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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 mixedcoordinate 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. In the report of Dillon et al., which appeared in 1995, the field of P-P bonded compounds was re-reviewed.

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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 R₄P⁺ cation that can be obtained by either protonation of the parent λ^3 -phosphane (phosphonium) or by hydride abstraction from the parent λ⁵-phosphane/phosphorane (λ⁵-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 P₄ is often used as a benchmark in order to classify the bonding situation in the title compounds. Although the sum of the van der Waals radii of the P-P bonded framework 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



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

	σ^2	σ^3	σ^4	σ^5		
σ^2	:-					
σ^3		⊕ :P-P P=P ⊕ H I				
σ^4	⊖	:P−P 	⊕			
σ^5	;;PP 	:P-P 	⊕			
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 $\sigma^2 - \sigma^2$ (diphosphenes)⁹ and $\sigma^3 - \sigma^3$ (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 PF₅). On the other hand, hyper-coordination with less electronegative atoms around the central phosphorus is less common and more sophisticated approaches (resonance stabilization, favorable ring size formation) are needed to stabilize such species".10

The discussion in the following section is divided in the combination of the σ -matrix as depicted in Table 1. Only for the combination of $\sigma^2 - \sigma^3$, $\sigma^2 - \sigma^4$, $\sigma^3 - \sigma^3$ and $\sigma^4 - \sigma^4$ 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.

$$\sigma^2 - \sigma^2$$

The parent motif of $\sigma^2 - \sigma^2$ phosphorus compounds is the wellknown 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 $(1^{-13}, 2^{-14}, 3^{-15}, 4^{-15}, 4^{-15})$ 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 representa tive 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 lowfield shifted compared to the adjacent two phosphorus atoms of which the chemical shift is observed at around 200 ppm (Table 2). Consistent with resonances structure I and II the central di-coordinate phosphorus atom is obviously involved in a normal conjugated allylic system and uses its p-type orbitals for both π - and σ -bonding. The 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-triphosphanediium cation 72+ (Scheme 2).

The protonation of 5⁺ is reversible and the addition of a base to a solution of 7²⁺ instantly forms a deep green solution of 5⁺. 19 Upon protonation the phosphaallyl anion $[(^tBu_3Si)_2P_3]^-$ (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 7²⁺ are observed in the characteristic range for cyclotriphosphanes. 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 $(7^{2+}: {}^{1}J(P_{\Delta}H) = 155.7 \text{ Hz}; \text{ compare } 9: {}^{1}J(P_{\Delta}H) = 137.1 \text{ Hz}). \text{ The}$ 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 $(7^{2+}: {}^{1}J(P_{A}P_{M}) = -158.8 \text{ Hz};$ compare 8: ${}^{1}J(P_{A}P_{X}) = -224.2 \text{ Hz}, 9: {}^{1}J(P_{A}P_{M}) = -226.6 \text{ Hz})$ contrasts the smaller coupling constant for the trans-arrangement involving the hydrogen-substituted P atom (7^{2+} : ${}^{1}J(P_{A}P_{X}) = -130.4$ Hz; compare 8: ${}^{1}/(P_{A}P_{X}) = -141.3 \text{ Hz}$, 9: ${}^{1}/(P_{A}P_{M}) = -144.1 \text{ Hz}$). A similar trend is observed for ²J(PH) coupling constants. Large values indicate a cis-arrangement of the hydrogen atom at PA and the lone pair of electrons at the adjacent P atom $(7^{2+}: {}^{2}J(P_{X}H) = 34.2 \text{ Hz}, 8:$ ${}^{2}J(P_{X}H) = 16.6 \text{ Hz}$), whereas small values indicate a transarrangement $(7^{2+}: {}^{2}J(P_{M}H) = 17.8 \text{ Hz}, 8: {}^{2}J(P_{M}H) = 6.9 \text{ Hz}).$

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

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

	$\mathrm{Li}[1]^a$	[Li(dme) ₃][2]	$[K(thf)_2][3]$	$[Li(triaz)_2][4]$	$[5][GaCl_4]$	[6][Cl]
Ref.	13	14	15 <i>c</i>	16 <i>b</i>	17	18
Colour	Red violet	Deep red	Purple	Violet	Green	Green
$\delta(^{31}P)_{adjacent}$ in ppm	208	494.1	232.1	199.8	199.4	190.6
$\delta(^{31}P)_{adjacent}$ in ppm $\delta(^{31}P)_{central}$ in ppm	548	295.5	730.0	717.2	597.9	591.9
$^{1}J_{\mathrm{PP}}$ in Hz	524	430	552.3	541	508.3	505.9
d(P−P) in Å		2.137(1)	2.072(2)	2.0730(8); 2.0774(8)	2.093(1); 2.091(1)	2.090(1); 2.097(1)
d(P−C/Si) in Å		1.687(3)	2.252(2); 2.260(2)	2.2459(8); 2.2454(9)	1.815(2); 1.814(3)	1.812(1); 1.811(1)
Angle P–P–P in °		88.3(1)	105.83(7)	105.52(3)	87.2(4)	92.76(2)

^a No structural parameter available.

Reversible protonation/deprotonation reaction between 5th Scheme 2 and 72+

Substituent arrangement in cyclo-triphosphanes 72+, 8 and 9

 $^{31}P\{^{1}H\}$ NMR parameters for 7^{2+} . 8 and 9

31 P	7 ²⁺	8	9
Ref.	19	13 <i>a</i>	20
Spin system	AMX	AMX	AMX
$\delta(P_A)$	-202.3	-260.1	-270.8
$\delta(P_M)$	-182.6	-259.5	-149.2
$\delta(P_X)$	-156.8	-240.9	-136.3
$^{1}J(P_{A}P_{M})$	-158.8	-224.2	-144.1
${}^{1}J(P_{A}P_{X})$	-130.4	-141.3	-226.6
${}^{1}J(P_{M}P_{X})$	-203.0	-188.0	-223.7
$^{1}J(P_{\Delta}H)$	155.7	137.1	<u>_</u> a
$^{2}J(P_{M}H)$	17.8	6.9	a a
${}^{2}J(P_{X}H)$	34.2	16.6	<u></u> _a
^a Coupling consta	nts are not reported	l.	

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 ³¹P NMR data. Thus, the more shielded central phosphorus atom is now observed at 295.5 ppm and the resonance for the adjacent phosphorus atoms is observed at significantly lower field at 494.1 ppm. The ¹J(PP) coupling constant of 430 Hz is only slightly affected but in accordance with a significant structural change of the P₃ bonded system. For triphosphaallyl ions 1⁻, 3⁻, 4⁻, 5⁺ and 6⁺ a significantly shortened P-P bond length (<2.1 Å) is observed indicating

$$R = SiMe_{3}$$

$$R = SiMe_{3}$$

$$R = R$$

Scheme 3 Rearrangement reaction of 2 upon protonation.

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 P₃-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 C₆H₅F shows two absorption bands of which the strongest band (I_{max}) is observed at 696 nm corresponding to an $n \to \pi^*$ transition. The second absorption maximum at 443 nm can be assigned to a $\pi \to \pi^*$ 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 $[Pn_3C_2R_2]^-$ (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 [Pn₇]³⁻ $(Pn = P, As)^{23}$ or the monoprotonated derivatives $[HPn_7]^{2-}$ with alkynes in dimethylformamide in the presence of a cation sequestering ligand like 2,2,2-crypt or 18-crown-6 (Scheme 5).²⁴

Noteworthy is that the electronic structures of these "carboncopy" ligands possess notable differences in comparison to

Scheme 4 Reduction of 6+ to neutral radical species 12•

$$[Pn_7]^{3-}$$
 or $[HPn_7]^{2-}$ + R $=$ R' = H, Aryl
 $Pn = P$, As

Scheme 5 1,2,3-Tripnictoolides 13 formed by the reaction of heptapnictides and alkynes.

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

catena-Tetraphosphene dianions of the general formula [R-PPPP-R]²⁻ may be described as doubly phosphanido substituted diphosphenes and are therefore related to the triphosphaallyl ions. The supersilyl-bearing ($R = {}^{t}Bu_{3}Si$) alkali salts²⁶ as well as the terphenyl substituted thallium analogue²⁷ (R = C_6H_3 -2,6- $(C_6H_2$ -2,6-iPr₂)₂) were isolated and characterized. The bond lengths compare well to [Li(dme)₃][2] (Fig. 1). All ³¹P chemical shifts are shifted to higher field. The alkali salts show highfield shifted resonances at 390-420 and -53 to 19 ppm for the inner and outer phosphorus atoms, respectively. The ³¹P NMR shifts of the thallium complex (285/180 ppm) could not be assigned.

Phosphanyl-substituted diphosphenes such as 14 represent another example related to bonding motif A and were first reported by Romanenko et al.28 The treatment of aminosubstituted diphosphene 15 with triflic acid (Scheme 6) eliminates [Pr2NH2][OTf] accompanied by the in situ formation of the highly reactive phosphorus-analogue of a diazonium ion 16^{+} which, due to its high reactivity, is not stable even at -78 °C and forms bicyclo[1.1.0]tetraphosphanes besides unidentified products.

In the presence of a tert-phosphane such as PPh3 the adduct 17a⁺ (R = R' = Ph) is formed with a $\sigma^2 - \sigma^2 - \sigma^4$ connectivity of the P3-backbone representing an example of bonding motif F (vide infra). The formation of 17a⁺ was confirmed by X-ray structure analysis and the obtained P-P bonding parameters of 2.025(1) Å and 2.206(1) Å are in the range of a double and a single bond, respectively. Employing a sec-phosphane such as ^tBu₂PH in the reaction with 16⁺, the initially formed cation 17b⁺ slowly liberates HOTf to give the first example of a σ^2 - σ^2 - σ^3 triphosphene 14 as an example of bonding motif B (vide infra).^{28,29}

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

Scheme 7 Two different approaches for the synthesis of NHC stabilized chlorodiphosphanes 19a-d comprising bonding motif B. For 19a,b: (i) +RPCl₂, +DABCO, -DABCO*HCl; for **19c**: (ii) +2 PCl(NMe₂)₂, +DABCO, -DABCO*HCl, $-P(NMe_2)_3$; for **19d**: (iii) +3 1,3-bis(2,6-diisopropylphenyl)-4,5-dichloro-imidazole-2-ylidene, -5+. Subsequent chloride abstraction yields polarized cationic diphosphenes 18a-d⁺. Only two resonance structures that indicate the polarization of 18a-d+ are shown.

Recently, Grützmacher et al. reported on the synthesis of three polarized, cationic diphosphenes 18a-c⁺. 30 Independently, a fourth derivative was also reported by our group.³¹ The synthesis of the precursor compound 19a-d, which belongs to bonding motif B, was achieved by two distinctly different synthetic strategies (Scheme 7). The group of Grützmacher followed the approach of DABCO (1,4-diaza[2.2.2]bicyclooctane) assisted condensation of the parent phosphinidene carbene adduct 20 with chlorophosphanes to synthesize 19a-c. Our group used the NHC induced [3+2] fragmentation reaction of the P5-cage cation 21a+ (bonding motif J, vide infra) yielding the triphosphaallyl compound 5⁺ as P₃-fragment (vide supra) besides the P₂-fragment **19d.**¹⁷ The subsequent chloride abstraction from all four derivatives 19a-d by GaCl3 leads to the formation of the polarized, cationic diphosphenes 18a-d⁺. The derivatives 18b,d⁺ with sterically more demanding substituents could be isolated and structurally characterized. The P-P bond lengths are in the expected range for polarized double bonds (18b⁺: 2.061(1) Å, 18d+: 2.038(1) Å).

The derivatives 18a,c+ with smaller residues on the phosphenium-type side prevent their isolation but enable dimerization to form dicationic cyclo-tetraphosphanes 22a,c²⁺ (Scheme 8, left) demonstrating the diphosphene-type reactivity. In contrast, the electrophilicity of the R-substituted P atom can be demonstrated by treatment of 18d⁺ with PMe₃ yielding the unique $\sigma^2 - \sigma^3 - \sigma^4$ species 23⁺ (Scheme 8, right) incorporating both bonding motif **B** and **J** (vide infra). The product may be depicted in another resonance structure including a phosphaalkene moiety, but a dihedral N-C-P-P angle of 50.5(3)° suggests a preference of the phosphanide structure. This is

Scheme 8 [2+2] dimerization reaction of diphosphenes 18a,c+ (left) and PMe₃ attacking the more electrophilic P atom of diphosphene **18d**⁺ forming $\sigma^2 - \sigma^3 - \sigma^4$ 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.

$$\sigma^2 - \sigma^3$$

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-phosphanyldiazaphosphene 24 produced by a base-catalysed elimination of Me₃SiCl from the corresponding phosphane.³³ The amino group at the nitrogen atom lengthens the P-N double bond, whereas the phosphanyl group at phosphorus itself exerts only negligible changes on the P-N bond. In this example the phosphanyl group acts as a σ -donor and the amino group simultaneously as a σ -acceptor and a π -donor. As a consequence, both substituents at the P-N double bond refer to the case of σ -push pull substitution and enforce enhanced lengthening of the P-N double bond.

