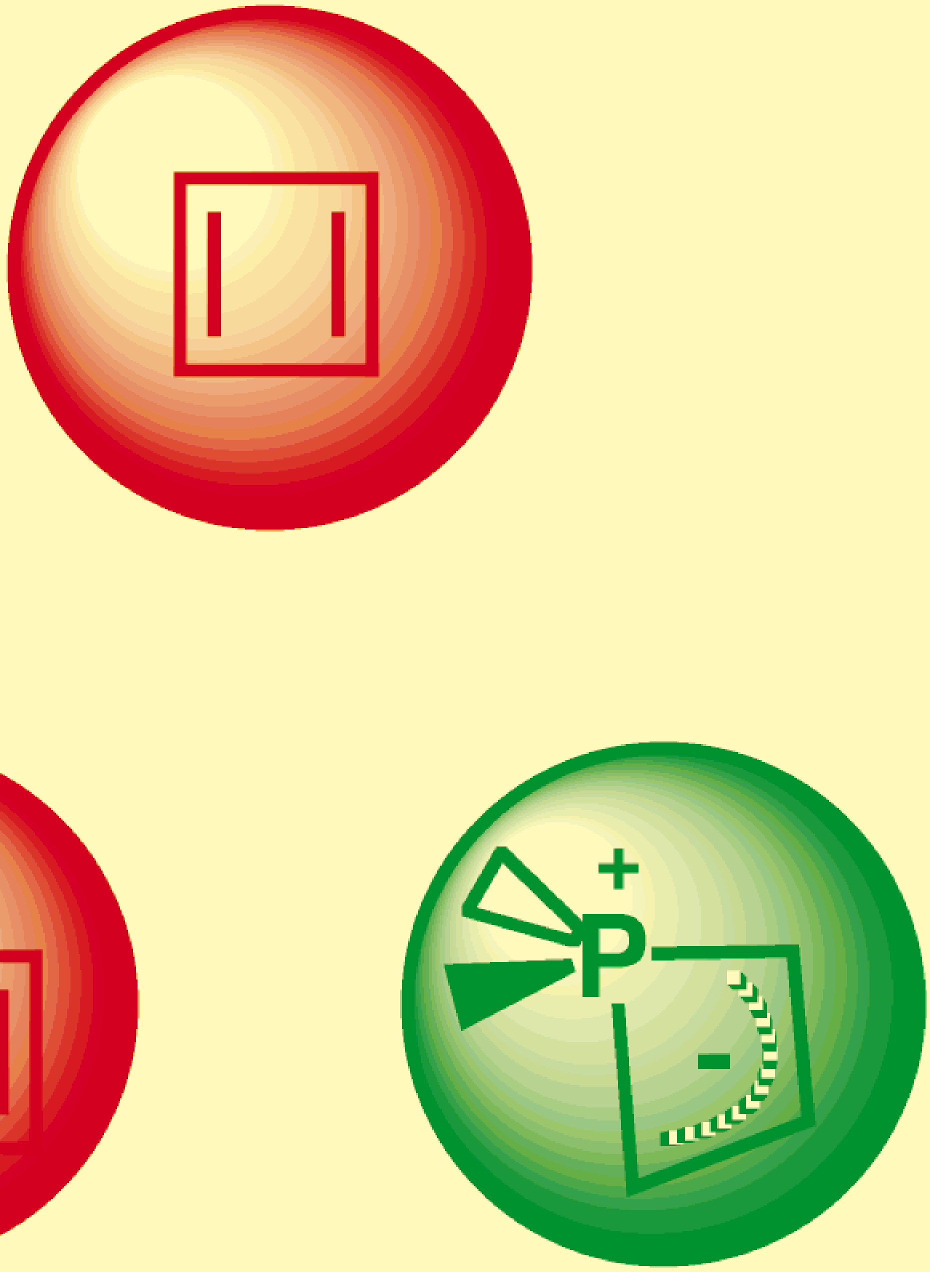
The escape from antiaromaticity in four π electron four-membered ring systems



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Ylidic Four π Electron Four-Membered λ^5-Phosphorus Heterocycles: Electronical Isomers of Heterocyclobutadienes

Guy Bertrand *

The first inorganic heterocycle, $(Cl_2PN)_3$, was discovered in the last century. Nevertheless, up to the beginning of the 1980s it was claimed that cyclodiphosphazenes $(R_2PN)_2$ could not exist because of ring strain and contraction of the N-P-N bond angles below 115°, which would cause serious interpenetration of the van der Waals boundaries of the nitrogen atoms. In 1984 we reported the synthesis and single-crystal X-ray structure analysis of the smallest member of the well-known family of cyclopolyphosphazenes, namely, tetrakis(diisopropylamino)-$1\lambda^5$,$3\lambda^5$-diphosphete. The parallel to the history of benzene and cyclobutadiene is striking, but here the comparison has to stop: Cyclobutadienes that contain λ^5-phosphorus atoms are not antiaromatic; they feature a strong ylide character with a four π electron system that follows either an island model or presents an interrupted cyclic delocalization. Despite the lack of antiaromaticity, the preparation of these heterocycles remains a challenging example of non-natural-product synthesis because of the ring strain. "Heterocyclobutadienes" of this type are very reactive, which makes them attractive precursors to a variety of novel heterocycles; the synthesis by Karsch of a spirocyclic ten-electron cation featuring an unprecedented pseudo-trigonal-bipyramidal PP_4 fragment is a good illustration. They also act as +ligands for transition metals, and preliminary results indicate that they could be used as building blocks for coordination polymers.

Keywords: antiaromaticity · phosphorus heterocycles · phosphorus ylides · strained molecules

1. Introduction

For more than a century, the synthesis and bonding description of six π electron six-membered and four π electron four-membered rings have attracted considerable attention.[1] Although benzoic acid has been known since the 16th century and benzene was discovered in 1825 by Faraday,[2] it was only in 1965 that Pettit[3] prepared an organometallic complex featuring cyclobutadiene as a ligand, and in 1968 that Gompper and Seybold[4] isolated a free cyclobutadiene derivative stabilized by push–pull effects. Outside the coordination sphere of transition metals, the parent cyclobutadiene is only stable in matrices at low temperature[5a–d] or in a molecular container, as recently shown by Cram.[5e, f]

Even by the end of the 19th century, Kekulé tried to rationalize the very peculiar stability of benzene. He stated that it was due to the structure of the ring exhibiting an alternance of single and double bonds, and introduced the oscillation theory:[6] This was the premise of aromaticity. The only mistake was to think that, as vinylogues of benzene, cyclobutadiene and cyclooctatetraene should also be aromatic and very stable, although this idea was reinforced by the synthesis of cyclooctatetraene by Willstätter in 1911.[7] In 1930 Hückel tried to rationalize the "mysterious" difference in behavior between benzene on the one hand and cyclobutadiene and cyclooctatetraene on the other using molecular-orbital theory.[8] According to the Hückel rules, annulenes of the type $(C_2H_2)_n$ have to be divided into two groups: 1) Compounds which have $(4n+2)$ π electrons, such as benzene, are stabilized by delocalization and thus aromatic. 2) Compounds which have $(4n)$ π electrons, such as cyclobutadiene, have no particular stabilization. Only one element was missing: the destabilizing effect called "antiaromaticity" in 1965 by Breslow and Dewar. Nowadays antiaromaticity accounts for 60% of the excess energy of cyclobutadiene (estimated at 35 kcal mol^{-1}); the remaining 40% is attributed to ring strain.[9] Even in the most recent book published on aromaticity (and antiaromaticity),[1a] the authors concluded: "at any rate, up to this time nobody has been able to produce a physically sound explanation to this effect"!

