 2.25 Å) in the cyclic dications is indicated by geometry and consideration of the frontier orbitals.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 *cyclo*-oligophosphanes are interesting objects of study since their structures give insight into the reactivity of *cyclo*-oligophosphanes and particularly into the relative nucleophilicity of the coordinated and uncoordinated phosphorus atoms. First reports by Cowley and Pinell on the treatment of *cyclo*-oligophosphanes *cyclo*-(PR)_{*n*} ($\text{R} = \text{Et, }^n\text{Pr, }^n\text{Bu, Ph}$)⁹⁹ with boron trihalides were recently complemented by Hey-Hawkins *et al.* They investigated the adduct formation of *cyclo*-oligophosphanes *cyclo*-(PPh)₅ (**68a**) and *cyclo*-($\text{P}_4\text{Ph}_4\text{CH}_2$) (**68b**) in the reaction with $\text{BH}_3(\text{SMe}_2)$ to form complexes **69a,b** (Scheme 25). The latter complex **69b** is of particular interest since they



Scheme 25 Formation of bis(borane) adducts of *cyclo*-phosphanes.



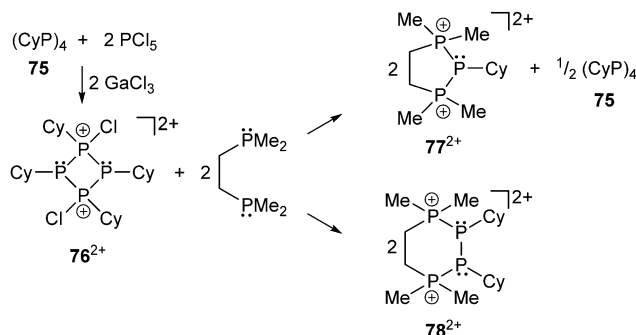


Scheme 28 Diverse reactivity of cation 52^+ in the reaction with a series of nucleophiles such as Me_2PCl , MePCL_2 , R_3P and dmap (4-(dimethylamino)pyridine).

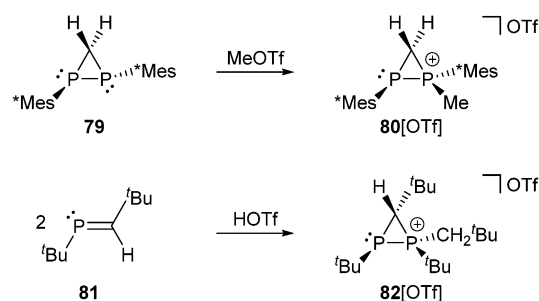
The prototypical phosphanylphosphonium framework can be decorated with halo-substituents ($X = \text{Cl}, \text{Br}, \text{I}$) at either the phosphane or the phosphonium centres to yield an array of acyclic and cyclic halo-functionalized cations (Fig. 15). In this context, the preparation of diphosphanes or *cyclo*-polyphosphanes from the reduction of respective chlorophosphanes can be applied to access catenated cationic polyphosphorus frameworks.^{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 (Scheme 28). Upon reaction with R_3P ($\text{R} = \text{Me}$ or ^nPr) or dmap the three-membered ring is opened to yield the adducts $[\text{R}_3\text{P}-\text{P}^t\text{Bu}-\text{P}^t\text{Bu}-\text{P}(\text{Me})^t\text{Bu}][\text{OTf}]$ ($\text{R} = \text{Me}$ (71a^+), ^nPr (71b^+)) and $[(\text{dmap})-\text{P}^t\text{Bu}-\text{P}^t\text{Bu}-\text{P}(\text{Me})^t\text{Bu}][\text{OTf}]$ (72^+). The complicated $^{31}\text{P}\{^1\text{H}\}$ 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

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 $[\text{Cy}_4\text{P}_4\text{Cl}]^+$ and $[\text{Cy}_4\text{P}_4\text{Cl}_2]^{2+}$ (76^{2+} , (Scheme 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 $[\text{PCy}]^{2+}$ and $[\text{P}_2\text{Cy}_2]^{2+}$ fragments, demonstrating the partially coordinative nature of the $\sigma^3-\sigma^4$ P–P bonds in *cyclo*-phosphanylhalophosphonium cations.¹⁰⁶

The methylation of the diphosphirane **79** with MeOTf allows the formation of the *P*-methylated diphosphiranium salt $80[\text{OTf}]$



Scheme 29 Synthesis of *cyclo*-phosphanylchlorophosphonium cation 76^{2+} (left) and release of $[\text{PCy}]^{2+}$ (top right) or $[\text{P}_2\text{Cy}_2]^{2+}$ fragments (bottom right).