Du Mont et al. investigated the reactions of the P-phosphanyl phosphaalkene 25 at its P=C and P-P bonds (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-Phosphanylphosphaalkene 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 (Me₃GeSiCl₃) they observed an unusual P=C bond cleavage accompanied by a double dichlorosilylene (SiCl₂) transfer, which represented an important contribution to the chemistry of stable Group 14 carbene analogues. The trichlorosilyltrimethylgermane represents a versatile reagent for the transfer of SiCl2 moieties to P-phosphanyl phosphaalkenes under very mild conditions.34b,c

Bonding motif C

The first phosphanylphosphenium 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 CH₂Cl₂ 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 SO₂₍₁₎ with very strong methylation reagents of the type $R[CHB_{11}Me_5X_6]$ (R = Me, Et, ⁱPr; X = Br) introduced by Reed et al. (Scheme 10).36 This class of potent electrophilic "R" alkylating agents uses the weakly nucleophilic carborane anions $[CHB_{11}Me_5X_6]^-$ (X = Cl, Br) as leaving groups. In this way the Reed group managed to transform alkanes into carbenium ions via hydride abstraction below room temperature or to methylate electron deficient phosphorus compounds that are otherwise inert to conventional alkylating agents such as methyl triflate. The mixture of Me[CHB11Me5Br6] and diphosphene 31b ($R = CF_3$) in $SO_{2(1)}$ 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 = t Bu): δ = 495 ppm). The large coupling constant of ¹/(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 \mathbf{D} and are the anionic congeners in the σ^2 – σ^3 category of P-P bonded phosphorus compounds. Surprisingly little is known about this class of compounds, unless considering phosphorus rich oligo- and polyphosphides. This might be due to their high tendency towards condensation reactions. Baudler *et al.* extensively described the reaction of P_2H_4 in liquid ammonia. They stated that the initial step represents the deprotonation by an amide anion. The resulting $P_2H_3^-$ anion in turn again attacks diphosphane and initiates a cascade of disproportionation and aggregation reactions. Under evolution of PH_3 gas the reaction ultimately leads to the formation of

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 $[P_7]^{3-}$, $[P_{14}]^{4-}$, $[P_{16}]^{2-}$, $[P_{19}]^{3-}$, $[P_{21}]^{3-}$, $[P_{22}]^{4-}$ and $[P_{26}]^{4-}$ is observed.²³ The reaction of P_2H_4 in ammonia in the presence of solvents such as THF yields hydrogen phosphides of which the selected examples $[H_3P_3]^{2-}$, $[H_8P_7]^-$, $[H_4P_7]^-$, $[H_5P_8]^-$, $[H_7]^{2-}$ (ref. 41) and $[H_2P_7]^-$ (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 phosphanyl-phosphanide motif also plays a key role, continue to attract attention which has led to numerous publications in the last decades. Parts of the interrelations between substituted oligophosphides, their reactivity and the mechanisms of their formation have been investigated employing *e.g.* bulky silanides and have been discussed elsewhere. ⁴³

Fritz *et al.* synthesized a series of bis-phosphanyl substituted lithium phosphanides 33a-d by treatment of the parent silyl phosphanes 34a-d with *n*-butyl lithium (Scheme 12). ⁴⁴ Interestingly, in the solid state, the lithium ion is not coordinated to the negatively charged phosphorus atom itself, but chelated by the two adjacent phosphane moieties instead. Several related acyclic and cyclic anions of the form $[P(PR_2)_2]^-$ 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. Fig. 5 depicts the tetraphosphane-1,4-diide [Na(solv) $_x$] $_2$ [34] as representative example, showing the characteristic M_2P_2 arrangement found in solid state structures of bis(alkali metal)-*catena*-oligophosphane- α , ω -diides [M $_2$ (solv) $_x$ (R_nP_n)]

SiMe₃

R

P

R

P

R

BuLi

THF

R

Li R'

thf

thf

a: R =
$${}^{t}Bu$$
; R' = ${}^{t}Bu$; Bu b: R = ${}^{i}Pr$; R' c: R = ${}^{i}Pr$; R' = ${}^{i}Pr$ d: R = ${}^{i}Pr$; R' = ${}^{t}Bu$ d: R = NEt₂; R' = ${}^{t}Bu$

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 [Na(solv), $_1$ 2[34] showing the characteristic bicyclobutane-shaped M_2P_2 arrangement (left); illustration of point charges and coulombic interactions (right).

(M = Li, Na, K; n = 2, 3, 4; R = Ph, Mes, tBu ; solv = solvent molecule or ligand). The formation of such bicyclobutane-shaped ion triples is found frequently for dianions as a result of a minimized net electrostatic energy. Four attractive Coulombic interactions $(r_{+,-})$ are opposed by only two repulsive ones $(r_{+,+})$ and $r_{-,-}$.

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

As may be expected, the P4 chains in both diastereomers adopt a 1,4-anti-conformation due to electrostatic repulsion. Interestingly, the dissolution of the slightly soluble crystals yields an orange solution which contains free diphenyldiphosphene radical anions [35] - resulting from the homolytic cleavage of the central P-P bond in [34]2-. The radical anions exhibit a strong EPR signal (g = 2.0089) with a triplet splitting ($a_{iso}[P] = 115$ MHz) resulting from two identical phosphorus nuclei. Further hyperfinecoupling to two non-equivalent ortho-protons $(a_{iso}[H] = 8.5 \text{ MHz},$ $a_{\rm iso}[{\rm H'}] = 4.0 {\rm MHz}$) indicates a hindered rotation of the phenyl groups on the EPR time scale along with a certain degree of π -type delocalization. Furthermore, the group of Grützmacher could show a complete reversibility of both reactions. Upon concentration of solutions of [35] again crystals of [Na(2,2,2crypt)]₂[34] are obtained and the addition of [Na(2,2,2-crypt)]₂[34] to a solution of NaOTf in THF reforms the ion triple $[Na(solv)_x]_2[34]$. Since the P-P bond lengths of the unstabilized [Ph₄P₄]²⁻-chains (central P-P: 2.224(2) Å, terminal P-P: 2.178(1) Å) in crystals of [Na(2,2,2-crypt)]₂[meso-34] refer to normal single bonds they reasoned that the dissociation process into radical anions must originate from the Coulombic repulsion. Similarly, the P-P bond cleavage, leading to [P₂Mes₂]• radical anions, was also reported by another group to occur in concentrated THF solutions

 $[Na(solv)_{x}]_{2}[\mathbf{34}] \xrightarrow{excess} Ph \xrightarrow{p} Ph \xrightarrow{p} Ph \xrightarrow{crystal} Ph \xrightarrow{r} Ph$ $[\mathbf{34}]^{2-} [Sa(2,2,2-crypt)]^{+} = 2[Na(2,2,2-crypt)]^{+} = 2[N$

Scheme 13 The sodium ions of [Na(solv), l_2 [34] can be sequestrated by 2,2,2-crypt. In solution the product splits into two radical anions [35] $^{\bullet-}$. Only one resonance structure of [35] $^{\bullet-}$ shown.

of the singly protonated species $[K(18\text{-crown-6})][P_4HMes_4]$. In contrast to solutions of the dianions, $[P_4HMes_4]^{\bullet-}$ was found to undergo redistribution reactions forming complex mixtures of neutral and anionic species.⁴⁶

$$\sigma^2 - \sigma^4$$

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-σ⁴-phosphoranes (R₂C⁻-P⁺R₃) or Wittig reagents and are thus called phosphanylidene-σ⁴-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 Me₃PPCF₃ adduct (36a) resulting from the reaction of PMe₃ and cyclic (PCF₃)_n (n = 4, 5; Scheme 14).47 Only very few examples are known (e.g. 36b,c (b: R = Mes, c: R = Mes*), 48 37, 49 38⁵⁰ and 39⁵¹) and synthetically accessible in their free form (Fig. 6). They are mainly obtained as transition metal-stabilized compounds $(L_nM-P(R)-PR_3)$, which are employed for P=C bond formation alternatively to terminal phosphinidene complexes $R-P = ML_n$ (for reviews see 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. The *peri*-substituted compound 39 is sterically less encumbered than previous examples. Similar to the BH₃ adduct 40, which is obtained from the reaction of 36a with B₂H₆ in Et₂O (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 ${\bf E}$.

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 phospha-derivatives of cyclo-phosphazenes as their cyclic congeners. Cyclic triphosphenium cations 41a,b⁺ with 5- or 6-membered rings are typically obtained from the reaction of an appropriate chelating bisphosphane ligand (e.g. a: dppe; b: dppp) and 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, n Bu) and [41a]Br (Scheme 16). Calculations confirm that these species are best considered as carbene-ligated P(1) 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: $R = {}^{i}Pr$). These ligands can undergo coordination to several transition metals as either two- or four-electron bridging donor to give stable and

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]⁺.

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

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(PiPr2)2 gives compound 45 in which two five-membered rings are linked via two phosphorus atoms. The mechanism of formation is unclear for both cases, however, their structural arrangement is confirmed by crystal structure analysis (Scheme 17).

The readily available Janus-head type diphosphorus compound 46[OTf] (pyr = 3,5-dimethylpyrazolyl) is an attractive precursor for the construction of cationic ring and cage systems.^{8b,62} The stepwise reaction of 46[OTf] with Cv₂PH gives the two novel cationic polyphosphorus frameworks [Cy4P4pyr]+ (47+) and $[Cy_6P_7]^+$ (48⁺) as well as 49[OTf] as one of the isolated sideproducts (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 18 Formation of cyclic (47+) and bicyclic (48+) cationic polyphosphorus frameworks comprising the triphosphenium motif. Equation is

Fig. 8 Molecular structure of cation 48⁺ in 48[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[AlCl₄] remains unchanged in solution, whereas 50[OTf] decomposes quantitatively into phosphaalkyne 51 under elimination of Me₃SiOTf and PPh₃ (Scheme 19). A reaction proceeding in the reverse manner has been reported in which the phosphonio-phosphaalkene 52⁺ is formed by a 1,2-addition reaction of [HPPh3][OTf] to the bulky adamantyl-substituted phosphaalkyne 53.65 Further reactions of phosphaalkynes leading to comparable derivatives comprising bonding motif **F** are described elsewhere.⁶⁶

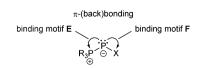


Illustration of π -(back)bonding in σ^2 - σ^4 phosphorus compounds.

Scheme 19 The phosphonio-phosphaalkene 50+ decomposes giving phosphaalkyne 51. In a reverse reaction 53 and triphenylphosphonium triflate form phosphonio-phosphaalkene 52[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 (Mes*PN)⁺ which can be described by a set of resonance structures I-III (Scheme 20). Although it was frequently described as a cation with a 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 sp² in well-stabilized to sp in poorly stabilized (Mes*NP)+ derivatives. Mes*NPCl is best described as covalent chloroiminophosphane (II) with a σ^2 P atom and a slightly elongated P-Cl single bond (2.142(4) Å). The P-N distance is rather short (1.495(4) Å) and the P-N-C angle $(154.8(4)^{\circ})$ is much larger than expected for an sp²-imine, thus indicating a starting transition to an iminophosphenium ion.⁶⁷ If X is a weakly coordinating anion such as [AlCl₄] the P-N distance

Scheme 20 Representative resonance structures I-III illustrating the bonding situation in phosphadiazonium ions (Mes*NP)+. L can be a neutral

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(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 $(\sim 3.55 \text{ Å})^7$ 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 (\sim 1.6 Å) than to the sum of the van der Waals radii ($\sim 3.3 \text{ Å}$), 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 σ^3 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, $^{1}J(PP) = 340 \text{ Hz}).^{70}$

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

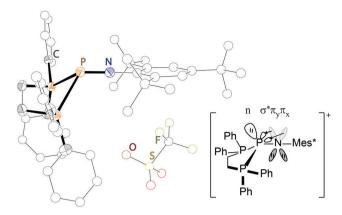


Fig. 11 Molecular structure of 54[OTf]; hydrogen atoms are omitted for clarity (left); illustration of negative hyperconjugation in 56[OTf].

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 σ^3 P atom (2.5708(9) Å and 2.5392(9) Å). A low temperature NMR study at -80 °C revealed that the P-P bonds also remain unequal in solution $(\delta(NP) = 36 \text{ ppm}, \delta(dppe1) = 10.2 \text{ ppm}, {}^{1}J(PP) = 492 \text{ Hz},$ $\delta(\text{dppe2}) = 10.3 \text{ ppm}, ^{1}J(\text{PP}) = 419 \text{ Hz}$). The coordination environment at the distorted trigonal pyramidal P atom may be rationalized by the occupied π_x - and π_v -orbitals of nitrogen overlapping the σ^* -orbitals of the P-P bonds, thus elongating them, but shortening the P-N bond (1.489(1) Å) and facilitating an effective sp-hybridization of the nitrogen atom (P-N-C: 179.3(7)°) (Fig. 11, right).