The aromatic and antiaromatic character is perturbed when one or more heteroatoms from the second row of the periodic system are present in the ring.[10] With an element from the third (or higher) row that possesses p orbitals for building the π system, the comparison is even more striking;[10] for

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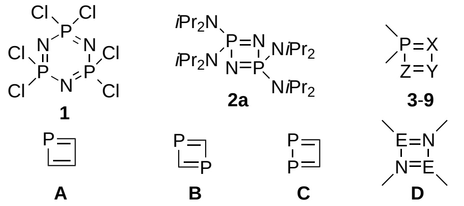
example, neither silabenzene[11] nor germabenzene[12] are stable. When the heteroatom has no p orbital available for the π system, the six-membered ring is no longer a Hückel aromatic system[13] and, consequently, the four-membered ring should not be antiaromatic.

Starting from this hypothesis, six π electron six-membered and four π electron four-membered rings featuring an element from the third row should not be particularly stable and unstable, respectively. However, it is amazing to realize that the first six-membered heterocycle of this type, the cyclotriphosphazene **1**,[14] was discovered in 1834, whereas the first vinylogue, the cyclodiphosphazene **2a** (Scheme 1), was reported by our group as recently as 1984![15]



3: X=Z: P, Y: PR$_2$;**4**: X=Z: CR, Y: PR'$_2$; **5**: X=Y=Z: CR;

6: X: N, Y=Z: CR; **7**: X: P, Y=Z: CR; **8**: X=Z: N, Y: CR;

9: X: P, Y:PR$_2$, Z: CR'; **9'**: X: As, Y:PR$_2$, Z: CR'.

E: B, Al, In.

Scheme 1. Cyclotriphosphazenes **1**, cyclodiphosphazenes **2**, and four π electron four-membered heterocycles containing phosphorus (**3**–**9**, **A**–**C**) or a Group 13 element (**D**).

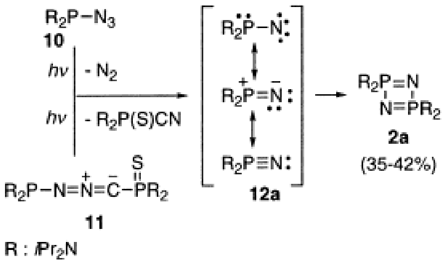
This review deals with the synthesis, bonding properties, and reactivity of four π electron four-membered rings **2**–**9**, which feature a λ^5-phosphorus atom.[16] So far, the related, but antiaromatic, λ^3-phosphete **A** and λ^3,λ^3-diphosphetes **B** and **C** (Scheme 1) are only known as transient species or as ligands for transition metal complexes; they are the subject of recent reviews.[17] On the other hand, there are very few four π electron four-membered rings featuring a main group element from the third (or higher) row. Indeed, to the best of our knowledge, there are no stable examples involving Group 14[18] or 16 elements (although some have been erroneously claimed for the latter),[19] and only a couple of compounds of type **D** involving Group 13 elements[20] (Scheme 1).

2. Synthesis

Several synthetic routes have been used to prepare the desired "λ^5-phosphacyclobutadiene" derivatives **2**–**9**. Although some routes can be used to prepare different classes of compound, none is general.

2.1. [2+2]Cycloadditions

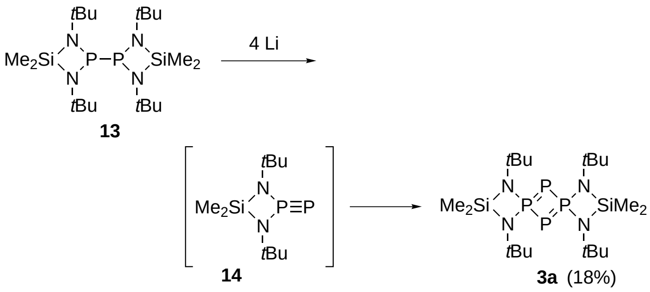
This story begins with calculations by Trinquier,[21] which predicted that the singlet phosphanylnitrene **12** (R = H; Scheme 2) will exhibit a phosphorus–nitrogen multiple bond due to delocalization of the lone pairs n_π(P) into p_π(N) and, to some extent, n_π(N) into d_π(P). We confirmed this hypothesis by irradiating bis(diisopropylamino)phosphanyl azide (**10**) in the presence of various trapping agents. As hoped, the products obtained resulted from simple addition across a formal phosphorus–nitrogen triple bond of the λ^5-phosphonitrile **12a**.[22] We then realized that irradiation of **10** in the absence of any trapping agent led to the head-to-tail cyclic dimer of **12a**, 2,2,4,4-tetrakis(diisopropylamino)-1,3,2λ^5,4λ^5-diazadiphosphete (**2a**, R = *i*Pr$_2$N), in 42% yield.[15] We more recently found that photolysis of the stable nitrilimine **11** also led to the cyclodiphosphazene **2a** in 35% yield along with bis(diisopropylamino)thiophosphorylnitrile (Scheme 2).[23] Since phosphanyl azides are in general highly explosive materials,[24] the use of N-phosphorus-substituted nitrilimines seems more attractive. Unfortunately only very few nitrilimines are stable,[25] and most rearrange under irradiation into carbodiimides[26] rather than undergoing nitrogen–nitrogen bond cleavage to give a phosphonitrile.



Scheme 2. Synthetic routes to the cyclodiphosphazene **2a**.