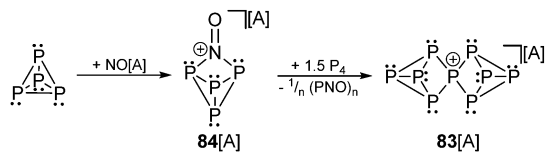


Scheme 30 Synthesis of diphosphiranium cations 80^+ by methylation of diphosphirane **79** (top) and 82^+ by acid-induced dimerization of phosphalkene **81** (bottom).

(Scheme 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 phosphalkene **81** upon addition of HOTf (Scheme 30, bottom). In contrast to $80[\text{OTf}]$ the diphosphiranium triflate $82[\text{OTf}]$ 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 ($\sigma^3-\text{P}$: 52.69(4)°, $\sigma^4-\text{P}$: 55.82(5)°, C: 71.49(5)°).¹¹⁰

The investigation of homoleptic polyphosphorus cations was limited to mass spectroscopy¹¹¹ and quantum chemical calculation¹¹² 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} Crossing *et al.* investigated the oxidation of P_4 with $[\text{NO}][\text{A}]$ ($\text{A} = \text{Al}(\text{OC}(\text{CF}_3)_3)_4^-$) which yields $[\text{P}_4\text{NO}]^+$ -cage compound $84[\text{A}]$ (Scheme 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 $[\text{NO}]^+$ as the interacting frontier orbitals.¹¹⁴ The reaction of $[\text{P}_4\text{NO}]^+$ -cage compound $84[\text{A}]$ with





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

additional 1.5 eq. of P_4 yields the P_9^+ -cage compound **83[A]** (Scheme 31).¹¹⁵ They suggest that cation **83⁺** forms *via* extrusion of $1/n$ (PNO)_{*n*} and intermediary formation of a P_3^+ -species. The ³¹P 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, tri-coordinate and one cationic, tetra-coordinate P atom the charge is almost evenly distributed over all nine atoms according to quantum chemical calculations.¹¹⁵

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 phosphonium 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 -substituted derivatives **86e,f** [$GaCl_4$].¹¹⁹ The cationic $[R_2P_5]^+$ -cage compounds **87d–k** [$GaCl_4$] 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** [$GaCl_4$])

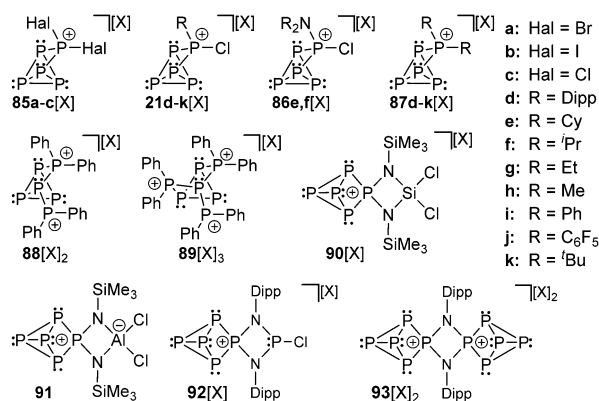


Fig. 16 Selected cationic cage compounds comprising bonding motif **J**.