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

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 σ^3 phosphorus atom to give compound 58 (Scheme 22). The phosphaalkene moiety occupies an equatorial position and

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

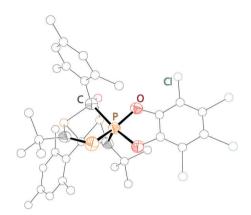


Fig. 12 Molecular structure of compound 58; hydrogen atoms are omitted

Scheme 23 Condensation of silvlated phosphaalkene 59 and chlorophosphorane **60** giving **61**, which features the rare $\sigma^2 - \sigma^5$ bonding motif **G**.

$$\begin{array}{c} \text{trip} \\ \text{:P-P:} \\ \text{trip} \end{array}
 \begin{array}{c} \text{trip} \\ \text{-2 Ag} \end{array}
 \begin{array}{c} \text{trip} \\ \text{-2 Ag} \end{array}
 \begin{array}{c} \text{trip} \\ \text{trip} \end{array}
 \begin{array}{c} \text{trip} \\ \text{-1 color} \\ \text{-2 Ag} \end{array}
 \begin{array}{c} \text{trip} \\ \text{-2 Ag} \end{array}
 \begin{array}{c} \text{-2 Ag} \\ \text{-2 Ag} \end{array}
 \begin{array}{c} \text{-2$$

Scheme 24 Oxidation of very bulky diphosphane 63 with silver salt of a very weakly coordinating anion yielding 622+, the only reported example of a diphosphenium dication.

the P-P bond length of 2.239(1) Å clearly indicates a regular P-P single bond (Fig. 12).72

Treatment of silylated phosphaalkene 59 with the chlorobis(catecholato)phosphorane 60 yields another example of a compound (61) featuring a σ^2 - σ^5 bonding motif. The reaction is accompanied by the formation of two eq. of Me₃SiCl and the product can be obtained in 80% yield after recrystallization (Scheme 23). Characterization of this compound included NMR, IR and elemental analysis.⁷³ Evidence of the structural arrangement was recently supported by a computational study of the same group on the mechanism of formation. They suggest a three step mechanism for the formation of the first experimentally observable intermediate, in which the P-P bond is already established, but the Si-O bond is still intact. The P=C bond is found to be in slightly disfavoured (8.9 kJ mol⁻¹) E-configuration.74

$$\sigma^3 - \sigma^3$$

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

Bonding motif H

This substance class contains compounds in which a phosphanyl moiety is linked to a σ^3 phosphorane. Predominantly in the early 1990's phosphanyl-bis(imino)phosphoranes and phosphanylbis(alkylidene)phosphoranes have been studied and discussed elsewhere. 37a, b, 75

Bonding motif I

To the best of our knowledge, only once such a dication has been synthesized and characterized.⁷⁶ Recognizing the relationship to the aforementioned σ^2 - σ^3 phosphanylphosphenium ions (bonding motif C) and the difficulties in accessing them, the necessity to employ a weakly coordinating anion such as $[Al(OR^F)_4]^-$ (R^F = C(CF₃)₃) seems obvious. The red dication 62²⁺ was obtained from the parent diphosphane 63 by two single electron oxidation steps with Ag[Al(ORF)4] via the radical monocation (trip = 2,4,6-triisopropylphenyl; Scheme 24). The ³¹P NMR resonance at 168.8 ppm is shifted to even higher field than that of the related phosphanylphosphenium ions (30⁺). The P-P bond length of 2.021(2) Å and the planar geometry in the crystal structure indicate a regular double bond (Fig. 13).

$$\sigma^3 - \sigma^4$$

Bonding motif J

The category of the σ^3 - σ^4 bonding motif J comprises neutral derivatives and a large variety of cations. The group of neutral derivatives (Fig. 14) includes the diphosphane monochalcogenides 64a (E = O, S). Although not many examples have appeared in the literature so far, they are of interest as flame retardants.⁷⁷ The applicability of the well-known diphosphane monooxides $R_2P(O)-PR_2$ (64a; E = O)^{1,2} is somehow restricted by their lability towards moisture and oxygen. The tautomer of these oxides are di(phosphanyl) oxides or anhydrides of phosphinous acids, $R_2P-O-PR_2$ (64b; E = O) which are in most cases less stable than the corresponding diphosphane monoxides (46a). For compounds with alkoxy- (OR) and aminosubstituents (NR₂) or mixtures of both equilibria between 64a and 64b are observed in certain

Fig. 13 Molecular structure of the diphosphenium dication 62²⁺; 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 substitutents such as fluoride,79 trifluoromethyl- (CF₃)80 or 2,4-bis(trifluoromethyl)phenyl- (2,4-(CF₃)₂C₆H₃) groups stabilize the anhydrides of the phosphinous acids. 81 The bis(bis(trifluoromethyl)phosphanyl) oxide, (CF₃)₂P-O-P(CF₃)₂, is stable with respect to its corresponding phosphane oxide tautomer, however, it deflagrates readily on contact with air. Hoge et al. succeeded to synthesize and crystallographically characterize the $(2,4-(CF_3)_2C_6H_3)_2P-O-P(2,4-(CF_3)_2C_6H_3)_2$ derivative ($\delta = 105.6$ ppm, ³¹P NMR in CDCl₃) but also observed small quantities of the isomeric diphosphane monoxide (2,4-(CF₃)₂C₆H₃)₂P(O)-P(2,4-(CF₃)₂C₆H₃)₂ in the reaction, identified by its characteristic resonance in the ³¹P NMR spectrum at 39 ppm for the oxygenbonded phosphorus atom and -32.5 ppm for the trivalent phosphorus atom (${}^{1}J(PP) = 247 \text{ Hz}$). The stability of **64a** is significantly improved for the heavier congeners with E = S or Se, however, large scale syntheses of these compounds in high purity are currently not available. Reported syntheses that are not suitable on an industrial scale involve desulfurization of diphosphane disulfides,82 oxidation reactions of diphosphanes with elemental sulfur,83 or comproportionation reactions of diphosphanes and diphosphane disulfides. 83a,84 The reaction of sodium thiophosphinites with R₂PCl 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 (R = Ph, Cy; E = 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; E = S) were obtained and used as ligands in ruthenium coordination complexes.86 To the best of our knowledge, synthetic protocols for diphosphane monoselenides (64a; E = Se) and -tellurides (64a; E = Te) are unreported. Only very few derivatives (R = t Bu, R₂N) of di(phosphanyl) selenides (64b; E = Se) and even fewer tellurides (64b; E = Te) are reported and prepared in a similar manner to the sulfur derivatives or via persistent phosphanyl radicals.87

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 diphosphane monochalcogenides 64a and are also tautomers of the more commonly encountered di(phosphanyl)amines 65b with an R₂P-NR-PR₂ 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 (PPh), with a deficiency of selenium in which one or two [PPh] units of the cyclo-phosphane are formally replaced by Se atoms. 95 The oxidation of cyclo-1,4- $(CH_2)_2(P^tBu)_4$ with chalcogens showed that the two antipodal CH2 units of the starting material provide structural braces that allow dichalcogenation to occur without disruption of the six-membered C₂P₄ ring giving dichalcogenated derivatives such as the 2,5-isomers **66** (Fig. 14, $R = {}^{t}Bu$; E = S, Se). ⁹⁶ Density functional theory (DFT) calculations for the 2,5-chalcogenated derivatives 66 (E = S, Se) and the corresponding radical cations and dications predict significant structural changes of the six-membered ring upon oxidation. The formation of a transannular P-P single bond (ca. 2.25 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 I 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- $(PR)_n$ (R = Et, ⁿPr, ⁿBu, 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-(P₄Ph₄CH₂) (68b) in the reaction with BH₃(SMe₂) 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.

reasoned that the coordination of the borane facilitates the formation of the respective tetraphosphacyclopentanide anion. 100 In their findings they concluded that the complexes 69a,b are readily formed from the 1:2 reaction of 68a,b with BH3. The formation of adducts with a higher ratio of BH3 per molecule appears to be disfavoured. The position of the BH₃ moieties in the cyclo-phosphane rings indicates a comparable high nucleophilicity of the respective P atoms in both cases. In solution, derivative 68a forms a mixture of two diastereomers which are related to each other by inversion of the tricoordinate P atoms, while a complex mixture of isomers is observed for 68b.

There is a large number of cationic species comprising bonding motif I. Phosphanylphosphonium ions consist of a tricoordinate phosphanyl moiety and a phosphonium centre which is analogous to an ammonium centre and conventionally defined as a tetracoordinate phosphorus center bearing a formal positive charge (iii, Scheme 26). According to another resonance structure, they are also termed phosphane stabilized phosphenium ions (ii). The question whether the σ^3 - σ^4 P-P bond possesses rather a covalent or a dative character was theoretically investigated by Pietschnig. 101 Calculations (MP2/6-311G(d)) on a model system (R = Me, X = Me or NH₂; Scheme 26) revealed that according to Wiberg bond indices (0.867 for X = Me, 0.807 for X = NH₂) the P-P bond in both derivatives are best described as single bonds. However, the heterolytic cleavage was only found to be slightly preferred over the homolytic P-P cleavage in case of the π -donating amino substituent. As already discussed in the context of phosphadiazonium ions (bonding motif F, Scheme 20) an efficient π -stabilization diminishes the necessity for stabilization by additional substituents/donors and may thus lead to a lower coordination number at the P atom. It is therefore not surprising that, to the best of our knowledge, no examples of isolated σ^2 phosphenium ions without a π -donating substituent have been reported.

Basically independent of the nature of the P-P bond in a wide range of phosphanylphosphonium ions, the σ^4 P atom represents a good nucleofuge and is therefore easily substituted by stronger Lewis bases. This inherent high reactivity makes cationic species containing polyphosphorus frameworks prominent synthetic targets. 102 Catenated and cyclic polyphosphanylphosphonium salts are most intensely studied within this diverse group of cations. 103 Typically phosphanylphosphonium

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

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

cations can be accessed from either the reaction of a chlorophosphane with a halide abstracting agent (Abs) (Scheme 27, top), the reaction of a chlorophosphane, a phosphane and a halide abstracting agent (Scheme 27, middle) or by protonation or alkylation of a diphosphane (Scheme 27, bottom).

A library of crystallographic data for several derivatives 104 is available and shows consistent P-P distances that are close to 2.2 Å for most cases. The most important of the many reported catena- and cyclo-phosphorus cations comprising bonding motif J are depicted in Fig. 15. 102c,105 They offer new synthetic approaches, not only for P-P bond formation, but also for other aspects in synthesis. 106 Phosphanylphosphonium cations with two phosphorus atoms typically exhibit two well separated doublets in 31P NMR spectra with the high field shifted resonance corresponding to the tricoordinate phosphorus atom and the low field shifted to the tetracoordinate phosphorus atom. ¹J(PP) coupling constants are normally observed in the range of 250–450 Hz. In the solid state phosphanylphosphonium cations contain a slightly distorted tetrahedral environment for the tetracoordinate and a pyramidal geometry for the tricoordinate phosphorus atom that is typical of a phosphane. As expected, the distortion can be more intense in more complex and cyclic systems as a result of ring strain or steric demand of the substituents.

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

Scheme 28 Diverse reactivity of cation 52⁺ in the reaction with a series of nucleophiles such as Me₂PCl, MePCl₂, R₃P and dmap (4-(dimethylamino)pyridine)

The prototypical phosphanylphosphonium framework can be decorated with halo-substituents (X = Cl, Br, I) at either the phosphane or the phosphonium centres to yield an array of acyclic and cyclic halo-functionalized cations (Fig. 15). In this context, the preparation of diphosphanes or cyclo-polyphosphanes from the reduction of respective chlorophosphanes can be applied to access catenated cationic polyphopshorus frameworks. 105d,e Cation 70+ readily reacts with Lewis bases such as 4-(dimethylamino)pyridine (dmap) and phosphanes (R₃P), providing approaches to new open-chain and cyclic phosphorus frameworks (Scheme 28). Upon reaction with R₃P (R = Me or ⁿPr) or dmap the three-membered ring is opened to yield the adducts $[R_3P-P^tBu-P^tBu-P(Me)^tBu][OTf]$ (R = Me (71a⁺), ⁿPr $(71b^+)$) and $[(dmap)-P^tBu-P^tBu-P(Me)^tBu][OTf]$ (7^{2+}) . The complicated ³¹P{¹H} NMR spectra of the three compounds were simulated, evidencing the presence of two diastereomeric forms of $71a^{+}$, and a single diastereomer of $71b^{+}$. This ringopening reactivity of the cation 70⁺ parallels the reactivity of isolobal epoxides with nucleophiles under acidic conditions. The reaction with Me₂PCl and Me₃SiOTf resulted in the unexpected formation of dication 732+, which is postulated to result from two consecutive ring-opening and ring-closing steps. In contrast, employing MePCl₂ 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 cyclotetraphosphane 75 by PCl₅ in the presence of the Lewis acid GaCl₃ which provides a stepwise approach to salts of the first cyclo-phosphanylchlorophosphonium cations [Cy₄P₄Cl]⁺ and $[Cy_4P_4Cl_2]^{2+}$ (76²⁺, (Scheme 29)). Reactions of the dication 76²⁺ with dmpe effect a dissociation of the cyclic framework resulting in the formation of the cyclic cations 77²⁺ and 78²⁺ with an extended ring size. The new cations represent phosphane complexes that are formed from 76²⁺ which dissociates formally via a retro [2+2] or [1+1+1'+1'] process releasing cationic $[PCy]^{2+}$ and $[P_2Cy_2]^{2+}$ fragments, demonstrating the partially coordinative nature of the σ^3 - σ^4 P-P bonds in *cyclo*-phosphanylhalophosphonium cations. 106

The methylation of the diphosphirane 79 with MeOTf allows the formation of the P-methylated diphosphiranium salt 80[OTf]

Scheme 29 Synthesis of cyclo-phosphanylchlorophosphonium cation 76²⁺ (left) and release of $[PCy]^{2+}$ (top right) or $[P_2Cy_2]^{2+}$ fragments (bottom right).