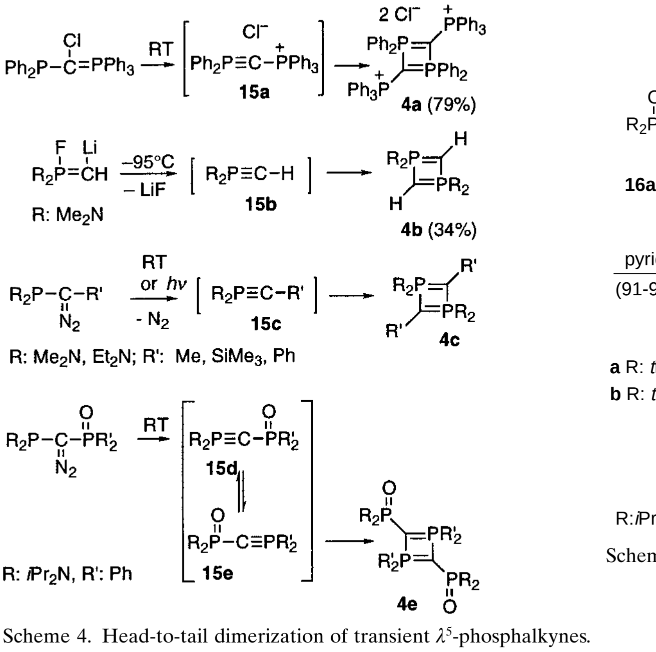
Guy Bertrand was born in Limoges (France) in 1952. He graduated from the University of Montpellier as ingénieur ENSCM and moved to Toulouse as an Attaché de Recherche CNRS in 1975. He defended his Thèse d'Etat at the University Paul Sabatier of Toulouse in 1979 and spent one year at Sanofi Recherche Company. Since 1988 he is Directeur de Recherche at the Laboratoire de Chimie de Coordination du CNRS at Toulouse. He has authored over 180 publications and patents, and his research spans a wide range of topics at the border between organic and inorganic chemistry. He received the International Council on Main Group Chemistry Award in 1993 and the Humbold Award in 1994, and was elected Membre Correspondant of the French Academy of Sciences in 1996.

The mixed-valent tetraphosphete **3**, which was recently obtained by Frank et al.,[27] formally results from dimerization of the phosphidophosphorane **14**. This transient species would be formed upon reduction of diphosphane **13** with lithium (Scheme 3).



Scheme 3. Synthesis of the mixed-valent tetraphosphete **3a**.

Head-to-tail dimerizations of transient λ^5-phosphalkynes **15** to $1\lambda^5,3\lambda^5$-diphosphetes **4** were observed by Appel et al.,[28] Fluck et al.,[29] and Regitz et al[30] (Scheme 4). It is noteworthy that diphosphete **4e** does not originate from the dimerization of the initially generated **15d**, but from that of isomeric **15e**, which forms after a 1→3 shift of the oxygen atom from one phosphorus atom to another.[30] This result suggests a possible equilibrium between the two isomeric *C*-phosphoryl-λ^5-phosphalkynes **15d** and **15e**; dimerization occurs with the least sterically hindered form. The very rare examples of compounds of type **15** which have been isolated do not dimerize even upon heating.[31]

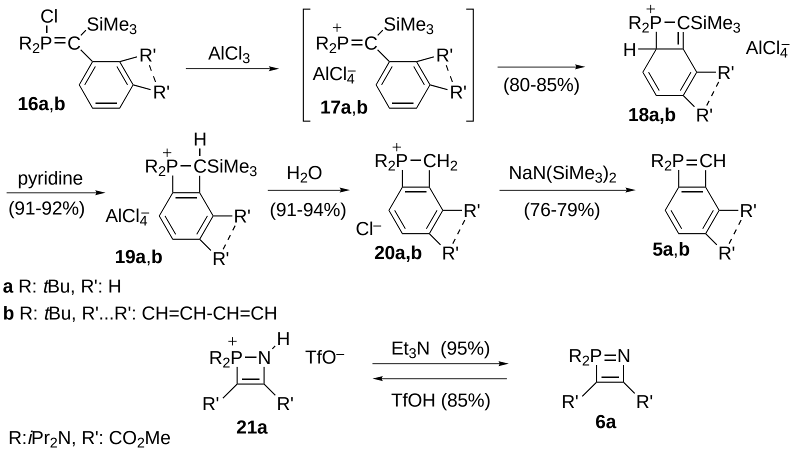


Scheme 4. Head-to-tail dimerization of transient λ^5-phosphalkynes.

So far, all attempts to prepare λ^5-phosphetes or λ^5-aza- or diazaphosphetes by [2+2]cycloaddition of λ^5-phosphalkynes **15** or λ^5-phosphonitriles **12** with alkynes or nitriles have failed.

2.2. 1,2-Eliminations

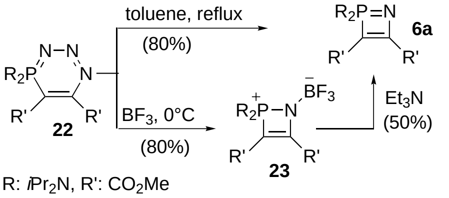
In 1968 Gompper and Seybold prepared the first stable cyclobutadiene by deprotonation of the corresponding cyclobutadienyl salt.[4] Similarly, addition of sodium bis(trimethylsilyl)amide to 1,2-dihydrophosphet-2-ylium salts **20a** and **20b** gives rise to benzo- and naphto-λ^5-phosphetes **5a** (76 % yield) and **5b** (79 % yield), respectively (Scheme 5).[32] The synthesis of derivatives **20a, b** deserves some comment, since it explains why non-benzo-λ^5-phosphetes are not available by this route. The key step in this synthesis is the generation of transient methylene phosphonium salts[33] **17a, b** from P-halogenated ylides[34] **16a, b**. Indeed, thanks to the high electrophilicity of the phosphorus atom in **17a, b**, an intramolecular ring closure leading to **18a,b** occurs. All attempts to generate the corresponding benzo-$1\lambda^5$-phosphetes from **18a, b** with a strong base failed. In the presence of pyridine an irreversible and quantitative isomerization to **19a, b** occurs. Deprotonation of **19a, b** was not clean in contrast to that of **20a, b**, which were generated by hydrolysis of the C–Si bond in **19a, b**. Deprotonation of **21a** with excess triethylamine affords $1,2\lambda^5$-azaphosphete **6a** in 95 % yield[32] (Scheme 5). However, this route is of no synthetic value, since **21a** is prepared by protonation of **6a**.



Scheme 5. Synthesis of benzo-λ^5-phosphetes **5a** and **5b**.

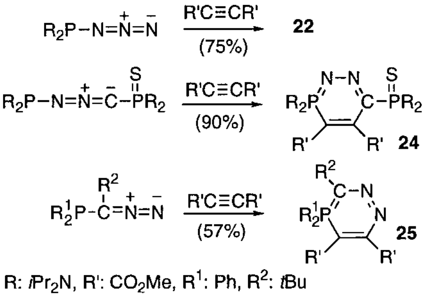
2.3. Ring Contractions

The thermal and photochemical elimination of dinitrogen from cyclic azoalkanes is an efficient method for preparing strained heterocycles,[35] including antiaromatic four-membered rings. Indeed, vapor flash pyrolysis of 1,2,3-triazines gives rise to azetes.[36] Similarly, heating $1,2,3,4\lambda^5$-triazaphosphinine **22** in toluene under reflux for 14 h affords the $1,2\lambda^5$-azaphosphete **6a** in 80 % yield (Scheme 6).[37] Compound **6a** can also be obtained in a two-step one-pot reaction by first adding boron trifluoride to **22** at 0 °C, which initially leads to the zwitterionic heterocycle **23**, followed by decomplexation with excess triethylamine.[37b]



Scheme 6. Synthesis of the $1,2\lambda^5$-azaphosphete **6a** by ring contraction.