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 ³¹P 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 phosphonium cations that are derived from four-membered phosphorus–nitrogen–metal heterocycles.¹²¹ Similarly, the reaction of P_4 with the *cyclo*-diphosphadiazane $[DippNPCI]_2$ ($Dipp = 2,6$ -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 **93²⁺** as $[Ga_2Cl_7]^-$ salt.¹²²

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 $[PI_2]^+$ -phosphonium 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 Crossing's silver salt $Ag[Al(OC(CF_3)_3)_4]$ giving the spiro-cyclic cage cation **97⁺**.¹²⁴ The formation of cation **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 alkylhalides (*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

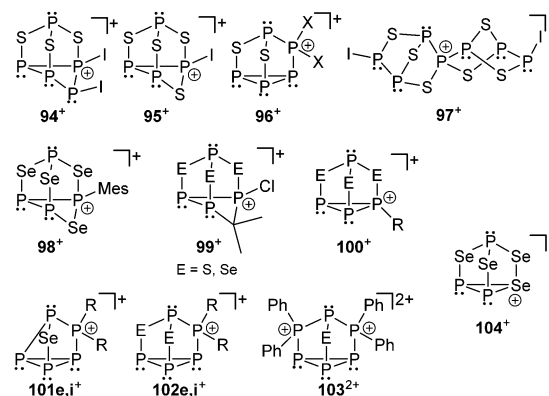
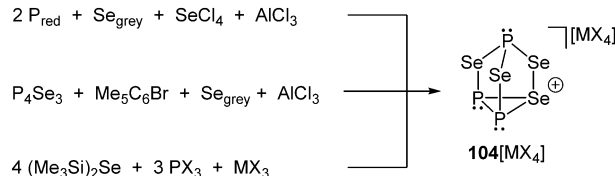


Fig. 17 Selected cationic polyphosphorus–chalcogen cages **94⁺–103²⁺** ($E = S, Se$) comprising bonding motif **J**; cation **104⁺** has been included since it represents the first binary SeP–cation and is related to the other cations.



starting materials. They constitute potentially versatile reagents due to the multitude of distinctly substituted derivatives which are all conveniently obtained in one step procedures from white phosphorus.¹²⁷ Chalcogenation reactions of $[\text{R}_2\text{P}_5]^+$ -cage compounds $\mathbf{87e,i}[\text{GaCl}_4]$ with elemental grey selenium yield the corresponding polyphosphorus-chalcogen cages $\mathbf{102}[\text{GaCl}_4]$ ($\text{E} = \text{Se}, \text{R} = \text{Cy}, \text{Ph}$; Fig. 17). Both cations are formed upon insertion of two selenium atoms into two P–P bonds adjacent to the phosphonium moieties in $\mathbf{87e,i}^+$. Their structural motif resembles that of nortricyclane, with a basal P_3 -ring, the tetra-coordinate P atom and the selenium atoms occupying the bridging positions, and one P atom defining the apex of the cage. This class of compound features interesting ^{31}P and ^{77}Se NMR characteristics. They reveal an AM_2OX spin system for the isotopologues without a ^{77}Se nucleus. These resonances are superimposed by the C_1 -symmetric isotopologues 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 $\mathbf{102e}^+$ ($\text{R} = \text{Cy}$), both spin systems were successfully simulated allowing for the exact determination of chemical shifts and coupling constants. A series of experiments employing variable temperatures, reaction times and stoichiometries gave meaningful insights into the mechanism of the chalcogenation. These experiments indicate that the insertion of Se atoms into P–P bonds of $\mathbf{87e,i}^+$ proceeds in a stepwise manner *via* the intermediates $\mathbf{101e,i}^+$.¹²⁷ The targeted preparation of $\mathbf{103}^+$ as $[\text{GaCl}_4]^-$ salt was achieved by utilizing a 2:1 stoichiometry of $\mathbf{48}^+$ and grey selenium ($\text{E} = \text{Se}$). Another synthetic approach for the preparation of $\mathbf{103}^+$ ($\text{E} = \text{S}, \text{Se}$) is the targeted substitution of one $[\text{Ph}_2\text{P}]^+$ -moiety in the tricationic cage $\mathbf{89}^{3+}$. This was achieved by reacting $\mathbf{89}^{3+}$ with grey selenium or sulfur under solvent-free conditions.¹²⁷ Dication $\mathbf{103}^{2+}$ was comprehensively characterized by X-ray crystallography as well as ^{31}P and ^{77}Se NMR spectroscopy ($\text{E} = \text{Se}$). The polyphosphorus cation $\mathbf{89}^{3+}$ and cationic polyphosphorus–chalcogen cages $\mathbf{103}^{2+}$ and $\mathbf{102i}^+$ are formally derived by stepwise isolobal exchange of $[\text{E}]$ atoms by $[\text{Ph}_2\text{P}]^+$ units in the bridging positions of the nortricyclane type structure of P_4E_3 derivatives ($\text{E} = \text{S}, \text{Se}$).