Scheme 30 Synthesis of diphosphiranium cations 80+ by methylation of diphosphirane 79 (top) and 82+ by acid-induced dimerization of phosphaalkene 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 phosphaalkene 81 upon addition of HOTf (Scheme 30, bottom). In contrast to 80[OTf] the diphosphiranium triflate 82[OTf] showed sufficient stability in solution to be isolated and crystallographically characterized. The P-P bond length of 2.1637(5) Å corresponds to a slightly shortened single bond and the strain in the P₂C ring is reflected by the small internal ring angles (σ^3 -P: 52.69(4)°, σ^4 -P: 55.82(5)°, C: 71.49(5)°). 110

The investigation of homoleptic polyphosphorus cations was limited to mass spectroscopy¹¹¹ and quantum chemical calculation 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_0^+ -cage 83⁺, which is composed of two C_{∞} -symmetric P₅-cages fused by a common phosphonium moiety. 112b Krossing et al. investigated the oxidation of P4 with [NO][A] (A = $Al(OC(CF_3)_3)_4^-)$ which yields $[P_4NO]^+$ -cage compound 84[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 $[NO]^+$ as the interacting frontier orbitals. 114 The reaction of [P4NO]+-cage compound 84[A] with

Scheme 31 Synthesis of the first homoleptic polyphosphorus cation 83^+ from P₄ and 84^+ .

additional 1.5 eq. of P_4 yields the P_9^+ -cage compound 83[A] (Scheme 31). They suggest that cation 83⁺ forms *via* extrusion of 1/n (PNO)_n and intermediary formation of a P_3^+ -species. The ^{31}P NMR spectrum of cation 83⁺ shows a characteristic $A_2A_2'BC_2C_2'$ spin system and confirms a D_{2d} symmetric Zintl-type structure. Despite the electron precise Lewis formula of eight neutral, tricoordinate and one cationic, tetracoordinate P atom the charge is almost evenly distributed over all nine atoms according to quantum chemical calculations.

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 PHal₃ and P₄ (Hal = Br, I; Fig. 16). 116,104d Utilizing PCl₃, 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(CF₃)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 RPCl₂ and a Lewis acid ECl₃ (E = Al, Ga) in fluorobenzene are potent sources of reactive equivalents of phosphenium ions [RPCl]+, which formally insert into P-P bonds of P₄. 118 Dissolution of P₄ in these mixtures yields white to yellowish precipitates of the corresponding [RP₅Cl]⁺-cage salts for a large range of distinct alkyl- and aryl-substituents R (21d-k[GaCl₄]; Fig. 16; [X] = [GaCl₄]). This approach can also be extended to R₂N-substituted derivatives **86e,f**[GaCl₄]. The cationic [R₂P₅]⁺-cage compounds 87d-k[GaCl₄] are synthesized via the stoichiometric reaction of R₂PCl, GaCl₃, and P₄. The reaction conditions depend on the substituent R. Alkyl-substituted derivatives (87d-h[GaCl₄]) are best synthesized using a solvent free melt reaction, whereas aryl-substituted derivatives (87i-k[GaCl₄])

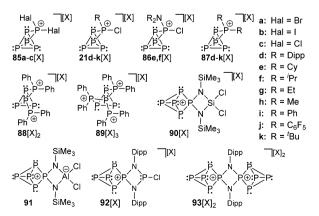


Fig. 16 Selected cationic cage compounds comprising bonding motif J.

are formed in C_6H_5F solution (Fig. 16; [X] = [GaCl₄]). 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 GaCl₃, 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 [Ph₂P]⁺ fragments into the P-P bonds of the P₄ tetrahedron. 120 This approach has been extended to highly functionalized cation 90^+ ([X] = [AlCl₄]) and the zwitterionic P5-cage 91, which are formed by the insertion of the corresponding phosphenium cations that are derived from four-membered phosphorus-nitrogen-metal heterocycles. 121 Similarly, the reaction of P4 with the cyclo-diphosphadiazane [DippNPCl]₂ (Dipp = 2,6-disopropylphenyl) and GaCl₃ in fluorobenzene yielded compound 92[GaCl₄]. The addition of an excess of GaCl₃ and a second eq. of P₄ to a solution of 92[GaCl₄] afforded the dicationic species 93²⁺ as [Ga₂Cl₇]⁻ 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 P₄S₃ reacts with in situ generated [PI₂]⁺-phosphenium ions yielding cation 94+ which disproportionates to cations 95⁺ and 96⁺ (Fig. 17). 123 The second approach is based on halide abstraction from α-P₄S₃I₂ using Krossing'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 P₃Se₄ with MesPCl₂ in the presence of AlCl₃ as Lewis acid. 125 Reacting P₄E₃ with Me₂CCl₂ in the presence of AlCl₃ the formation of cations 99 (E = S, Se) is observed. The cations are only formed in small amounts but their connectivity was confirmed by extensive NMR investigation and X-ray analysis of suitable single crystals. 126 Basal alkylation of P4E3 is observed in the reaction with secondary alkyhalides (sec-RX) to give cations of the type 100^+ (E = S, Se). 126

Another approach to generate cationic chalcogen-phosphorus cages (E = S, Se) is based on cationic polyphosphorus cages as

Fig. 17 Selected cationic polyphosphorus—chalcogen cages 94^+ – 103^{2+} (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 derivates which are all conveniently obtained in one step procedures from white phosphorus. 127 Chalcogenation reactions of [R₂P₅]⁺-cage compounds 87e,i[GaCl₄] with elemental grey selenium yield the corresponding polyphosphorus-chalcogen cages 102[GaCl₄] (E = Se, R = Cy, Ph; Fig. 17). Both cations are formed upon insertion of two selenium atoms into two P-P bonds adjacent to the phosphonium moieties in 87e,i⁺. Their structural motif resembles that of nortricyclane, with a basal P3-ring, the tetracoordinate P atom and the selenium atoms occupying the bridging positions, and one P atom defining the apex of the cage. This class of compound features interesting ³¹P and ⁷⁷Se NMR characteristics. They reveal an AM₂OX spin system for the isotopologues without a ⁷⁷Se nucleus. These resonances are superimposed by the C_1 -symmetric isotopologues featuring one ⁷⁷Se atom in one of the bridging positions. This gives rise to an AMNOXZ spin system which is strongly influenced by higher order effects. However, in the case of $102e^+$ (R = Cy), both spin systems were successfully simulated allowing for the exact determination of chemical shifts and coupling constants. A series of experiments employing 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 87e,i⁺ proceeds in a stepwise manner via the intermediates 101e,i⁺. The targeted preparation of 103⁺ as [GaCl₄]⁻ salt was achieved by utilizing a 2:1 stoichiometry of 48⁺ and grey selenium (E = Se). Another synthetic approach for the preparation of 103^+ (E = S, Se) is the targeted substitution of one [Ph₂P]⁺-moiety in the tricationic cage 893+. This was achieved by reacting 893+ with grey selenium or sulfur under solvent-free conditions. 127 Dication 1032+ was comprehensively characterized by X-ray crystallography as well as ³¹P and ⁷⁷Se NMR spectroscopy (E = Se). The polyphosphorus cation 89³⁺ and cationic polyphosphorus-chalcogen cages 103²⁺ and 102i+ are formally derived by stepwise isolobal exchange of [E] atoms by $[Ph_2P]^+$ units in the bridging positions of the nortricyclane type structure of P_4E_3 derivatives (E = S, Se).

Despite the fairly large number of binary group 15/16 element cations that have been reported, an example involving phosphorus in combination with a group 16 element has not been synthesized and characterized until very recently. Although cation $[P_3Se_4]^+$ (104⁺) does not belong to bonding motif J it complements the series of polyphosphorus-selenium cages. Three distinct synthetic routes for salts of the nortricyclane type cation 104⁺ were independently discovered. Cation 104⁺ is obtained as metallate salt $104[MX_4]$ (M = Al, Ga; X = Cl, Br), either via a melt approach from elemental red or white phosphorus, grey selenium and selenium tetrachloride in the Lewis-acidic ionic liquid BMImCl/AlCl₃ (M = Al; X = Cl, Scheme 32, top) or an arylation reaction of P₄Se₃ with pentamethylbromobenzene (Me₅C₆Br) in the presence of AlCl₃ in CH_2X_2 (M = Al; X = Cl, Br, Scheme 32, middle) or the addition of (Me₃Si)₂Se to a solution of PX₃ and MX₃ in CH₂X₂ at ambient temperature (M = Al, Ga; X = Cl, Br, Scheme 32, bottom). 128 The materials have been structurally characterized by single-crystal

$$2 P_{red} + Se_{grey} + SeCl_4 + AlCl_3$$

$$P_4Se_3 + Me_5C_6Br + Se_{grey} + AlCl_3$$

Scheme 32 Three different approaches for the synthesis of the first binary phosphorus chalcogen cation P₃Se₄⁺ (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 P₃Se₄⁺ cation presents a ¹/₍₃₁P⁷⁷Se) 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 -diaction 105^{2+} is obtained by substitution of the AsPh₃ moieties of **106**²⁺ by PPh₃ (Scheme 33). The experimental and iteratively fitted ³¹P{¹H} NMR spectrum reveals an A₂MM'XX' spin system (Fig. 18). The large ³¹P-³¹P coupling constants observed in 105^{2+} (${}^{2}J(MM') = 339 \text{ Hz}$, ${}^{3}J(MX') =$ -139 Hz and ${}^{4}I(XX') = 39$ 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 P5N cage compound 107 obtained from the insertion reaction of a room temperature stable phosphanylnitrene¹³⁰ 108 into one edge of a P₄ tetrahedron (Scheme 34). The zwitterionic cage compound 107 reveals an A₂CMX spin system with ³¹P chemical shifts in the expected

Scheme 33 AsPh₃ can be substituted by PPh₃ in the bicyclic compound 106²⁺ to give the analogous dicationic polyphosphorus framework 105²⁺

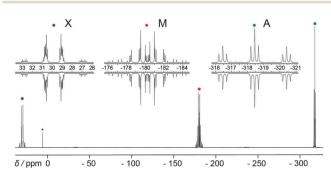


Fig. 18 ³¹P(¹H) NMR spectrum of the butterfly-shaped diaction 105²⁺ (upwards) and simulation (downwards). This figure has been reproduced from Angewandte Chemie with permission from John Wiley and Sons. 129

$$\begin{bmatrix} \vdots \\ N \vdots \\ R \end{bmatrix} \xrightarrow{P_{1}} \begin{bmatrix} \vdots \\ R \end{bmatrix} \xrightarrow{P_{2}} \begin{bmatrix} \vdots \\ R \end{bmatrix} \xrightarrow{P_{3}} \xrightarrow{P_{3$$

Scheme 34 Insertion of a phosphanylnitrene 108 into one edge of the P₄ 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 PA and PM (2.288(3) and 2.275(3) Å) are significantly longer than those between P_A and $P_{\rm C}$ (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 $(N-P_M 1.614(4) \text{ Å})$ therefore loosening the P_A-P_M bonds.

$$\sigma^3 - \sigma^5$$

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

Bonding motif K

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

Compound 109 was obtained by reduction of the corresponding phosphane oxide 110 (bonding motif N) with chloroform (Scheme 35). 131 The 31P 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, CDCl₃, $\delta(P_A) = -28.2$, $\delta(P_B) = 40.9$ ppm, ${}^{1}J(PP) =$ 341.3 Hz). The crystal structure of 109 (Fig. 19) comprises a central σ^3 phosphorus atom bearing three σ^5 phosphoranyl moieties. The P-P bonds are in the expected range of single bonds (2.244 Å) and occupy the equatorial positions of the trigonal bipyramidal coordinate σ^5 phosphorus atom. Since normal phosphane oxides (e.g. Ph₃PO or ⁿBu₃PO) 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 CHCl₃ to triphosphoranylphosphane 109.