Like **22**, $1,2,3\lambda^5$- and $1,2,4\lambda^5$-diazaphosphinines **24**[38] and **25**[39] are readily available since phosphanyl-substituted 1,3-dipoles are able to react as formal 1,4-dipoles (Scheme 7).



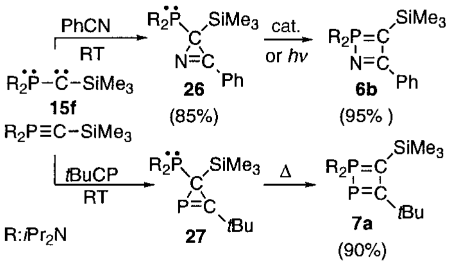
Scheme 7. Phosphanyl-substituted 1,3-dipoles react as formal 1,4-dipoles.

However, all attempts to eliminate dinitrogen from **24** and **25** failed. The reluctance of **24** to loose N_2 is consistent with the high stability of phosphazo derivatives. Indeed, **24** features the same $R_3P{=}N{-}N{=}C<$ sequence as Staudinger–Meyer adducts (phosphane+diazo derivative), which are not precursors of phosphorus ylides.[40] In contrast, **22** features a phosphazide skeleton in a *cis* configuration, which has been postulated to be the geometry of the transition state[41] in the Staudinger reaction (phosphane+azide →phosphazene+N_2). The high stability of **25** is more difficult to rationalize. Therefore, the ring-contraction route is so far restricted to the synthesis of $1,2\lambda^5$-azaphosphetes.

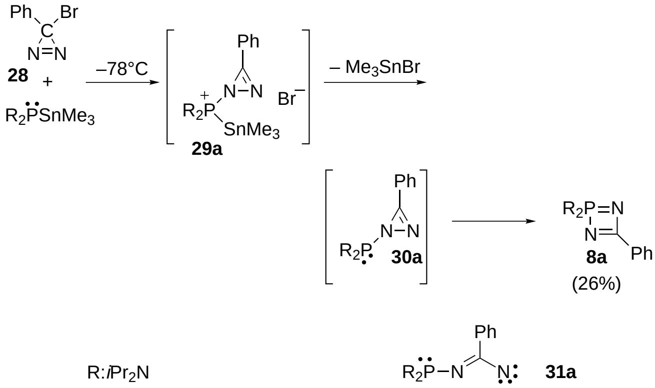
2.4. Ring Expansions

A few cyclobutadienes and azetes were prepared by ring expansions involving transient cyclopropenyl carbenes and nitrenes.[42] Similarly, 2-phosphanyl-2*H*-azirine **26** and 2-phosphanyl-2*H*-phosphirene **27** rearrange into $1,2\lambda^5$-azaphosphete **6b** (95% yield)[43] and $1\lambda^5,2\lambda^3$-diphosphete **7a** (90% yield),[44] respectively (Scheme 8). Both starting materials were prepared from our stable "carbene" **15f**.[31a–d] Although the only other example of a stable 2*H*-phosphirene was prepared using a transient carbene,[45] **26** is the first 2*H*-azirine prepared by a [1+2]cycloaddition.

The third example of a ring expansion leading to a four π electron four-membered heterocycle involves the transient 1-phosphanyl-1*H*-diazirine **30a**. This antiaromatic four π electron three-membered ring was prepared by adding bis(diisopropylamino)trimethylstannylphosphane to 3-bromo-3-phenyldiazirine (**28**) followed by elimination of bromotrimethylstannane (Scheme 9).[46]



Scheme 8. From the stable carbene **15f** to $1,2\lambda^5$-azaphosphete **6b** and $1\lambda^5,2\lambda^3$ diphosphete **7a** by ring expansions of unsaturated three-membered heterocycles **26** and **27**, respectively.

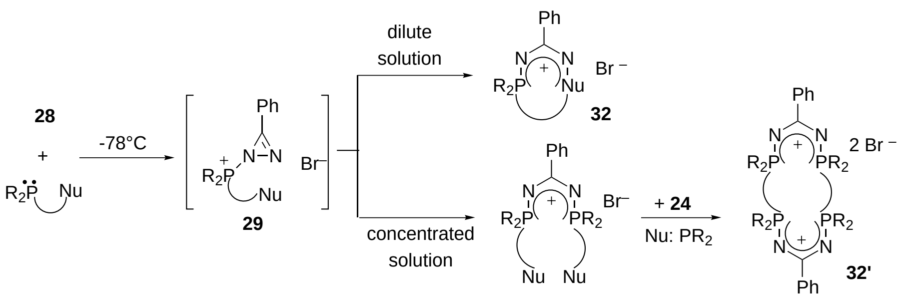


Scheme 9. Synthesis of the transient 1-phosphanyl-1*H*-diazirine **30a** and its ring expansion to the $1,3,2\lambda^5$-diazaphosphete **8a**.

We were able to prove that the first step of the reaction proceeds by an S_N2' mechanism and leads to *N*-phosphoniodiazirine **29a**; this is in agreement with independent works by Creary[47] and Dailey[48] with other nucleophiles. We also demonstrated experimentally and with ab initio calculations that the rearrangement of **30a** to **8a** involves nucleophilic attack by the phosphorus lone pair at the second nitrogen atom of the diazirine, and not the imidoylnitrene intermediate **31a** (Scheme 9).[46b] Indeed, the parent parent compound **31** (R = H) is an unstable species on the singlet hypersurface and rearranges without requiring any activation energy to the corresponding carbodiimide. On the other hand, diazaphosphete **8a** is over 23 kcal mol^{-1} more stable than the corresponding 1-phosphino-1*H*-diazirine **30a**, and the activation energy for the rearrangement of **30a** to **8a** is around 24 kcal mol^{-1}. Interestingly, *N*-phosphoniodiazirines **29** have a reasonable lifetime, probably due to the presence of the phosphonio group, which decreases the effect of the destabilizing antiaromatic energy through "negative hyperconjugation".[49] The relative stability of **29** allows inter and intramolecular S_N2 reactions to compete. This makes the reaction of bromodiazirine with phosphanes possessing a second nucleophilic center of synthetic interest, as proven by the high-yield synthesis of mono- and dicationic heterocycles **32** and **32'**[46b] (Scheme 10).