Despite the fairly large number of binary group 15/16 element cations that have been reported, an example involving phosphorus in combination with a group 16 element has not been synthesized and characterized until very recently. Although cation $[\text{P}_3\text{Se}_4]^+$ ($\mathbf{104}^+$) 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 $\mathbf{104}^+$ were independently discovered. Cation $\mathbf{104}^+$ is obtained as metallate salt $\mathbf{104}[\text{MX}_4]$ ($\text{M} = \text{Al}, \text{Ga}$; $\text{X} = \text{Cl}, \text{Br}$), either *via* a melt approach from elemental red or white phosphorus, grey selenium and selenium tetrachloride in the Lewis-acidic ionic liquid $\text{BImCl}/\text{AlCl}_3$ ($\text{M} = \text{Al}$; $\text{X} = \text{Cl}$, Scheme 32, top) or an arylation reaction of P_4Se_3 with pentamethylbromobenzene ($\text{Me}_5\text{C}_6\text{Br}$) in the presence of AlCl_3 in CH_2X_2 ($\text{M} = \text{Al}$; $\text{X} = \text{Cl}, \text{Br}$, Scheme 32, middle) or the addition of $(\text{Me}_3\text{Si})_2\text{Se}$ to a solution of PX_3 and MX_3 in CH_2X_2 at ambient temperature ($\text{M} = \text{Al}, \text{Ga}$; $\text{X} = \text{Cl}, \text{Br}$, Scheme 32, bottom).¹²⁸ The materials have been structurally characterized by single-crystal

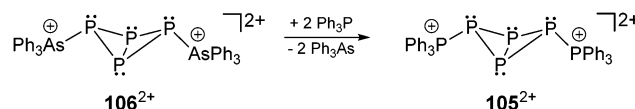


Scheme 32 Three different approaches for the synthesis of the first binary phosphorus chalcogen cation P_3Se_4^+ ($\mathbf{104}^+$) as metallate salt.

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 $^1J(^{31}\text{P}^{77}\text{Se})$ 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

The symmetrical butterfly-shaped P_6 -dication $\mathbf{105}^{2+}$ is obtained by substitution of the AsPh_3 moieties of $\mathbf{106}^{2+}$ by PPh_3 (Scheme 33). The experimental and iteratively fitted $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum reveals an $\text{A}_2\text{MM}'\text{XX}'$ spin system (Fig. 18). The large ^{31}P – ^{31}P coupling constants observed in $\mathbf{105}^{2+}$ ($^2J(\text{MM}') = 339 \text{ Hz}$, $^3J(\text{MX}') = -139 \text{ Hz}$ and $^4J(\text{XX}') = 39 \text{ Hz}$) indicate a substantial degree of trough space coupling between the *cis*-orientated free-lone pairs located at each “butterfly-wing”.¹²⁹

Bertrand *et al.* reported on the P_5N cage compound $\mathbf{107}$ obtained from the insertion reaction of a room temperature stable phosphanylnitrene¹³⁰ $\mathbf{108}$ into one edge of a P_4 tetrahedron (Scheme 34). The zwitterionic cage compound $\mathbf{107}$ reveals an A_2CMX spin system with ^{31}P chemical shifts in the expected



Scheme 33 AsPh_3 can be substituted by PPh_3 in the bicyclic compound $\mathbf{106}^{2+}$ to give the analogous dicationic polyphosphorus framework $\mathbf{105}^{2+}$.