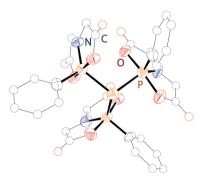


Fig. 19 Molecular structure of triphosphoranyl phosphane 109; hydrogen atoms are omitted for clarity

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** ($\sigma^3 - \sigma^5$) and **M** ($\sigma^4 - \sigma^4$) 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). Thus, the σ^3 - σ^5 diphosphorus compound 112

Scheme 36 Transformation of 111 (bonding motif M) into 112 (bonding motif \mathbf{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 $(\sim 2.3 \text{ Å})^{135}$ and comparable to the $[PCl_4]^-$ anion, ¹³⁶ the P-F distance (1.628 Å) is only slightly longer than those observed in PF₅ (1.577(5) Å). 137

$\sigma^4 - \sigma^4$

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 (113²⁺), ¹³⁸ unsymmetrically substituted alkyl-derivatives (1142+)139 or a polycyclic framework (115²⁺, 140 116²⁺ (vide infra), 141 117²⁺ (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 elimation processes or methylation of P-P phosphanylphosphonium cations are versatile synthetic approaches to fundamentally important prototypical examples of diphosphonium dications (Fig. 20) that define the origin of a potentially extensive and diverse catena-phosphorus chemistry, paralleling catena-carbon chemistry. The quantitative nature of the reactions bodes well for the development of polyphosphonium chemistry. Very recently 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 ($\delta = -61.9$ 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, $\delta(P_{acc}) = 78.5$ ppm, ${}^{1}J(PP) = 450.3$ Hz). The crystal structure of 118 (Fig. 22) shows the typical disphenoidal geometry of the phosphoranide P atom with the phosphonio and one bromo substituent occupying the two equatorial positions. While these bond lengths (P-P 2.264(2) Å, P-Br_{eq} 2.250(2) Å) correspond to single bonds the two axially bonded bromo substituents display elongated P-Br distances (P-Brax: 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 $(3.74 \text{ Å})^7$ 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.

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

1. MeOH
2.
$$S_8$$
 or Se

$$|P_{r_2}P: P: Pr_2 | Pr_$$

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 ³¹P NMR spectra (PCl₂ 68.8 and PⁱPr₂ 40.4 ppm) and the observation of a ¹J(PP) coupling constant of 363 Hz are consistent with the retention of the P-P bond upon redissolution. 135d

The reaction of the anthracene derived triphosphane 10 usith P₂I₄ 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 ³¹P 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).

$$\sigma^4 - \sigma^5$$

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 tricvclic propellane-type diphosphonium dications (bonding motif L) of different ring sizes gives phosphoniophosphoranes. Although some aspects of this work have already been summarized elsewhere, 150 the different extent of transannular P-P bonding with respect to the applied nucleophiles and ring sizes is worthy to be mentioned here. 151 Crystal structure analyses are available for the benzyl-, hydroxo- and hydrido-substituted derivatives indicating a different degree of pyramidalization of the 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 123²⁺ initially gives the monoprotonated bicyclic cation out,out-124⁺ which undergoes in,out-inversion of the free lone pair (Scheme 38). 152 While out,out-124⁺ shows broad signals in the ³¹P NMR spectra, in,out-124 shows two doublets with a 1/(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

Schmutzler 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

$$H-P \oplus P-H \xrightarrow{\cdot H^+} : P \oplus P-H \xrightarrow$$

Deprotonation of 123²⁺ 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 3c4ebonding interaction.

Kilian et al. reported on the isomeric diphosphonium dications meso-1302+ and rac-1302+ 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 σ^4 - σ^5 phosphoniophosphoranes to be stable towards dissociation to phosphanes and phosphonium cations and whether they can exist unless restrained by a bridging ligand forcing them to close contact. Besides charged phosphoniophosphoranes, phosphane oxides 131,156 (see also 110) and sulfides 133,157 adjacent to the σ^5 phosphorane unit exhibit similar bonding motifs. Although they have been discussed earlier,² we like to point out that they are sometimes surprisingly stable and some of them have been also structurally characterized. They feature the tetracoordinate phosphorus atom in an equatorial position. This is in sharp contrast to the aforementioned phosphoniophosphoranes, as the few which could be isolated so far, feature the tetracoordinate phosphorus

Scheme 40 Single and double methylation of 1,8-naphthalene bridged diphosphane 131 to meso- or rac-1302+ (top) and interconversion in the presence of fluoride ions (bottom)

in an apical position. 158 These inherent differences might be explained by the fact that the Lewis adduct formation occurs between a cationic phosphonium ion and in one case a neutral phosphane and in the other case an anionic $\sigma^3 - \lambda^3$ 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 σ^4 - σ^5 environment.

$$\sigma^4$$
- σ^6

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

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 σ^4 – σ^6 P–P compound 134 from an electron deficient trifluoro-λ⁵-dioxophospholane was published by Röschenthaler et al. 160 The molecular structure displays a tetrahedral phosphonio moiety bonded to an octahedral σ^6 -phosphate. The P-P bond length (2.234(5) Å) lies well in the expected range for a single bond. Other examples comprising bonding motif O (Fig. 23) display comparable bond lengths with those of 135¹⁶¹ and 136¹³³ 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

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

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

a relaxed σ^3 - σ^5 phosphanylphosphorane without P-P-bond and a C-C-P angle of 120° at the sp²-hybridized carbon atoms would imply a much higher distance between the two P atoms. Therefore, the distance of 2.2962(6) Å clearly indicates a strong attractive interaction between both phosphorus atoms. In the oxidation product 136 of the phosphoniophosphoranide 111 (bonding motif **M**) by o-chloranil, the hexacoordinate phosphorus comprises a regular octahedral environment and a bond length of 2.165 Å to the phosphonium moiety. The tetracoordinate phosphorus 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 135161 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 $(\sigma^5 - \sigma^5)$ similar to the equilibrium between molecular PCl₅ and its ionic form [PCl₄][PCl₆]. The optimized geometry of the calculated diphosphorane intermediate shows an axial-apical connection of the phosphorus moieties.

$$\sigma^5 - \sigma^5$$

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 $P_{ax}\text{-}P_{ax}\left(2.255(1\right)\mathring{A}\right)^{166}$ connection of both phosphorus moieties. However, compound 139 is of particular interest (Fig. 24), as both phosphorus atoms are in a different pentacoordinate environment which allows for the observation of a large ¹J(PP) coupling constant of 749.6 Hz. Although no crystal structure is available, it was proposed that the P-P bond is in equatorial position for both pentacoordinate moieties which can also explain the large ¹J(PP) value observed. ¹⁶⁷

Abbreviations

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

Ad Adamantyl Abs Halide abstracting agent

Bu Butvl

Cp Cyclopentadienide

Cyclohexyl Cy

DABCO 1,4-Diaza[2.2.2]bicyclooctane

Dipp 2,6-Diisopropylphenyl

1,2-Bis(dimethylphosphanyl)ethane dmpe dppe 1.2-Bis(diphenylphosphanyl)ethane dppp 1,3-Bis(diphenylphosphanyl)propane

Et Ethyl

eq. Equivalent(s)

Iso i

Me Methyl

2,4,6-Trimethylphenyl Mes Mes* 2,4,6-Tri(tert-butyl)phenyl Normal/unbranched N-heterocyclic carbene NHC

OTf Triflate/trifluoromethanesulfonate

Propyl Pr Ph Phenyl

3,5-Dimethylpyrazolyl pyr

1,3,5-Trimethylhexahydro-1,3,5-triazine triaz

2,4,6-Triisopropylphenyl trip

See below vide infra vide supra See above

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References

- 1 A. H. Cowley, Chem. Rev., 1965, 65, 617-634.
- 2 (a) L. Lamandé, K. Dillon and R. Wolf, Phosphorus, Sulfur Silicon Relat. Elem., 1995, 103, 1-24; (b) R. R. Holmes, Phosphorus, Sulfur Silicon Relat. Elem., 1996, 109, 1-42.
- 3 IUPAC, Compendium of Chemical Terminology, 2nd edn. (the "Gold Book"), Compiled by A. D. McNaught and A. Wilkinson, Blackwell Scientific Publications, Oxford, 1997, XML on-line corrected version: http://goldbook.iupac.org (2006) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins, ISBN 0-9678550-9-8, DOI: 10. 1351/goldbook.
- 4 W. H. Powell, Pure Appl. Chem., 1993, 65, 1357-1455.
- 5 J. J. Weigand and N. Burford, in Comprehensive Inorganic Chemistry II, ed. J. R. Poeppelmeier, Elsevier, Amsterdam, 2nd edn, 2013, pp. 119-149.
- 6 (a) L. R. Maxwell, S. B. Hendricks and V. M. Mosley, J. Chem. Phys., 1935, 3, 699-709; (b) N. J. Brassington, H. G. M. Edwards and D. A. Long, J. Raman Spectrosc., 1981, 11, 346-348; (c) A. Simon, H. Borrmann and H. Craubner, Phosphorus Sulfur Relat. Elem., 1987, 30,

- 507-510; (d) M. Haser and O. Treutler, J. Chem. Phys., 1995, **102**, 3703-3711.
- 7 A. Bondi, J. Phys. Chem., 1964, 68, 441-451.
- 8 (a) A. Karaçar, V. Klaukien, M. Freytag, H. Thönnessen, J. Omelanczuk, P. G. Jones, R. Bartsch and R. Schmutzler, Z. Anorg. Allg. Chem., 2001, 627, 2589-2603; (b) K.-O. Feldmann, Dissertation, Westfälische Wilhelms-Universität Münster, 2012.
- 9 (a) B. D. Ellis and C. L. B. Macdonald, Coord. Chem. Rev., 2007, 251, 936-973; (b) L. Weber, Eur. J. Inorg. Chem., 2000, 2425-2441.
- 10 P. Kilian and A. M. Z. Slawin, Dalton Trans., 2007, 3289-3296.
- 11 L. Farrugia, J. Appl. Crystallogr., 1997, 30, 565.
- 12 M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu and T. Higuchi, J. Am. Chem. Soc., 1981, 103, 4587-4589.
- 13 (a) P. Jutzi and U. Meyer, Phosphorus Sulfur Relat. Elem., 1988, **40**, 275–277; (b) M. Scheer, C. Kuntz, M. Stubenhofer, M. Linseis, R. F. Winter and M. Sierka, Angew. Chem., Int. Ed., 2009, 48, 2600–2604; (c) M. Scheer, C. Kuntz, M. Stubenhofer, M. Linseis, R. F. Winter and M. Sierka, Angew. Chem., 2009, 121, 2638-2642.
- 14 (a) V. Thelen, D. Schmidt, M. Nieger, E. Niecke and W. W. Schoeller, Angew. Chem., 1996, 108, 354-356; (b) V. Thelen, D. Schmidt, M. Nieger, E. Niecke and W. W. Schoeller, Angew. Chem., Int. Ed. Engl., 1996, 35, 313-315.
- 15 (a) N. Wiberg, A. Wörner, H.-W. Lerner, K. Karaghiosoff, D. Fenske, G. Baum, A. Dransfeld and P. von Ragué Schleyer, Eur. J. Inorg. Chem., 1998, 833-841; (b) H.-W. Lerner, I. Sanger, F. Schodel, A. Lorbach, M. Bolte and M. Wagner, *Dalton Trans.*, 2008, 787–792; (c) H.-W. Lerner, M. Bolte, K. Karaghiosoff and M. Wagner, Organometallics, 2004, 23, 6073-6076.
- 16 (a) V. Cappello, J. Baumgartner, A. Dransfeld, M. Flock and K. Hassler, Eur. J. Inorg. Chem., 2006, 2393-2405; (b) S. Yao, Dissertation, Johannes Gutenberg-University of Mainz, 2005.
- 17 (a) M. H. Holthausen, S. K. Surmiak, P. Jerabek, G. Frenking and J. J. Weigand, Angew. Chem., Int. Ed., 2013, 52, 11078-11082; (b) M. H. Holthausen, S. K. Surmiak, P. Jerabek, G. Frenking and J. J. Weigand, Angew. Chem., 2013, 125, 11284-11288.
- 18 A. M. Tondreau, Z. Benko, J. R. Harmer and H. Grützmacher, Chem. Sci., 2014, 5, 1545-1554.
- 19 M. H. Holthausen, Dissertation, Westfälische Wilhelms-Universität Münster, 2013.
- 20 M. Baudler, B. Makowka and K. Langerbeins, Z. Naturforsch., B: J. Chem. Sci., 1985, 40, 1274-1276.
- 21 (a) M. Baudler, J. Hahn, H. Dietsch and G. Fuerstenberg, Z. Naturforsch., B: J. Chem. Sci., 1976, 31, 1305-1310; (b) J. Hahn, M. Baudler, C. Krueger and Y. H. Tsay, Z. Naturforsch., B: J. Chem. Sci., 1982, 37, 797-805.
- 22 M. Baudler and J. Hahn, Z. Naturforsch., B: J. Chem. Sci., 1990, 45, 1139-1142.
- 23 (a) S. Scharfe, F. Kraus, S. Stegmaier, A. Schier and T. F. Fässler, Angew. Chem., Int. Ed., 2011, 50, 3630-3670;