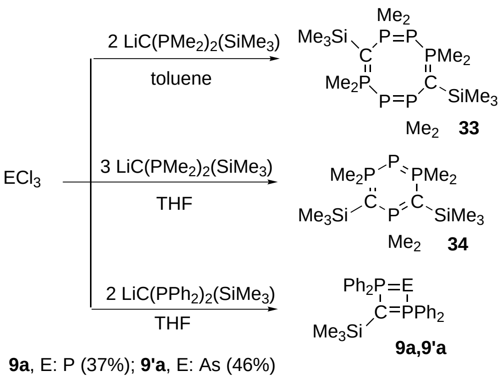
2.5. Use of Diphosphanylmethanides

Diphosphanylmethanides are suitable starting materials for synthesizing *n* π electron *n*-membered phosphorus hetero-



Scheme 10. Transient *N*-phosphoniodiazirines **29** as precursors for cationic and dicationic heterocycles.

cycles.[50] It is particularly interesting that Li[C(PMe$_2$)$_2$(SiMe$_3$)] reacts with PCl$_3$ in toluene to afford the eight-membered heterocycle **33**, whereas the six-membered ring **34** is formed in THF (Scheme 11).[50a] Heterocycle **34** is an analogue of cyclotriphosphazenes in which the three nitrogen atoms have been replaced by a phosphorus atom and two CR groups. With the more sterically crowded Li[C(PPh$_2$)$_2$(SiMe$_3$)], the $1\lambda^5,2\lambda^3,3\lambda^5$-triphosphete **9a** was obtained in 37% yield.[50b] The same synthetic route allowed Karsch et al. to obtain the corresponding $2\lambda^3,1\lambda^5,3\lambda^5$-arsadiphosphete **9′a** in 46% yield.[50b]

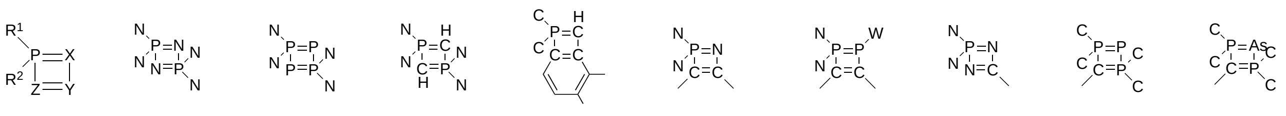


Scheme 11. Diphosphanylmethanides as precursors of *n* π electron *n*-membered heterocycles.

3. Structural and Spectroscopic Data

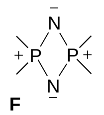
Single-crystal X-ray diffraction studies were performed on several λ^5-phosphacyclobutadienes. The most important geometric parameters of derivatives **2a**,[15a] **3**,[27] **4b**,[29a] **5b**,[32] **6a**,[37a] **7′a** (a W(CO)$_5$ complex of **7a**),[44] **8a**,[51] **9a**, and **9′a**[50b] are listed in Table 1. In $1\lambda^5,3\lambda^5$-diphosphetes **2**, **3**, and **4** of type P$_2$X$_2$, the four-membered ring is organized around a crystallographically imposed symmetry center, which highlights the absolute planarity of the ring. All endocyclic P–X bond lengths are equal and lie between those of single and double bonds. Of special interest is the pinching of the ring around the nitrogen atom of **2a**, which induces a P⋯P distance (2.22 Å) as short as that in diphosphines.[52] Ab initio calculations[53a, b] rationalized these experimental data. Cyclodiphosphazenes **2** can be conceptualized as a sequence of amide and phosphonium units in which the negative charge of nitrogen is carried by a pure p lone pair that is perpendicular to the mean plane of the ring. Formally, this charge is equal to – 1, but is in fact reduced due to σ polarization and to a certain amount of conjugation with the phosphorus atoms. The electrostatic repulsion between the nitrogen atoms explains the acute angle at nitrogen and the short P⋯P distance; there is no transannular P⋯P bonding interaction, as shown by the strongly negative overlap population. In conclusion, the four π electron system of **2** and related P$_2$X$_2$ heterocycles **3** and **4** as well as the six π electron system of cyclotriphospha-

Table 1. Selected bond lengths [Å] and angles [°] determined from X-ray diffraction studies

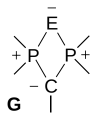


	2a	**3a**	**4b**	**5b**	**6a**	**7′a**	**8a**	**9a**	**9′a**
P-R^1	1.645(8)		1.681(11)	1.840(6)	1.629(3)	1.664(6)	1.625(4)		
P-R^2	1.644(9)		1.680(1)	1.852(6)	1.626(3)	1.651(6)	1.644(3)		
P-X	1.651(8)	2.139(1)	1.725(1)	1.772(8)	1.702(3)	2.176(3)	1.670(4)	2.1489(5)	2.2710(7)
P-Z	1.648(8)	2.142(1)	1.725(1)	1.773(6)	1.764(4)	1.804(7)	1.675(4)	1.729(1)	1.741(2)
X-Y	1.651(8)	2.139(1)	1.725(1)	1.401(8)	1.352(5)	1.842(7)	1.368(7)	2.1530(6)	2.2692(7)
Y-Z	1.648(8)	2.142(1)	1.725(1)	1.406(7)	1.406(6)	1.391(10)	1.377(6)	1.738(1)	1.731(2)
P-Y	2.22	2.736	2.410	2.206	2.109		1.987	2.548	2.601
Z-P-X	95.0(6)	100.6(1)	91.4(1)	78.9(3)	81.2(2)	83.1(2)	86.0(2)	96.44(5)	96.21(8)
P-X-Y	85.0(5)	79.4(1)	88.6(1)	87.2(5)	86.5(2)	71.9(3)	81.1(3)	72.65(2)	69.90(2)
X-Y-Z	95.0(6)	100.6(1)	91.4(1)	106.7(6)	109.7(3)	109.6(5)	112.4(3)	96.03(5)	96.59(8)
Y-Z-P	85.0(5)	79.4(1)	88.6(1)	87.1(5)	82.6(3)	95.1(5)	80.6(3)	96.64(7)	97.0(1)
Abw.[a]	0	0	0	0.022	0.003	0.028	0.006	0.074	0.088

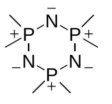
[a] Mean deviation from the best plane of the four-membered ring.



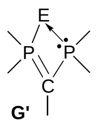
F



G



F'

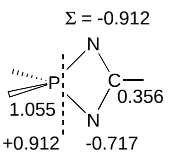


G'

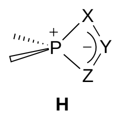
zenes **1** basically follow the island models **F** and **F'**,[13] respectively.

In the nonsymmetrical 1λ^5,3λ^5-diphosphetes **9a** and **9'a**[50b] the four-membered rings are not completely planar: The dicoordinated phosphorus and arsenic atoms project out of the P-C-P plane, and once again there is a pinching of the ring at the σ^2-P* (or As) atom, which induces a relatively short nonbonding λ^5-P–λ^5-P distance. The structural parameters suggest a representation of **9a** and **9'a** as cyclic bis(ylides) **G**, very comparable to **F**, or alternatively as internally donor-stabilized phosphinidenes and arsinidenes **G'**, respectively.