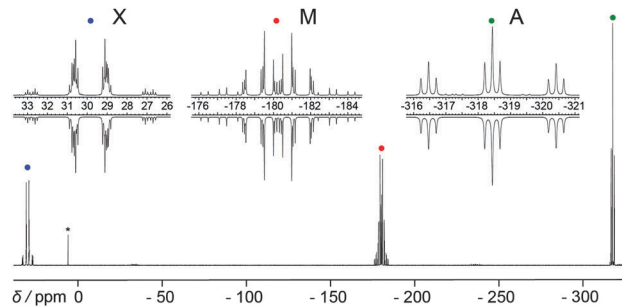
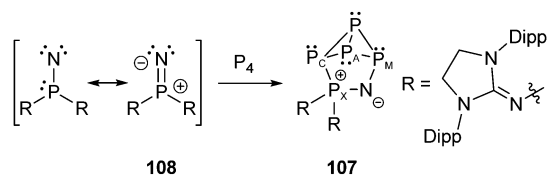


Fig. 18 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the butterfly-shaped dication $\mathbf{105}^{2+}$ (upwards) and simulation (downwards). This figure has been reproduced from *Angewandte Chemie* with permission from John Wiley and Sons.¹²⁹



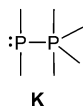


Scheme 34 Insertion of a phosphanyl nitrene **108** into one edge of the P_4 tetrahedron giving **107**.

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

σ^3 – σ^5

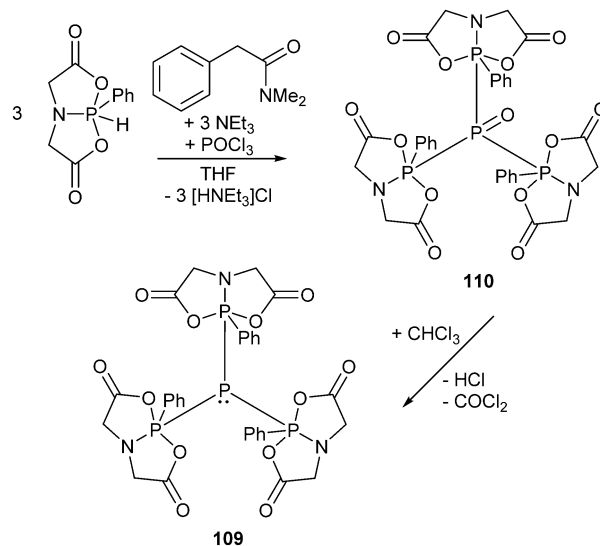
The class of σ^3 – σ^5 diphosphorus compounds comprises basically only phosphanylphosphoranones (bonding motif **K**), as no example of the combination of a σ^3 – σ^5 phosphorus atom adjacent to a σ^5 phosphorane has been reported.



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.

Compound **109** was obtained by reduction of the corresponding phosphane oxide **110** (bonding motif **N**) with chloroform (Scheme 35).¹³¹ The ^{31}P NMR spectrum displays a complex A_3B 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, $CDCl_3$, $\delta(P_A) = -28.2$, $\delta(P_B) = 40.9$ ppm, $^1J(PP) = 341.3$ 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 nBu_3PO) 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



Scheme 35 Synthesis of **110** and reduction with $CHCl_3$ to triphosphoranyl-phosphane **109**.

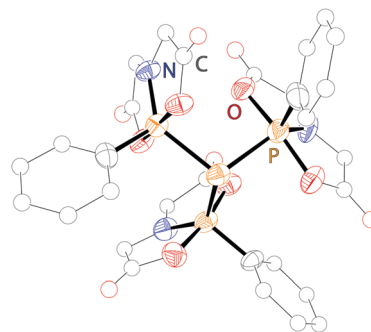
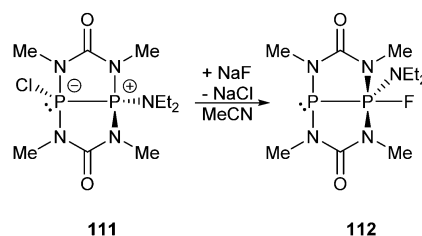


Fig. 19 Molecular structure of triphosphoranyl phosphane **109**; hydrogen atoms are omitted for clarity.

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 (Scheme 36).¹³³ Thus, the σ^3 – σ^5 diphosphorus compound **112**



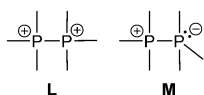
Scheme 36 Transformation of **111** (bonding motif **M**) into **112** (bonding motif **K**) by halide exchange.