- (b) S. Scharfe, F. Kraus, S. Stegmaier, A. Schier and T. F. Fässler, Angew. Chem., 2011, 123, 3712-3754.
- 24 (a) R. S. P. Turbervill and J. M. Goicoechea, Chem. Commun., 2012, 48, 6100-6102; (b) R. S. P. Turbervill, A. R. Jupp, P. S. B. McCullough, D. Ergöçmen and J. M. Goicoechea, Organometallics, 2013, 32, 2234-2244.
- 25 (a) P. Le Floch and F. Mathey, Coord. Chem. Rev., 1998, 179-180, 771-791; (b) F. Mathey, Angew. Chem., Int. Ed., 2003, 42, 1578-1604; (c) F. Mathey, Angew. Chem., 2003, 115, 1616-1643; (d) P. Le Floch, Coord. Chem. Rev., 2006, 250, 627-681; (e) J. F. Nixon, Chem. Soc. Rev., 1995, 24, 319-328; (f) K. B. Dillon, F. Mathey and J. F. Nixon, Phosphorus: The Carbon Copy: From Organophosphorus to Phospha-organic Chemistry, Wiley, Chichester, Toronto, 1st edn, 1998.
- 26 (a) A. Lorbach, A. Nadj, S. Tüllmann, F. Dornhaus, F. Schödel, I. Sänger, G. Margraf, J. W. Bats, M. Bolte, M. C. Holthausen, M. Wagner and H.-W. Lerner, Inorg. Chem., 2009, 48, 1005-1017.
- 27 (a) A. R. Fox, R. J. Wright, E. Rivard and P. P. Power, Angew. Chem., Int. Ed., 2005, 44, 7729-7733; (b) A. R. Fox, R. J. Wright, E. Rivard and P. P. Power, Angew. Chem., 2005, 117, 7907-7911.
- 28 V. D. Romanenko, V. L. Rudzevich, E. B. Rusanov, A. N. Chernega, A. Senio, J.-M. Sotiropoulos, G. Pfister-Guillouzo and M. Sanchez, J. Chem. Soc., Chem. Commun., 1995, 1383-1385.
- 29 L. N. Markovskii, V. D. Romanenko, M. I. Povolotskii, A. V. Ruban and E. O. Klebanskii, Zh. Obshch. Khim., 1986, 56, 2157-2158.
- 30 A. Beil, R. J. Gilliard Jr. and H. Grützmacher, *Dalton Trans.*, 2016, 45, 2044-2052.
- 31 K. Schwedtmann, M. H. Holthausen, C. H. Sala, F. Hennersdorf, R. Fröhlich and J. J. Weigand, Chem. Commun., 2016, 52, 1409-1412.
- 32 (a) R. Appel and U. Kündgen, Angew. Chem., Int. Ed. Engl., 1982, 21, 219-220; (b) R. Appel and U. Kündgen, Angew. Chem., 1982, 94, 227.
- 33 O. Altmeyer, E. Niecke, M. Nieger, T. Busch, W. W. Schoeller and D. Stalke, Heteroat. Chem., 1990, 1, 191-194.
- 34 (a) J. Mahnke, A. Zanin, W.-W. du Mont, F. Ruthe and P. G. Jones, Z. Anorg. Allg. Chem., 1998, 624, 1447-1454; (b) W.-W. du Mont, T. Gust, E. Seppälä, C. Wismach, P. G. Jones, L. Ernst, J. Grunenberg and H. C. Marsmann, Angew. Chem., Int. Ed., 2002, 41, 3829-3832; (c) W.-W. du Mont, T. Gust, E. Seppälä, C. Wismach, P. G. Jones, L. Ernst, J. Grunenberg and H. C. Marsmann, Angew. Chem., 2002, 114, 3977-3979.
- 35 (a) S. Loss, C. Widauer and H. Grützmacher, Angew. Chem., Int. Ed., 1999, 38, 3329-3331; (b) S. Loss, C. Widauer and H. Grützmacher, Angew. Chem., 1999, 111, 3546-3548.
- 36 T. Kato, E. Stoyanov, J. Geier, H. Grützmacher and C. A. Reed, J. Am. Chem. Soc., 2004, 126, 12451-12457.
- 37 (a) P. Becker, H. Brombach, G. David, M. Leuer, H.-J. Metternich and E. Niecke, Chem. Ber., 1992, 125, 771-782; (b) E. Niecke, V. von der Gönna and M. Nieger,

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Chem. Ber., 1990, **123**, 2329–2333; (c) W. W. Schoeller and T. Busch, Chem. Ber., 1992, **125**, 1319–1323; (d) R. Streubel and E. Niecke, Chem. Ber., 1990, **123**, 1245–1251; (e) R. Streubel, M. Nieger and E. Niecke, Chem. Ber., 1993, **126**, 645–648.

- 38 (a) M. Baudler, Angew. Chem., 1982, 94, 520-539; (b) M. Baudler, Angew. Chem., Int. Ed. Engl., 1982, 21, 492-512; (c) M. Baudler, Angew. Chem., 1987, 99, 429-451; (d) M. Baudler, Angew. Chem., Int. Ed. Engl., 1987, 26, 419-441; (e) M. Baudler and K. Glinka, Chem. Rev., 1993, 93, 1623-1667; (f) M. Baudler and K. Glinka, Chem. Rev., 1994, 94, 1273-1297.
- 39 N. Korber and J. Aschenbrenner, *J. Chem. SocDalton Trans.*, 2001, 1165–1166.
- 40 M. Baudler and P. Winzek, Z. Anorg. Allg. Chem., 1999, 625, 417–422.
- 41 (a) J. C. Aschenbrenner and N. Korber, Z. Anorg. Allg. Chem., 2004, 630, 31–32; (b) F.-R. Dai and L. Xu, Inorg. Chim. Acta, 2006, 359, 4265–4273.
- 42 N. Korber and H.-G. von Schnering, *J. Chem. SocChem. Commun.*, 1995, 1713–1714.
- 43 (a) M. Scheer, G. B. Balázs and A. Seitz, Chem. Rev., 2010,
 110, 4236–4256; (b) S. Gómez-Ruiz and E. Hey-Hawkins,
 Coord. Chem. Rev., 2011, 255, 1360–1386; (c) W. T. K. Chan,
 F. García, A. D. Hopkins, L. C. Martin, M. McPartlin and
 D. S. Wright, Angew. Chem., 2007, 119, 3144–3146;
 (d) W. T. K. Chan, F. García, A. D. Hopkins, L. C. Martin,
 M. McPartlin and D. S. Wright, Angew. Chem., Int. Ed.,
 2007, 46, 3084–3086.
- 44 (a) I. Kovacs, E. Matern and G. Fritz, Z. Anorg. Allg. Chem., 1996, 622, 935–941; (b) I. Kovacs, H. Krautscheid, E. Matern, E. Sattler, G. Fritz, W. Hönle, H. Borrmann and H. G. Von Schnering, Z. Anorg. Allg. Chem., 1996, 622, 1564–1572.
- 45 (a) R. Wolf, A. Schisler, P. Lönnecke, C. Jones and E. Hey-Hawkins, Eur. J. Inorg. Chem., 2004, 3277–3286; (b) R. Wolf and E. Hey-Hawkins, Z. Anorg. Allg. Chem., 2006, 632, 727–734; (c) J. Geier, J. Harmer and H. Grützmacher, Angew. Chem., Int. Ed., 2004, 43, 4093–4097; (d) J. Geier, J. Harmer and H. Grützmacher, Angew. Chem., 2004, 116, 4185–4189.
- 46 R. Wolf, S. Gomez-Ruiz, J. Reinhold, W. Böhlmann and E. Hey-Hawkins, *Inorg. Chem.*, 2006, **45**, 9107–9113.
- 47 A. B. Burg and W. Mahler, *J. Am. Chem. Soc.*, 1961, 83, 2388–2389.
- 48 S. Shah, G. P. A. Yap and J. D. Protasiewicz, *J. Organomet. Chem.*, 2000, **608**, 12–20.
- 49 M. Sanchez, R. Réau, C. J. Marsden, M. Regitz and G. Bertrand, *Chem. Eur. J.*, 1999, 5, 274–279.
- 50 A. Schmidpeter and G. Burget, *Z. Naturforsch., B: J. Chem. Sci.*, 1985, **40**, 1306–1313.
- 51 (a) B. A. Surgenor, M. Bühl, A. M. Z. Slawin, J. D. Woollins and P. Kilian, *Angew. Chem., Int. Ed.*, 2012, 51, 10150–10153; (b) B. A. Surgenor, M. Bühl, A. M. Z. Slawin, J. D. Woollins and P. Kilian, *Angew. Chem.*, 2012, 124, 10297–10300.

- 52 (a) S. Shah and J. D. Protasiewicz, Coord. Chem. Rev., 2000, 210, 181–201; (b) H. Aktaş, J. C. Slootweg and K. Lammertsma, Angew. Chem., Int. Ed., 2010, 49, 2102–2113; (c) H. Aktaş, J. C. Slootweg and K. Lammertsma, Angew. Chem., 2010, 122, 2148–2159; (d) A. Schmidpeter, in Multiple Bonds and Low Coordination in Phosphorus Chemistry, ed. M. Regitz, O. J. Scherer and R. Appel, Thieme, Stuttgart, 1990, pp. 338–351; (e) F. Mathey, A. Marinetti, S. Bauer and P. Le Floch, Pure Appl. Chem., 1991, 63, 855–858; (f) F. Mathey, N. H. T. Huy and A. Marinetti, Helv. Chim. Acta, 2001, 84, 2938–2957; (g) N. A. Piro and C. C. Cummins, J. Am. Chem. Soc., 2009, 131, 8764–8765.
- 53 (a) S. Shah and J. D. Protasiewicz, Chem. Commun., 1998, 1585–1586; (b) S. Shah, M. C. Simpson, R. C. Smith and J. D. Protasiewicz, J. Am. Chem. Soc., 2001, 123, 6925–6926; (c) D. V. Partyka, M. P. Washington, J. B. Updegraff, R. A. Woloszynek and J. D. Protasiewicz, Angew. Chem., Int. Ed., 2008, 47, 7489–7492; (d) D. V. Partyka, M. P. Washington, J. B. Updegraff, R. A. Woloszynek and J. D. Protasiewicz, Angew. Chem., 2008, 120, 7599–7602; (e) U. J. Kilgore, H. Fan, M. Pink, E. Urnezius, J. D. Protasiewicz and D. J. Mindiola, Chem. Commun., 2009, 4521–4523.
- 54 B. A. Surgenor, B. A. Chalmers, K. S. Athukorala Arachchige, A. M. Z. Slawin, J. D. Woollins, M. Bühl and P. Kilian, *Inorg. Chem.*, 2014, 53, 6856–6866.
- (a) E. L. Norton, K. L. S. Szekely, J. W. Dube, P. G. Bomben and C. L. B. Macdonald, *Inorg. Chem.*, 2008, 47, 1196–1203;
 (b) B. D. Ellis and C. L. B. Macdonald, *Inorg. Chem.*, 2006, 45, 6864–6874.
- 56 (a) D. Weber, G. Heckmann and E. Fluck, Z. Naturforsch., B:
 J. Chem. Sci., 1976, 31, 81–84; (b) A. Schmidpeter,
 S. Lochschmidt and W. S. Sheldrick, Angew. Chem., 1985,
 97, 214–215; (c) A. Schmidpeter, S. Lochschmidt and
 W. S. Sheldrick, Angew. Chem., Int. Ed. Engl., 1985, 24,
 226–227; (d) K. B. Dillon and R. J. Olivey, Heteroat. Chem.,
 2004, 15, 150–154; (e) J. D. Burton, R. M. K. Deng,
 K. B. Dillon, P. K. Monks and R. J. Olivey, Heteroat. Chem.,
 2005, 16, 447–452.
- 57 (a) J. W. Dube, C. L. B. Macdonald, B. D. Ellis and P. J. Ragogna, *Inorg. Chem.*, 2013, 52, 11438–11449;
 (b) J. W. Dube, C. L. B. Macdonald and P. J. Ragogna, *Angew. Chem.*, *Int. Ed.*, 2012, 51, 13026–13030; (c) J. W. Dube, C. L. B. Macdonald and P. J. Ragogna, *Angew. Chem.*, 2012, 124, 13203–13207.
- 58 J. F. Binder, A. A. Swidan, M. Tang, J. H. Nguyen and C. L. B. Macdonald, *Chem. Commun.*, 2015, **51**, 7741–7744.
- 59 P. K. Coffer, R. M. K. Deng, K. B. Dillon, M. A. Fox and R. J. Olivey, *Inorg. Chem.*, 2012, 51, 9799–9808.
- 60 A. Schmidpeter, F. Steinmüller and W. S. Sheldrick, *Z. Anorg. Allg. Chem.*, 1989, **579**, 158–172.
- 61 S. C. Kosnik, G. J. Farrar, E. L. Norton, B. F. T. Cooper, B. D. Ellis and C. L. B. Macdonald, *Inorg. Chem.*, 2014, 53, 13061–13069.
- 62 (a) J. J. Weigand, K.-O. Feldmann, A. K. C. Echterhoff, A. W. Ehlers and K. Lammertsma, *Angew. Chem.*, 2010, 122,

Chem Soc Rev

6314–6317; (b) J. J. Weigand, K. O. Feldmann, A. K. C. Echterhoff, A. W. Ehlers and K. Lammertsma, Angew. Chem., Int. Ed., 2010, 49, 6178–6181; (c) K.-O. Feldmann and J. J. Weigand, Angew. Chem., 2012, 124, 6670–6672; (d) K.-O. Feldmann and J. J. Weigand, Angew. Chem., Int. Ed., 2012, 51, 6566–6568.