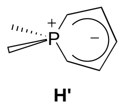
The four π electron system of 1λ^5-phosphetes **5**–**8** cannot follow the island model, and one should therefore find an alternative way to escape from the concept of antiaromaticity. Also these four-membered rings are nearly planar, as shown by the mean deviation from the best plane (Table 1). The exocyclic P–N bonds of **6a**, **7'a**, and **8** (as in **2a** and **4b**) are rather short and are comparable to those observed in bis(diisopropylamino)phosphenium salts (1.61 Å).[54] This indicates a positive charge located on the $(R_2N)_2P$ fragment, although according to calculations[51] a delocalization of this charge towards the exocyclic amino groups seems unpronounced. All the X–Y and Y–Z bond lengths are between those of single and double bonds, indicating that the XYZ part of the rings can be regarded as an anionic propenyl system. This zwitterionic formulation of **5**–**8** is illustrated by the calculated electron density Σ (Mulliken charges) for the parent compound **8**. The value of the inner ring angle at phosphorus is small and that of the opposite angle is large, which induces a short P$\cdots$Y distance across the diagonal. Since the P–X and P–Z bond distances are long in all the derivatives, these results as a whole demonstrate that λ^5-phosphetes **5**–**8** have a rhomboidal zwitterionic structure of type **H**.



8



H

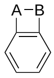


H'

Interestingly, the related six π electron six-membered heterocycles can be almost planar, such as various λ^5-di- and triphosphinines,[55] or have a boat conformation, such as the 1λ^5,3λ^5,5λ^5,2λ^3-tetraphosphinine **34** reported by Karsch (interplanar angle 127°).[50a] λ^5-Diaza- and triazaphosphinines such as **24**, **25**, and **22** have a zwitterionic structure of type **H'**.[37b, 39, 51] Clearly, all these heterocycles are not aromatic.

Ab initio SCF calculations were performed on the parent benzannulated derivatives **5** and **35**–**40**.[32] Apart from the geometric parameters, the anisotropy of magnetic susceptibilies $\Delta\chi$ (Table 2) gives an indication of the degree of aromatic or antiaromatic character.[56] For instance, the calculated value of $\Delta\chi$ is strongly negative in benzene (-63.4×10^{-6} cm^{3}mol^{-1}), while much larger anisotropies are observed for π systems possessing antiaromatic character; $\Delta\chi$ is even positive in cyclobutadiene. Annulation of a saturated four-membered cyclic system on a benzene ring (**37** and **40**) reduces the value of $\Delta\chi$ by about 15%, which signifies relatively little perturbation of the electronic properties of the aromatic moiety. The small negative values of $\Delta\chi$ for **35**, **38**, and **39** are indicative of antiaromatic π systems. Compounds **38** and **39** are formally derived from benzocyclobutadiene **35** by replacement of one CH unit by a P or PH$^+$ group; both groups are able to participate in the π-electron system by (p,p)-π interactions. On the other hand, the $\Delta\chi$ values for the cyclic hydrocarbon anion **36** and λ^5-benzophosphete **5** are similar; this confirms that four π electron four-membered heterocycles possessing one heteroatom that has no suitable p orbital show an interrupted cyclic π delocalization.

Table 2. Calculated anisotropy of magnetic susceptibilities, $\Delta\chi$ [10^{-6} cm^{3}mol^{-1}].[32]



	35	36	37	38	39	50	5
A	CH	CH_2	CH_2	P	PH^+	PH_2^+	PH_2
B	CH	CH^-	CH_2	CH	CH	CH_2	CH
$\Delta\chi$[a]	−11	−26	−55	−8	−2	−54	−29

[a] $\Delta\chi = \chi_{op} - \chi_{ip}$, where χ_{ip} is the average of the difference of the in-plane components of the susceptibility (op = out-of-plane; ip = in-plane).

Table 3 summarizes the most important NMR data for compounds **2**–**9**. There are some striking features. The ^{31}P NMR chemical shifts for the λ^5-phosphorus atom of all heterocycles bearing dialkylamino groups are similar; these atoms are more deshielded than those in analogous six-membered rings and linear systems. The ylid character of the P–X or P–Z bonds is indicated by the high-field chemical shifts of the corresponding nuclei, which are, however, less shielded in **5**–**7** than in **3**, **4**, and **9**; this supports the representations **F**, **G**, and **H** for **2**–**4**, **9**, and **5**–**8**, respectively. The very low field chemical shift of the signal for the carbon atom (Y) in **5**–**8** is typical of unsaturated small rings, including the antiaromatic cyclobutadienes and azetes.

The HOMO of the four-membered rings **2**–**9** is located at the X or Z atom. For example, in the parent compound **8** the

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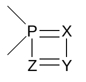
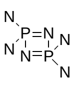
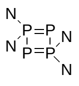
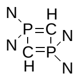
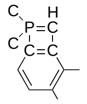
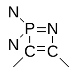
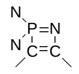
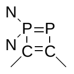
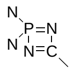
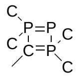
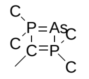
[*] Editorial comment: If the bonding number of a ring atom deviates from its standard value, according to IUPAC rules the actual bonding number is expressed by an Arabic number cited as a superscript to the Greek letter lambda, which follows the corresponding locant. In contrast to this recommendation, the Greek letter sigma is used here to indicate the structural features. The exponent gives the number of σ bonds that originate at phosphorus ring atoms.

Table 3. Selected NMR data; coupling constants are given in Hz.

	 **2a**	 **3a**	 **4b**	 **5b**	 **6a**	 **6b**	 **7a**	 **8a**	 **9a**	 **9′a**
$\delta(^{31}P)$	+40.0	+102.4	+48.9	+73.0	+52.5	+52.3	+49.2	+54.2	+20.2	−0.5
$\delta(X)$		+62.6	8.2	41.3			+58.4		−86.3	
$J(PX)$		372	97.3	77.6			201.2		261.0	
$\delta(Y)$	+40.0	+102.4	+48.9	170.1	182.4	192.4	224.3	194.7	+20.2	−0.5
$J(PY)$				3.8	28.0	46.7	9.9	48.4		
$\delta(Z)$		+62.6	8.2	106.0	91.9	84.9	105.7			
$J(PZ)$		372	97.3	76.9	81.6	42.9	36.8			

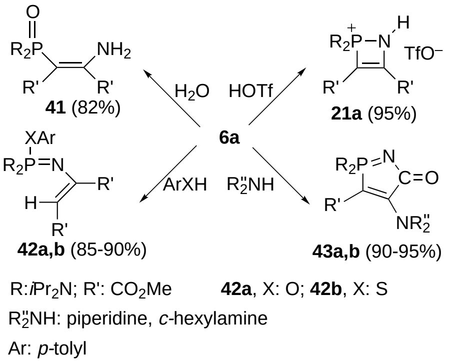
HOMO is a mixture of the nonbonding orbitals of the lone pair of the endocyclic nitrogen atoms and the nonbonding allylic π orbital of the ring (computed to be −8.7 eV).[51] Not surprisingly, the LUMO is at the carbon atom β to the λ^5-phosphorus atom. These theoretical results may serve as a good model for explaining the reactivity of **2**–**9**.