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 [PCl₄][−] anion,¹³⁶ the P–F distance (1.628 Å) is only slightly longer than those observed in PF₅ (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**).



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 [Me₃PPMe₃][PF₆]₂ (**96**²⁺, R = R' = Me) has first been assigned on the basis of elemental analysis data and IR spectroscopy.¹⁴⁴

Polyphosphane adducts of electrophilic antimony,¹⁴⁵ thallium,¹⁴⁴ copper,¹⁴⁴ or iron¹⁴⁶ acceptors are known to spontaneously eliminate diphosphonium dications [R₃PPR₃]²⁺. Dialkylation of diphosphines, reductive elimination processes or methylation of P–P phosphanylphosphonium cations are versatile synthetic approaches to fundamentally important prototypical examples of diphosphonium dications (Fig. 20) that define the origin of a potentially extensive and diverse *catena*-phosphorus chemistry, paralleling *catena*-carbon chemistry. The quantitative nature of the reactions bodes well for the development of polyphosphonium chemistry. Very recently diphosphonium dications

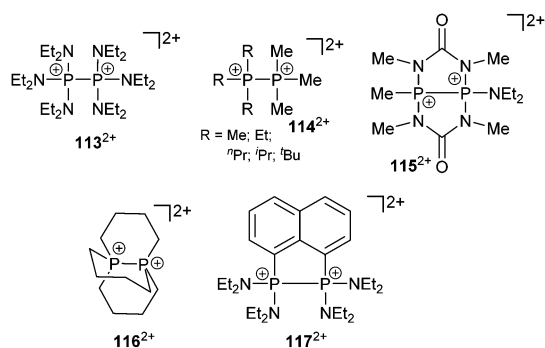


Fig. 20 Selected examples of diphosphonium dications comprising bonding motif L.

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.

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 PMe₃ into a solution of PBr₃ 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 PMe₃ (δ = −61.9 ppm in C₆D₆) and PBr₃ (228.5 ppm in CD₂Cl₂) the resonance of the donating PMe₃ unit (P_{don}) is shifted to lower field, whereas that of the accepting PBr₃ unit (P_{acc}) is shifted to significantly higher field (δ (P_{don}) = 29.5 ppm, δ (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 bromo 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 PBr₃ unit resulting in two edge-sharing distorted square pyramids. Although the distances between two monomeric units of **118** are closer to the sum of the van der Waals radii (3.74 Å)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 PCl₂[−] and an electron donating ⁱPr₂P-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

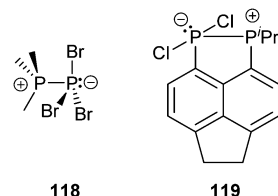


Fig. 21 Selected examples of compounds comprising bonding motif M.



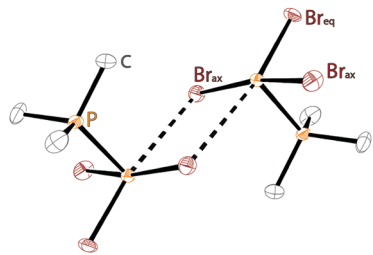
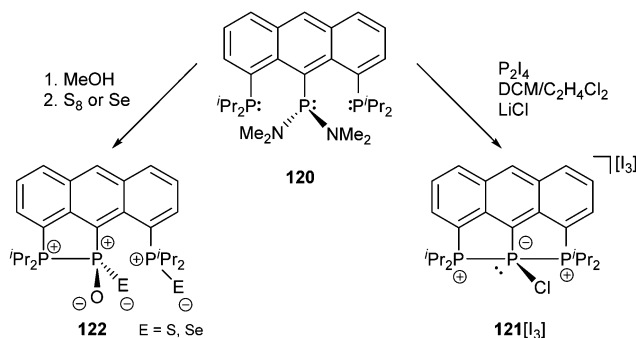


Fig. 22 Molecular structure of **118** displaying two phosphoniophosphoranide units forming a dimeric bridge; hydrogen atoms are omitted for clarity.