- 63 (a) K.-O. Feldmann and J. J. Weigand, Angew. Chem., Int. Ed., 2012, 51, 7545-7549; (b) K.-O. Feldmann and J. J. Weigand, Angew. Chem., 2012, 124, 7663-7667.
- 64 G. David, E. Niecke, M. Nieger, J. Radseck and W. W. Schoeller, J. Am. Chem. Soc., 1994, 116, 2191–2192.
- 65 J. A. C. Clyburne and M. J. Schriver, *Inorg. Chem.*, 1996, 35, 3062–3063.
- 66 (a) B. Breit, A. Hoffmann, U. Bergsträßer, L. Ricard, F. Mathey and M. Regitz, Angew. Chem., 1994, 106, 1541–1543; (b) B. Breit, A. Hoffmann, U. Bergsträsser, L. Ricard, F. Mathey and M. Regitz, Angew. Chem., Int. Ed. Engl., 1994, 33, 1491–1493; (c) E. A. Ishmaeva, E. V. Popova, V. F. Mironov, R. M. Aminova, Y. A. Vereshchagina, V. I. Galkin, K. Moeller and R. Schmutzler, Russ. J. Org. Chem., 2004, 40, 1076–1079.
- 67 (a) E. Niecke, M. Nieger and F. Reichert, Angew. Chem.,
 1988, 100, 1781–1782; (b) E. Niecke, M. Nieger and
 F. Reichert, Angew. Chem., Int. Ed. Engl., 1988, 27,
 1715–1716.
- 68 (a) N. Burford, H. A. Spinney, M. J. Ferguson and R. McDonald, *Chem. Commun.*, 2004, 2696–2697;
 (b) E. Niecke, R. Detsch, M. Nieger, F. Reichert and W. W. Schoeller, *Bull. Soc. Chim. Fr.*, 1993, 130, 25–31.
- 69 N. Burford, T. S. Cameron, J. A. C. Clyburne, K. Eichele, K. N. Robertson, S. Sereda, R. E. Wasylishen and W. A. Whitla, *Inorg. Chem.*, 1996, 35, 5460-5467.
- 70 E. Niecke, G. David, R. Detsch, B. Kramer, M. Nieger and P. Wenderoth, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1993, 76, 25–28.
- 71 N. Burford, A. D. Phillips, H. A. Spinney, M. Lumsden, U. Werner-Zwanziger, M. J. Ferguson and R. McDonald, J. Am. Chem. Soc., 2005, 127, 3921–3927.
- 72 A. Mack, U. Bergsträßer, G. J. Reiß and M. Regitz, Eur. J. Org. Chem., 1999, 587–595.
- 73 E. V. Popova, V. F. Mironov, E. A. Ishmaeva and I. I. Patsanovskii, *Russ. J. Gen. Chem.*, 1999, **69**, 48–50.
- 74 E. A. Ishmaeva, D. V. Chachkov, A. Z. Alimova and Y. A. Vereshchagina, *Russ. J. Org. Chem.*, 2014, **50**, 608–610.
- 75 D. Gudat, E. Niecke, A. Ruban and V. von der Gönna, *Magn. Reson. Chem.*, 1996, 34, 799–806.
- 76 X. Pan, Y. Su, X. Chen, Y. Zhao, Y. Li, J. Zuo and X. Wang, J. Am. Chem. Soc., 2013, 135, 5561–5564.
- 77 (a) M. Staal and P. Charoensirisomboon, *Germany Pat.*, WO2009121821A1, 2009; (b) B. M. Balbo, J. Ferbitz,
 O. S. Henze, C. Fleckenstein and K. Massonne, *Germany Pat.*, WO2011092232A1, 2011.
- 78 I. F. Lutsenko and V. L. Foss, *Pure Appl. Chem.*, 1980, **52**, 917–944.
- 79 R. W. Rudolph, R. C. Taylor and R. W. Parry, *J. Am. Chem. Soc.*, 1966, 88, 3729–3734.

- 80 (a) J. E. Griffiths and A. B. Burg, J. Am. Chem. Soc., 1960, 82, 1507–1508; (b) J. E. Griffiths and A. B. Burg, J. Am. Chem. Soc., 1962, 84, 3442–3450.
- 81 (a) B. Hoge and B. Kurscheid, *Angew. Chem.*, 2008, **120**, 6920–6922; (b) B. Hoge and B. Kurscheid, *Angew. Chem.*, *Int. Ed.*, 2008, **47**, 6814–6816.
- 82 L. Maier, J. Inorg. Nucl. Chem., 1962, 24, 275-283.
- 83 (a) L. Maier, Helv. Chim. Acta, 1962, 45, 2381–2383;
 (b) H. Matschiner, F. Krech and A. Steinert, Z. Anorg. Allg. Chem., 1969, 371, 256–262.
- 84 M. Gruber, P. G. Jones and R. Schmutzler, *Chem. Ber.*, 1990, 123, 1313–1317.
- 85 V. L. Foss, Y. A. Veits, P. L. Kukhmisterov and I. F. Lutsenko, *Zh. Obshch. Khim.*, 1977, 47, 478–479.
- 86 P. E. Sues, A. J. Lough and R. H. Morris, *Chem. Commun.*, 2014, **50**, 4707–4710.
- 87 (a) R. C. Dobbie and M. J. Hopkinson, J. Fluorine Chem., 1974,
 3, 367–374; (b) W.-W. du Mont, R. Hensel, W. McFarlane,
 I. J. Colquhoun, M. L. Ziegler and O. Serhadli, Chem. Ber.,
 1989, 122, 37–41; (c) H. Westerman, M. Nieger and
 E. Niecke, Chem. Ber., 1991, 124, 13–16; (d) N. J. Hill,
 G. Reeske and A. H. Cowley, Main Group Chem., 2010, 9,
 5–10; (e) N. A. Giffin, A. D. Hendsbee, T. L. Roemmele,
 M. D. Lumsden, C. C. Pye and J. D. Masuda, Inorg. Chem.,
 2012, 51, 11837–11850.
- 88 E. Ciganek, J. Org. Chem., 1970, 35, 3631-3636.
- 89 (a) A. Sola, F. Oton, A. Espinosa, A. Tarraga and P. Molina, *Dalton Trans.*, 2011, 40, 12548–12559; (b) Á. Lorenzo, E. Aller and P. Molina, *Tetrahedron*, 2009, 65, 1397–1401; (c) M. Alajarín, A. Vidal and R.-A. Orenes, *Eur. J. Org. Chem.*, 2002, 4222–4227.
- 90 (a) T. Q. Ly and J. D. Woollins, Coord. Chem. Rev., 1998, 176, 451–481; (b) Z. Fei and P. J. Dyson, Coord. Chem. Rev., 2005, 249, 2056–2074.
- 91 (a) Z. Fei, E. Păunescu, W. H. Ang, R. Scopelliti and P. J. Dyson, Eur. J. Inorg. Chem., 2014, 1745–1750;
 (b) H. Rossknecht, W. P. Lehmann and A. Schmidpeter, Phosphorus, 1975, 5, 195–201; (c) A. Schmidpeter and H. Rossknecht, Z. Naturforsch., B: J. Chem. Sci., 1971, 26, 81–82.
- 92 (a) M. S. Balakrishna, V. S. Reddy, S. S. Krishnamurthy, J. F. Nixon and J. C. T. R. Burckett St. Laurent, *Coord. Chem. Rev.*, 1994, **129**, 1–90; (b) T. Appleby and J. Derek Woollins, *Coord. Chem. Rev.*, 2002, **235**, 121–140.
- 93 (a) Z. Fei, R. Scopelliti and P. J. Dyson, Eur. J. Inorg. Chem., 2004, 530–537; (b) Z. Fei, R. Scopelliti and P. J. Dyson, Dalton Trans., 2003, 2772–2779; (c) Z. Fei, N. Biricik, D. Zhao, R. Scopelliti and P. J. Dyson, Inorg. Chem., 2004, 43, 2228–2230; (d) Z. Fei, W. H. Ang, D. Zhao, R. Scopelliti and P. J. Dyson, Inorg. Chim. Acta, 2006, 359, 2635–2643.
- 94 (a) P. Bhattacharyya, A. M. Z. Slawin and J. D. Woollins, Chem. Eur. J., 2002, 8, 2705–2711; (b) K. Karaghiosoff, K. Eckstein and R. Motzer, Phosphorus, Sulfur Silicon Relat. Elem., 1994, 93, 185–188; (c) G. Großmann, G. Ohms, K. Krüger, K. Karaghiosoff, K. Eckstein,

Review Article

J. Hahn, A. Hopp, O. L. Malkina and P. Hrobarik, *Z. Anorg. Allg. Chem.*, 2001, **627**, 1269–1278.

- 95 (a) G. Hua and J. D. Woollins, *Angew. Chem.*, 2009, **121**, 1394–1403; (b) G. Hua and J. D. Woollins, *Angew. Chem.*, *Int. Ed.*, 2009, **48**, 1368–1377.
- 96 P. J. W. Elder and T. Chivers, *Inorg. Chem.*, 2013, 52, 7791–7804.
- 97 P. J. W. Elder, T. L. Roemmele, M. Taghavikish, T. A. Engesser, H. Scherer, I. Krossing, R. T. Boeré and T. Chivers, *Heteroat. Chem.*, 2014, 25, 501–513.
- 98 (a) A. B. Burg, J. Inorg. Nucl. Chem., 1959, 11, 258; (b) H. L. Carrell and J. Donohue, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 1968, 24, 699–707; (c) H. Schmidbaur, T. Wimmer, A. Grohmann, O. Steigelmann and G. Müller, Chem. Ber., 1989, 122, 1607–1612.
- 99 A. H. Cowley and R. P. Pinnell, *Inorg. Chem.*, 1966, 5, 1463–1464.
- 100 R. Wolf, M. Finger, C. Limburg, A. C. Willis, S. B. Wild and E. Hey-Hawkins, *Dalton Trans.*, 2006, 831–837.
- 101 R. Pietschnig, J. Organomet. Chem., 2007, 692, 3363-3369.
- 102 (a) N. Burford, T. S. Cameron, D. J. LeBlanc, P. Losier, S. Sereda and G. Wu, *Organometallics*, 1997, 16, 4712–4717;
 (b) N. Burford, T. S. Cameron, P. J. Ragogna, E. Ocando-Mavarez, M. Gee, R. McDonald and R. E. Wasylishen, *J. Am. Chem. Soc.*, 2001, 123, 7947–7948; (c) N. Burford, P. J. Ragogna, R. McDonald and M. J. Ferguson, *J. Am. Chem. Soc.*, 2003, 125, 14404–14410.
- 103 (a) N. Burford, C. A. Dyker and A. Decken, Angew. Chem., Int. Ed., 2005, 44, 2364–2367; (b) N. Burford, C. A. Dyker, M. Lumsden and A. Decken, Angew. Chem., 2005, 117, 6352–6355; (c) C. A. Dyker and N. Burford, Chem. Asian J., 2008, 3, 28–36.
- (a) M. B. Abrams, B. L. Scott and R. T. Baker, *Organometallics*, 2000, 19, 4944–4956; (b) J. M. Slattery, C. Fish, M. Green, T. N. Hooper, J. C. Jeffery, R. J. Kilby, J. M. Lynam, J. E. McGrady, D. A. Pantazis, C. A. Russell and C. E. Willans, *Chem. Eur. J.*, 2007, 13, 6967–6974; (c) M. Gee, R. E. Wasylishen, P. J. Ragogna, N. Burford and R. McDonald, *Can. J. Chem.*, 2002, 80, 1488–1500; (d) M. Gonsior, I. Krossing, L. Müller, I. Raabe, M. Jansen and L. van Wüllen, *Chem. Eur. J.*, 2002, 8, 4475–4492; (e) N. Burford, D. E. Herbert, P. J. Ragogna, R. McDonald and M. J. Ferguson, *J. Am. Chem. Soc.*, 2004, 126, 17067–17073.
- 105 (a) N. Burford, P. J. Ragogna, R. McDonald and M. J. Ferguson, *Chem. Commun.*, 2003, 2066–2067; (b) C. A. Dyker, N. Burford, G. Menard, M. D. Lumsden and A. Decken, *Inorg. Chem.*, 2007, 46, 4277–4285; (c) C. A. Dyker, N. Burford, M. D. Lumsden and A. Decken, *J. Am. Chem. Soc.*, 2006, 128, 9632–9633; (d) Y.-y. Carpenter, N. Burford, M. D. Lumsden and R. McDonald, *Inorg. Chem.*, 2011, 50, 3342–3353; (e) Y.-y. Carpenter, C. A. Dyker, N. Burford, M. D. Lumsden and A. Decken, *J. Am. Chem. Soc.*, 2008, 130, 15732–15741.
- 106 J. J. Weigand, N. Burford, R. J. Davidson, S. Cameron and P. Seelheim, *J. Am. Chem. Soc.*, 2009, **131**, 17943–17953.