4. Reactivity

The λ^5-phosphacyclobutadienes **2**–**9** are quite reactive. It would take too long to provide a comprehensive review, and, therefore, only a few representative reactions will be presented here. They highlight the versatility of these heterocycles as well as their usefulness as starting materials in several fields.

4.1. Addition of Protic Reagents

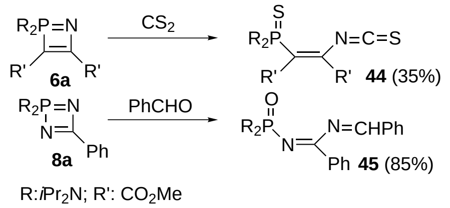
All λ^5-phosphacyclobutadienes considered in this review are moisture-sensitive. For example, **6a** in dichloromethane reacts to give the phosphoranyl compound **41** (82% yield, Scheme 12) after contact with air for a few minutes.[37b] The first step is certainly protonation at nitrogen. The ring opening is induced by the formation of a strong P=O bond, which converts the phosphonium center into a phosphorane. Indeed, with triflic acid, cyclic phosphonium salt **21a** was isolated in 95% yield.[32] The behavior of **6a** towards protic nucleophiles appears to depend dramatically on the nature of the nucleophiles. Although P–N bond cleavage occurs in the presence of water, P–C bond cleavage takes place upon adding *p*-cresol or *p*-thiocresol[57] to afford **42a**, **b** (85–90% yield). With primary or secondary amines a ring expansion is observed leading to five-membered heterocycles **43a**, **b** in excellent yields.[57] Derivatives of type **42** are starting materials for the synthesis of electron-poor 2-azadienes,[58] and five-membered cyclic phosphazenes **43** are not readily available by other routes.



Scheme 12. Reactivity of the 1,2λ^5-azaphosphete **6a** towards protic reagents. Tf = F_3CSO_2.

4.2. Addition of Unsaturated Compounds

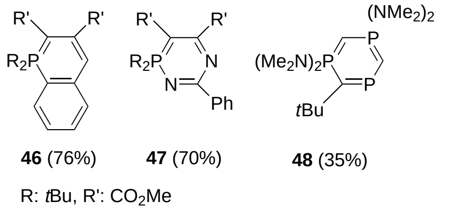
The Wittig reaction is one of the most famous and useful reactions in chemistry. Not surprisingly, classical aza-Wittig reactions were observed when azaphosphete **6a** or diazaphosphete **8a** was treated with carbon disulfide and benzaldehyde to afford thiophosphoryl and phosphoryl derivatives **44**[37b] and **45**[51] as single isomers in 35 and 85% yield, respectively (Scheme 13).



Scheme 13. Two examples of classical aza-Wittig reactions.

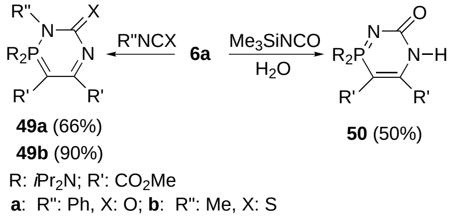
Electron-poor alkynes are known to insert into P–C and P–N ylidic bonds.[40] Indeed, dimethylacetylene dicarboxylate cleanly inserts into the P–X bond of **5a** and **8a** at room temperature to lead to the expected benzophosphinine **46**[32] and diazaphosphinine **47**[51] in 76 and 70% yield, respectively (Scheme 14). Noteworthy is the reaction of diphosphete **4b** with *tert*-butylphosphaethyne, which provided the first triphosphabenzene **48** in 35% yield.[59]

In fact, **6a** and its congeners very often react as nonclassical Wittig reagents. For example, isocyanates and isothiocyanates



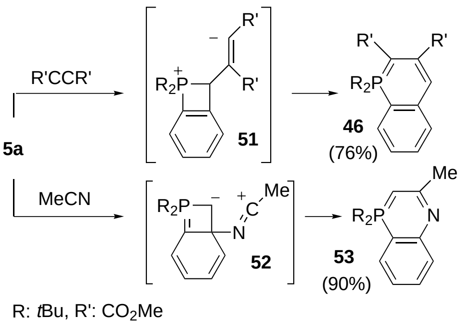
Scheme 14. Some six π electron six-membered heterocycles available by addition of alkynes or phosphalkyne to four π electron four-membered phosphorus heterocycles.

have been widely employed in aza-Wittig reactions to give unsymmetrical carbodiimides and the corresponding phosphoryl and thiophosphoryl derivatives.[40] In marked contrast, phenyl isocyanate and methyl isothiocyanate react with **6a** to provide the corresponding ring insertion products **49a** (66% yield) and **49b** (90% yield), respectively;[37b] these results are reminiscent of the Dimroth rearrangement.[40b, 60] Compound **6a** also reacts with trimethylsilyl isocyanate to afford, after hydrolysis, heterocycle **50** (50% yield),[37b] which formally results from the insertion of the cumulene into the N–C bond (Scheme 15). However, insertion into the P–N bond of **6a** followed by a 1,3-silyl or hydrogen shift is more likely. Intriguingly, **50** exists as a hydrogen-bonded dimer in the solid state and has a structure very similar to that of cytosine. The $C(NH_2)$ is replaced by a $P(N\mathit{i}Pr_2)_2$ group; **50** could be considered as a "labeled" cytosine.



Scheme 15. Reactivity of $1,2\lambda^5$-azaphosphete **6a** towards cumulenes.

The only clear example for the expansion of a four-membered to a six-membered ring involving the X–Y and not the P–X or P–Z bonds is the reaction of λ^5-phosphete **5a** with acetonitrile, which leads to $1,4\lambda^5$-azaphosphinine **53** (Scheme 16).[32] The striking difference in the behavior of **5a** towards dimethylacetylene dicarboxylate (insertion into the P–C bond to form **46**) and acetonitrile can be explained by considering that the HOMO of **5a** is located at the α-carbon atom, while the LUMO is at the carbon atom β to the phosphorus atom. Therefore, the electron-poor alkyne reacts with **5a** to give **51** as an intermediate, whereas the nitrogen end of the nitrile adds to the β-carbon atom to form **52** initially (Scheme 16).



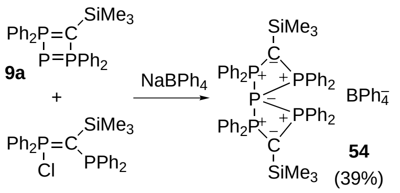
Scheme 16. Versatile behavior of the naphto-λ^5-phosphete **5a** towards reagents with triple bonds.

In contrast to the other four-membered heterocycles discussed in this review, the $1\lambda^5,2\lambda^3$-diphosphetes **3**, **7a**, and **9** seem reluctant to undergo any kind of insertion.