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

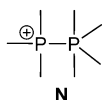
substituent in the equatorial and the chlorine atoms in the axial positions. The resonances of solution ^{31}P NMR spectra (PCl_2 68.8 and P^iPr_2 40.4 ppm) and the observation of a $^1J(\text{PP})$ coupling constant of 363 Hz are consistent with the retention of the P–P bond upon redissolution.^{135d}

The reaction of the anthracene derived triphosphane¹⁰ **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 (Scheme 37). The rather long P–P bond lengths are unequal in the solid state (2.382(5) and 2.528(5) Å). In contrast, the solution ^{31}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.

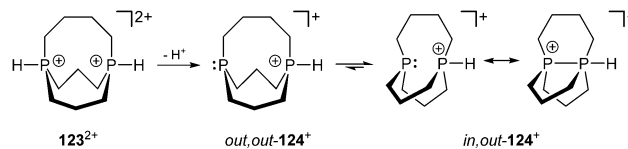


Bonding motif N

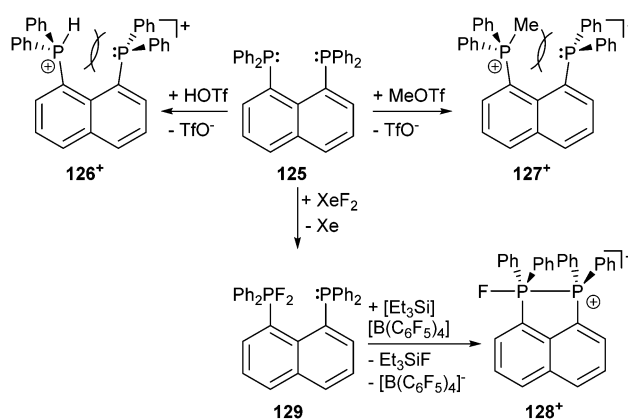
Alder *et al.* showed that the addition of nucleophiles to tricyclic propellane-type diphosphonium dication (bonding motif L) of different ring sizes gives phosphoniophosphoranides. Although some aspects of this work have already been summarized elsewhere,¹⁵⁰ the different extent of transannular P–P 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.

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 monoprotinated bicyclic cation out,out-**124**⁺ which undergoes in,out-inversion of the free lone pair (Scheme 38).¹⁵² While out,out-**124**⁺ shows broad signals in the ^{31}P NMR spectra, in,out-**124**⁺ shows two doublets with a $^1J(\text{PP})$ coupling constant of 253 Hz. The energy barrier of inversion in **124**⁺ was determined to be only 70 kJ mol⁻¹, an extraordinary low value for trialkylphosphanes. The phosphoniophosphorane was calculated to be 24 kJ mol⁻¹ more stable.¹⁵³

Schmützler *et al.* reinvestigated the single protonation (Scheme 39, left) and methylation (Scheme 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



Scheme 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.



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



the Alder systems (*vide supra*). Very recently, Stephan *et al.* synthesized the phosphoniofluorophosphorane as perfluorinated borate salt **128**[B(C₆F₅)₄] by fluorination of **125** and subsequent fluoride ion abstraction from the difluorophosphorane **129** (Scheme 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.

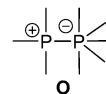
Kilian *et al.* reported on the isomeric diphosphoniumdications *meso*-**130**²⁺ and *rac*-**130**²⁺ that are formed by two consecutive methylation steps of the diphosphaacenaphthene **131** *via* a phosphanylphosphonium intermediate **132**⁺ (Scheme 40, top). The formation of the respective diastereomer strongly depends on the methylation agent used. An interesting interconversion process of both stereoisomers is facilitated by the presence of fluoride ions which was supported by quantum chemical calculations and ³¹P-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 σ⁴–σ⁵ 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 σ⁵ 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 σ³–λ³ phosphane (phosphinite, R₂PO[−] or phosphinothioite, R₂PS[−]). 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 σ⁴–σ⁵ environment.