- 107 A. P. M. Robertson, C. A. Dyker, P. A. Gray, B. O. Patrick, A. Decken and N. Burford, *J. Am. Chem. Soc.*, 2014, **136**, 14941–14950.
- 108 M. H. Holthausen, D. Knackstedt, N. Burford and J. J. Weigand, *Aust. J. Chem.*, 2013, **66**, 1155–1162.
- 109 S. Loss, C. Widauer, H. Ruegger, U. Fleischer, C. M. Marchand, H. Grützmacher and G. Frenking, *Dalton Trans.*, 2003, 85–91.
- 110 J. I. Bates and D. P. Gates, J. Am. Chem. Soc., 2006, 128, 15998–15999.
- 111 T. P. Martin, Z. Phys. D: At., Mol. Clusters, 1986, 3, 211-217.
- 112 (a) M. D. Chen, R. B. Huang, L. S. Zheng, Q. E. Zhang and C. T. Au, *Chem. Phys. Lett.*, 2000, 325, 22–28; (b) T. Xue, J. Luo, S. Shen, F. Li and J. Zhao, *Chem. Phys. Lett.*, 2010, 485, 26–30.
- 113 I. Krossing, in *Molecular Clusters of the Main Group Elements*, ed. M. Driess and H. Nöth, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2005, pp. 209–229.
- 114 (a) T. Köchner, S. Riedel, A. J. Lehner, H. Scherer, I. Raabe, T. A. Engesser, F. W. Scholz, U. Gellrich, P. Eiden, R. A. Paz Schmidt, D. A. Plattner and I. Krossing, Angew. Chem., Int. Ed., 2010, 49, 8139–8143; (b) T. Köchner, S. Riedel, A. J. Lehner, H. Scherer, I. Raabe, T. A. Engesser, F. W. Scholz, U. Gellrich, P. Eiden, R. A. Paz Schmidt, D. A. Plattner and I. Krossing, Angew. Chem., 2010, 122, 8316–8320.
- 115 (a) T. Köchner, T. A. Engesser, H. Scherer, D. A. Plattner, A. Steffani and I. Krossing, Angew. Chem., Int. Ed., 2012, 51, 6529–6531; (b) T. Köchner, T. A. Engesser, H. Scherer, D. A. Plattner, A. Steffani and I. Krossing, Angew. Chem., 2012, 124, 6635–6637.
- 116 I. Krossing and I. Raabe, *Angew. Chem., Int. Ed.*, 2001, **40**, 4406–4409.
- 117 A. Bihlmeier, M. Gonsior, I. Raabe, N. Trapp and I. Krossing, *Chem. Eur. J.*, 2004, **10**, 5041–5051.
- 118 M. H. Holthausen, K.-O. Feldmann, S. Schulz, A. Hepp and J. J. Weigand, *Inorg. Chem.*, 2012, 51, 3374–3387.
- 119 M. H. Holthausen and J. J. Weigand, *Z. Anorg. Allg. Chem.*, 2012, **638**, 1103–1108.
- 120 (a) J. J. Weigand, M. Holthausen and R. Fröhlich, Angew. Chem., Int. Ed., 2009, 48, 295–298; (b) J. J. Weigand, M. Holthausen and R. Fröhlich, Angew. Chem., 2009, 121, 301–304.
- 121 M. H. Holthausen, C. Richter, A. Hepp and J. J. Weigand, *Chem. Commun.*, 2010, **46**, 6921–6923.
- 122 M. H. Holthausen and J. J. Weigand, *J. Am. Chem. Soc.*, 2009, **131**, 14210–14211.
- 123 M. Gonsior, I. Krossing and E. Matern, *Chem. Eur. J.*, 2006, **12**, 1703–1714.
- 124 (a) M. Gonsior, I. Krossing and E. Matern, *Chem. Eur. J.*, 2006, **12**, 1986–1996; (b) I. Krossing, *Chem. Eur. J.*, 2001, 7, 490–502.
- 125 (a) K. Eckstein, *Dissertation*, LMU München, 1997; (b) C. Strauhal, *Diploma thesis*, LMU München, 1996.
- 126 O. Schön, Dissertation, LMU München, 2007.

127 M. H. Holthausen, A. Hepp and J. J. Weigand, *Chem. – Eur. J.*, 2013, **19**, 9895–9907.

Chem Soc Rev

- 128 K.-O. Feldmann, T. Wiegand, J. Ren, H. Eckert, J. Breternitz, M. F. Groh, U. Müller, M. Ruck, B. Maryasin, C. Ochsenfeld, O. Schön, K. Karaghiosoff and J. J. Weigand, *Chem. Eur. J.*, 2015, **21**, 9697–9712.
- 129 (a) M. Donath, E. Conrad, P. Jerabek, G. Frenking, R. Fröhlich, N. Burford and J. J. Weigand, Angew. Chem., Int. Ed., 2012, 51, 2964–2967; (b) M. Donath, E. Conrad, P. Jerabek, G. Frenking, R. Fröhlich, N. Burford and J. J. Weigand, Angew. Chem., 2012, 124, 3018–3021.
- 130 F. Dielmann, O. Back, M. Henry-Ellinger, P. Jerabek, G. Frenking and G. Bertrand, *Science*, 2012, 337, 1526–1528.
- 131 W. Wang, R. Cao and L. Liu, J. Chem. Soc., Perkin Trans. 1, 2000, 1673–1675.
- 132 W.-H. Wang, G.-Y. Xu, R.-Z. Cao and L.-Z. Liu, *Heteroat. Chem.*, 2000, **11**, 512–517.
- 133 G. Bettermann, H. Buhl, R. Schmutzler, D. Schomburg and U. Wermuth, *Phosphorus Sulfur Relat. Elem.*, 1983, **18**, 77–80.
- 134 D. Schomburg, Acta Crystallogr., Sect. A: Found. Crystallogr., 1984, 40, C265.
- 135 (a) K. Schwedtmann, M. H. Holthausen, K.-O. Feldmann and J. J. Weigand, Angew. Chem., 2013, 125, 14454–14458;
 (b) K. Schwedtmann, M. H. Holthausen, K.-O. Feldmann and J. J. Weigand, Angew. Chem., Int. Ed., 2013, 52, 14204–14208; (c) T. Böttcher, B. S. Bassil, L. Zhechkov, T. Heine and G.-V. Röschenthaler, Chem. Sci., 2013, 4, 77–83; (d) P. Wawrzyniak, A. L. Fuller, A. M. Z. Slawin and P. Kilian, Inorg. Chem., 2009, 48, 2500–2506.
- 136 K. B. Dillon, A. W. G. Platt, A. Schmidpeter, F. Zwaschka and W. S. Sheldrick, *Z. Anorg. Allg. Chem.*, 1982, 488, 7–26.
- 137 K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, 1965, 4, 1775–1776.
- 138 E. V. Nikitin, A. S. Romakhin, V. A. Zagumennov and Y. A. Babkin, *Electrochim. Acta*, 1997, **42**, 2217–2224.
- 139 J. J. Weigand, S. D. Riegel, N. Burford and A. Decken, *J. Am. Chem. Soc.*, 2007, **129**, 7969–7976.
- 140 D. Schomburg, G. Bettermann, L. Ernst and R. Schmutzler, *Angew. Chem., Int. Ed. Engl.*, 1985, 24, 975–976.
- 141 R. W. Alder, C. Ganter, C. J. Harris and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1992, 1170–1172.
- 142 P. Kilian, A. M. Z. Slawin and J. D. Woollins, *Dalton Trans.*, 2006, 2175–2183.
- 143 (a) Y. P. Makovetskii, N. G. Feshchenko, V. V. Malovik, V. Y. Semenii, I. E. Boldeskul, V. A. Bondar and N. P. Chernukho, *Zh. Obshch. Khim.*, 1980, 50, 1967;
 (b) Y. P. Makovetskii, V. E. Lidkovskii, I. E. Boldeskul, N. G. Feshchenko and N. N. Kalibabchuk, *Zh. Obshch. Khim.*, 1989, 52, 1989.
- 144 R. M. Siddique and J. M. Winfield, *Can. J. Chem.*, 1989, **67**, 1780–1784.
- 145 (a) S. S. Chitnis, Y.-Y. Carpenter, N. Burford, R. McDonald and M. J. Ferguson, *Angew. Chem., Int. Ed.*, 2013, 52,

- 4863–4866; (*b*) S. S. Chitnis, A. P. M. Robertson, N. Burford, J. J. Weigand and R. Fischer, *Chem. Sci.*, 2015, **6**, 2559–2574; (*c*) S. S. Chitnis, N. Burford, J. J. Weigand and R. McDonald, *Angew. Chem., Int. Ed.*, 2015, **54**, 7828–7832; (*d*) S. S. Chitnis, N. Burford, J. Weigand and R. McDonald, *Angew. Chem.*, 2015, **127**, 7939–7943; (*e*) A. P. M. Robertson, N. Burford, R. McDonald and M. J. Ferguson, *Angew. Chem., Int. Ed.*, 2014, **53**, 3480–3483; (*f*) A. P. M. Robertson, N. Burford, R. McDonald and M. J. Ferguson, *Angew. Chem.*, 2014, **126**, 3548–3551.
- 146 G. Bellachioma, G. Cardaci, A. Macchioni, C. Venturi and C. Zuccaccia, *J. Organomet. Chem.*, 2006, **691**, 3881–3888.
- 147 M. H. Holthausen, J. M. Bayne, I. Mallov, R. Dobrovetsky and D. W. Stephan, *J. Am. Chem. Soc.*, 2015, 137, 7298–7301.
- 148 R. R. Holmes and E. F. Bertaut, J. Am. Chem. Soc., 1958, 80, 2980–2983.
- 149 G. Müller, H.-J. Matheus and M. Winkler, *Z. Naturforsch., B: J. Chem. Sci.*, 2001, **56**, 1155–1162.
- 150 I. Bauer and W. D. Habicher, *Collect. Czech. Chem. Commun.*, 2004, **69**, 1195–1230.
- 151 R. W. Alder, D. D. Ellis, R. Gleiter, C. J. Harris, H. Lange, A. G. Orpen, D. Read and P. N. Taylor, J. Chem. Soc., Perkin Trans. 1, 1998, 1657–1668.
- 152 R. W. Alder, C. P. Butts, A. G. Orpen, D. Read and J. M. Oliva, J. Chem. Soc., Perkin Trans. 2, 2001, 282–287.
- 153 (a) R. W. Alder and D. Read, Angew. Chem., 2000, 112, 3001–3004; (b) R. W. Alder and D. Read, Angew. Chem., Int. Ed., 2000, 39, 2879–2882.
- 154 M. H. Holthausen, R. R. Hiranandani and D. W. Stephan, *Chem. Sci.*, 2015, **6**, 2016–2021.
- 155 D. M. U. K. Somisara, M. Bühl, T. Lebl, N. V. Richardson, A. M. Z. Slawin, J. D. Woollins and P. Kilian, *Chem. – Eur. J.*, 2011, 17, 2666–2677.
- 156 H. W. Roesky and H. Djarrah, *Inorg. Chem.*, 1982, 21, 844–845.
- 157 (a) D. Schomburg, N. Weferling and R. Schmutzler, J. Chem. Soc., Chem. Commun., 1981, 609–610;
 (b) L. Lamande and A. Munoz, Phosphorus Sulfur Relat. Elem., 1987, 32, 1–17.
- 158 R. W. Alder, C. P. Butts, A. G. Orpen and D. Read, *J. Chem. Soc.*, *Perkin Trans.* 2, 2001, 288–295.
- 159 C. W. Schultz and R. W. Rudolph, *J. Am. Chem. Soc.*, 1971, 93, 1898–1903.
- 160 (a) J. A. Gibson, G.-V. Röschenthaler and R. Schmutzler, J. Chem. Soc., Dalton Trans., 1975, 918–924; (b) W. S. Sheldrick, J. A. Gibson and G.-V. Röschenthaler, Z. Naturforsch., B: J. Chem. Sci., 1978, 33, 1102–1105.
- 161 P. Kilian, D. Philp, A. M. Z. Slawin and J. D. Woollins, *Eur. J. Inorg. Chem.*, 2003, 249–254.
- 162 (a) M. Sanchez, R. Réau, F. Dahan, M. Regitz and G. Bertrand, Angew. Chem., 1996, 108, 2386–2388;
 (b) M. Sanchez, R. Réau, F. Dahan, M. Regitz and G. Bertrand, Angew. Chem., Int. Ed. Engl., 1996, 35, 2228–2230.

163 (a) H. Luo, R. McDonald and R. G. Cavell, Angew. Chem.,
1998, 110, 1172–1174; (b) H. Luo, R. McDonald and
R. G. Cavell, Angew. Chem., Int. Ed., 1998, 37, 1098–1099.

Review Article

- 164 (a) R. W. Suter, H. C. Knachel, V. P. Petro, J. H. Howatson and S. G. Shore, J. Am. Chem. Soc., 1973, 95, 1474–1479; (b) K. B. Dillon and T. A. Straw, J. Chem. Soc., Chem. Commun., 1991, 234–235.
- 165 J. E. Richman, R. O. Day and R. R. Holmes, *J. Am. Chem. Soc.*, 1980, **102**, 3955.
- 166 H. W. Roesky, D. Amirzadeh-Asl and W. S. Sheldrick, *J. Am. Chem. Soc.*, 1982, **104**, 2919–2920.
- 167 L. Lamande and A. Munoz, *Tetrahedron*, 1990, **46**, 3527–3534.