4.3. Reactions with Retention of the Four-Membered Ring

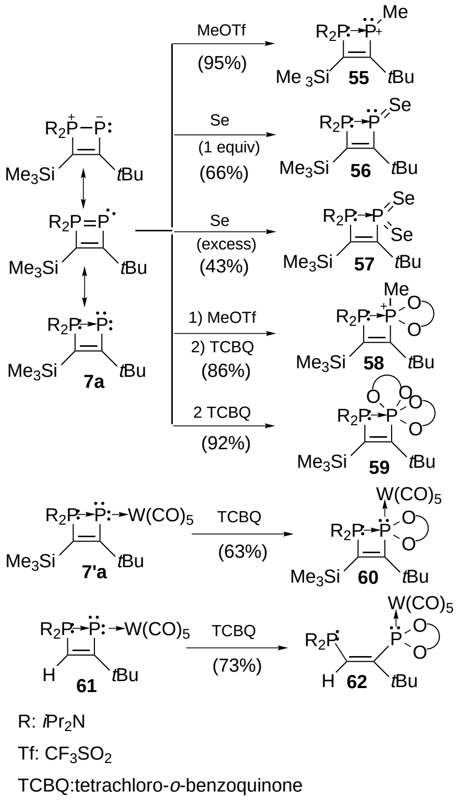
These reactions are surprisingly numerous, but the most striking results were obtained with the $1\lambda^5,2\lambda^3,3\lambda^5$-triphosphete **9a**[50b] and the $1\lambda^5,2\lambda^3$-diphosphete **7a**.[61]

The reaction of **9a** with $[Ph_2PC(PPh_2)(SiMe_3)]^+BPh_4^-$ results in formation of the spirocyclic ten-electron cation **54** (Scheme 17), which features an unprecedented pseudo-trigonal-bipyramidal PP_4 skeleton.[50b] Compound **54** can also be described as a tetraphosphonio-substituted phosphoranide[62] with partial charge compensation by two internal carbanion functionalities.



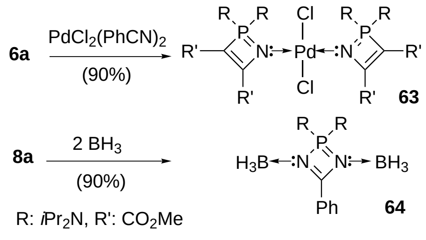
Scheme 17. Synthesis of a spirocyclic ten-electron cation with a pseudo-trigonal-bipyramidal PP_4 skeleton.

Methyltrifluoromethane sulfonate, a stoichiometric amount or two equivalents of elemental selenium, and two equivalents of tetrachloro-*o*-benzoquinone cleanly react with **7a** at its dicoordinate phosphorus atom to provide the corresponding heterocycles **55**, **56**, **57**, and **59** (Scheme 18), which can be regarded as phosphenium–, selenoxophosphane–, diselenoxophosphorane– and phosphorane–phosphane adducts, respectively.[61] The four-membered ring is also retained when tetrachloro-*o*-benzoquinone is added to **55**; the resulting derivative **58** is an example of a phosphonium–phosphane adduct. In other words, the σ^2-phosphorus atom of **7a** (a phosphanylidene-phosphane adduct) can extend its coordination number up to six without destroying the four-membered ring! The tendency of derivatives of **7a** and **55**–**57** to retain the ring structure can be explained by the presence of an electrophilic low-coordinate phosphorus center. It was only recently that the cyclic structure of derivatives **58** and **59**, which feature a high-coordinate phosphorus atom, was rationalized.[63] The presence of bulky substituents at the two carbon atoms of the ring induces small C-C-P angles, as proven by the formation of heterocycle **60** on the one hand and the linear adduct **62** on the other in the reaction of diphosphetes **7′a** and **61**, respectively, with tetrachloro-*o*-benzoquinone (Scheme 18).



Scheme 18. The persistence of the P–P bond in $1\sigma^4,2\sigma^x$-diphosphetes.

In contrast to their organic analogues—in particular the azetes,[42c, 64] which give η^4-complexes—**2**–**8** usually[65] act as η^1-ligands towards transition metal complexes.[44, 66] For example, azaphosphete **6a** reacts at room temperature with half an equivalent of $[PdCl_2(PhCN)_2]$ to lead to the bis(η^1-azaphosphete)palladium(II) complex **63** in 90% yield (Scheme 19). Interestingly, two equivalents of a neutral Lewis acid, such as BH_3, react with diazaphosphete **8a** to provide the bis-adduct **64** in 90% yield.[51] In both cases the geometric parameters and NMR data for the free and the coordinated ring are very similar, which suggests that the four π electron system is not perturbed upon complexation. From the results of both reactions presented in Scheme 19, it seems quite likely that mixed inorganic–organometallic polymers could be prepared with **8a**.



Scheme 19. λ^5-Aza- and -diazaphosphetes as η^1 ligands.

5. Summary and Outlook

These results as a whole clarify the bonding situation in four π electron four-membered heterocycles with a phosphorus atom that possesses no available p orbital for the π system. When two phosphorus atoms are present in the 1,3-positions, the four π electron system basically follows the island model. However, when there is only one phosphorus atom the negative charge is delocalized on an allylic fragment, and the positive charge is localized at the phosphorus center. In all cases there is an interrupted cyclic π delocalization, and, therefore, these compounds are not antiaromatic. Similarly, six π electron six-membered heterocycles with a λ^5-phosphorus atom are not aromatic.

Some of these four π electron four-membered heterocycles can be prepared on a multi-gram scale and are no longer laboratory curiosities. They are valuable precursors for highly functionalized neutral or cationic heterocycles and polycycles that exhibit unusual bonding situations; they are also interesting ligands for transition metals.

Most of the "λ^5-phosphacyclobutadiene derivatives" prepared so far bear bulky substituents at phosphorus atom with the exception of **9a** and **9′a**, which have phenyl substituents. Although all attempts[67] to prepare stable cyclodiphosphazenes **2** with other substituents failed, it is important to continue trying to prepare phosphacyclobutadienes bearing small substituents if one wants to use these compounds as starting materials for polymers. We have to keep in mind that phosphorus polymers (such as polyphosphazenes) have numerous peculiar and industrially important properties.

We have shown that the presence of a λ^5-phosphorus atom is sufficient to stabilize four π electron four-membered rings. Clearly other heteroatoms possessing no available p orbital should also allow the synthesis of analogous heterocycles.

At the end of this review I would like to make clear the main motivations of this work. We wanted to play tricks with the concept of antiaromaticity while seriously keeping in mind that the search for the physical reality in which this concept may be rooted is an important issue for future studies. To nonspecialists, natural-product synthesis appears to be just an intellectual game; this review deals with nonnatural-product synthesis. However, novel properties can only be discovered if new families of compounds are prepared, and history has demontrated that it is difficult to predict the impact and development of new materials or new reactions. Let us wait and see what the future of these heterocycles will be.

I would like to thank all my co-workers for their dedication, intellectual contribution, and hard work, and the CNRS for generous support of this work

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