σ⁴–σ⁶

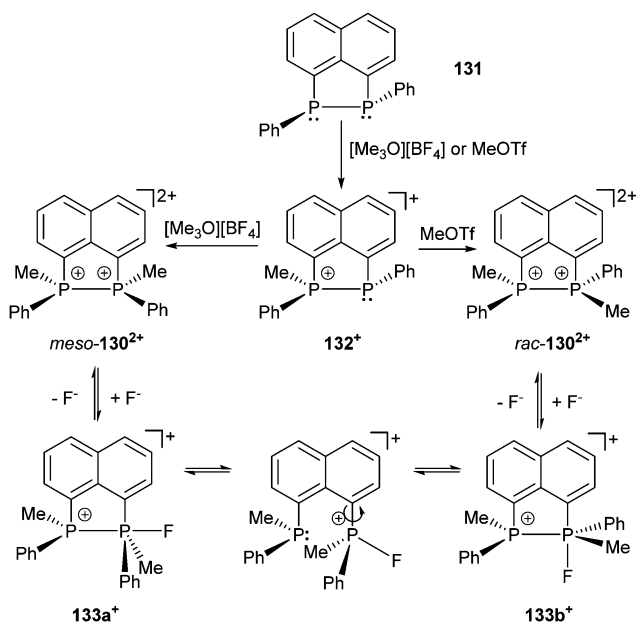
The only phosphorus moiety bonded to a hexacoordinate phosphate forming stable products that have been observed so far is the phosphonium moiety. Phosphoniophosphates are described by bonding motif **O**.



Bonding motif O

Only few reports on phosphoniophosphates have appeared in the literature. At first, adducts of PF₅ and alkylphosphanes were studied by NMR spectroscopy.¹⁵⁹

The first isolated and structurally characterized σ⁴–σ⁶ P–P compound **134** from an electron deficient trifluoro-λ⁵-dioxophospholane was published by Röschenenthaler *et al.*¹⁶⁰ The molecular structure displays a tetrahedral phosphonio moiety bonded to an octahedral σ⁶-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



Scheme 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).

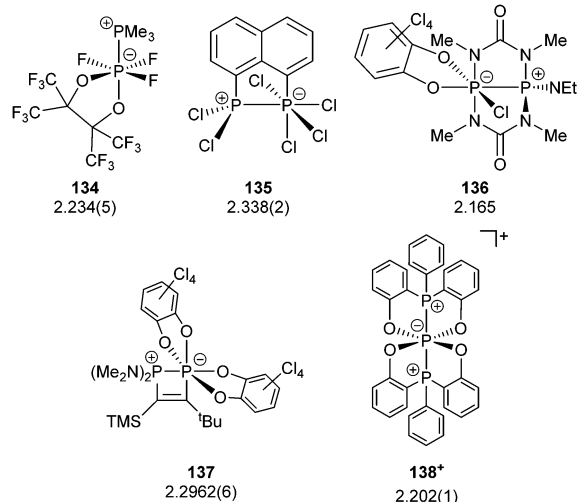


Fig. 23 Selected derivatives comprising bonding motif **O** with respective P–P bond lengths in Å.



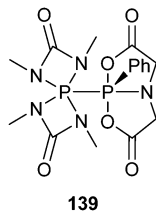


Fig. 24 Compound **139** comprising the very rare example of bonding motif **P**.

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 phosphoniophosphorane **111** (bonding motif **M**) by *o*-chloranil, the hexacoordinate phosphorus comprises a regular octahedral environment and a bond length of 2.165 Å to the phosphonium moiety. The tetracoordinate phosphorus atom is in a heavily distorted tetrahedral environment due to the urea ligand forcing the two P-P-N angles to be rather small at 97° .¹³³ The structures of the cation **138**⁺ (ref. 163) and the unsymmetrically chlorinated diphosphaacenaphthene **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



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 penta-coordinate 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

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(<i>tert</i> -butyl)phenyl
n	Normal/unbranched
NHC	N-heterocyclic carbene
OTf	Triflate/trifluoromethanesulfonate
Pr	Propyl
Ph	Phenyl
pyr	3,5-Dimethylpyrazolyl
<i>t</i>	<i>tert</i>
triaz	1,3,5-Trimethylhexahydro-1,3,5-triazine
trip	2,4,6-Triisopropylphenyl
<i>vide infra</i>	See below
<i>vide supra</i>	See above

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