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Aromaticity of Phosphorus Heterocycles

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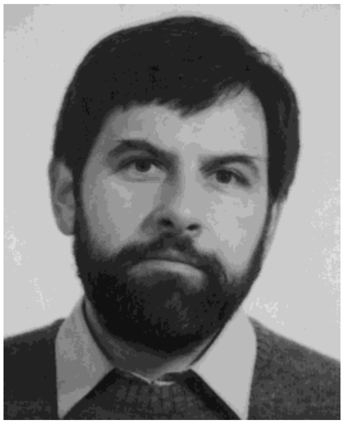
Contents

I. Scope, Time Frame

The present work is dealing with the aromaticity of heterocycles containing phosphorus in different bonding environments. The main emphasis of the work is to show to what an extent and under what circumstances a phosphorus-containing system can be aromatic. Aromaticity can be indicated by different criteria including experimental evidences as well as theoretical measures. Experimental data, although usually more accurate than computed results, are not always directly comparable because of the effect of different substituents or experimental techniques (e.g., X-ray structures of solids differ from geometries obtained by gas electron diffraction). Difficulties in comparison are usually much less severe in the case of theoretical calculations, provided that a uniform level of theory has been used. Thus, the main emphasis in this paper is on the theoretical results, taking care to use data obtained at the same level of the theory when comparing different systems. Wherever possible (i.e., available for comparison), experimental facts (NMR data, structures, chemical behavior) will be discussed as well. Also, the first synthesis of a given class of compounds will be given. In the case of the two most important classes of compounds, phospholes and phosphinines, some other important synthetic routes will also be mentioned. For detailed synthetic procedures, reactivity, or other details, the reader should consult with recent reviews and books.[1a−1o] This review covers the literature until the summer of 2000.



Professor Nyulászi was born in Budapest and received his M.S. degree at the Technical University of Budapest. He received his doctoral degree at the same institution in 1986 and became a staff member there. In 1990 he visited the photoelectron spectroscopic research group of Professor J. M. Dyke at Southampton University for one year, and in 1997 with an Alexander von Humboldt fellowship he spent one year at the phosphorus research group of Professor Manfred Regitz in Kaiserslautern, Germany, and in the computational chemistry group of Professor Paul von Rague Schleyer in Erlangen, Germany. Since 1999 he became Head of the Inorganic Chemistry Department at the Budapest University of Technology and Economics. His research interests are primarily directed toward computational studies of structure, stability, and reactivity of main-group-element-containing molecules.

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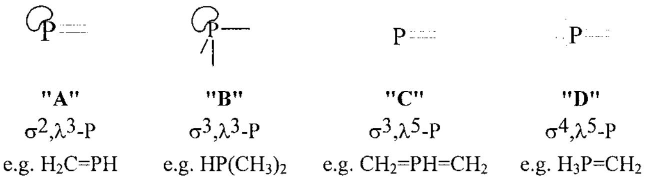
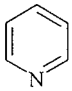
II. Introduction

Phosphorus is a group 15 element of the periodic table. It is analogous with nitrogen, perhaps the most common heteroatom in different aromatic systems (see pyridine **1** and pyrrole **2**). Another important property of phosphorus is its analogy to carbon, mainly for compounds with low-valent phosphorus. This similarity has been pointed out only recently,[11] although such diagonal relationships in the periodic table (Li–Mg, Be–Al, B–Si) are widely discussed in inorganic chemistry textbooks. Phosphorus has a medium electronegativity (2.1) and five valence electrons. Thus, it is able to form a large variety of covalent bonds, which are usually depicted as having different valencies[1c] (see Scheme 1). In the "**A**"-type case, the P=C double bond can be part of a conjugated system like phosphinine (**3**), the phosphorus analogue of **1**. In the "**B**"-type case, with the lone pair on phosphorus, a pyrrole-type system, phosphole (**4**), can be formed. While the ylidic versus ylenic character of the formally doubly bonded "**C**"- and "**D**"-type structures is disputable (see section V), this type of phosphorus, having p orbitals of proper symmetry, might be considered as a building block of π-aromatic systems. Therefore, in a study of unsaturated phosphorus cycles, several important aspects of heteroaromaticity can be covered.

Scheme 1





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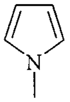

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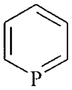

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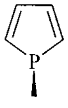


4

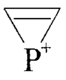
The possible aromaticity of phosphorus compounds has been disputed for a long time in the literature, and even the existence of the P=C double bond has been questioned till the mid-1960s. According to the classical "double-bond rule" (which was mainly an empirical rule based on a lot of unsuccessful experiments),[2] no stable double bond between carbon and heavy elements can be formed. Accordingly, while pyridine (**1**) had been known since the end of the 19th century, the first phosphinine (**3**) derivative was synthesized in 1966 by Märkl.[3] It was shown later that double bonds involving heavy elements are rather stable;[4] the double-bond strength of the P=C bond amounts about 60–70% that of the C=C bond,[5] as a result of the symmetry allowed overlap between the atomic p_z orbitals.[6] The aromatic character of **3** was recognized soon: "Beyond any doubt λ^3-phosphinines are Hückel aromatic systems but the character of λ^3-phosphinines is much more sophisticated as compared to that of the pyridines" (Märkl, G.).[7] The case of phosphole (**4**)—the phosphorus analogue of pyrrole (**2**)—was even much more complicated. Contrary to pyrrole, phospholes are not planar, due to the high inversion barrier of the tricoordinate phosphorus (cf. the 6 kcal/mol inversion barrier of ammonia with the 35 kcal/mol inversion barrier of phosphine).[8] As a consequence, "unfortunately phospholes are not aromatic" (Mathey, F.).[1d] Although the aromaticity of phospholes has been disputed in the past, Mislow considered first that phospholes with pyramidal phosphorus are nonaromatic while with planar tricoordinate phosphorus aromatic phospholes could be obtained.[9] It was just recently found that phosphorus can be flattened or even fully planarized (as discussed comprehensively[10]), resulting in aromatic systems (see section IV.B.1).

The aromaticity of the phosphorus compounds with the "**A**–**D**" bonding type (shown in Scheme 1) will be discussed below, using structural, energetic, and magnetic criteria. The chemical reactivity—in relation to the aromatic stabilization—will be mentioned as well.

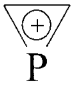
III. "A"-Type Bonding, P=C Bond in Aromatic Systems

A. Three-Membered Ring: Phosphirene Cation (5)

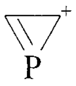
The phosphirene cation (**5**) (with two resonance structures **5a** and **5b**) has been predicted to possess a 2π aromatic system for quite some time.[11] The aromaticity of the corresponding cyclopropenylium cation ($C_3H_3^+$) is well-known.[12] Substituted derivatives of **5**, however, have only recently been observed in solution[13] and in complexed form.[14] **5** is the global minimum on the $C_2H_2P^+$ potential energy surface.[15] The surmised aromaticity of the phosphirenium cation has clearly been shown[16] by the homodesmotic reaction, eq 1, with a stabilization of 32.5 kcal/mol (G2 theory).[17] The PC bonds reported in the study of Eisfeld and Regitz[16] are shorter for **5** than for the 1*H*-phosphirenes, while the C=C bond lengths are somewhat longer. This behavior is in accordance with the expected aromatic character of **5**.



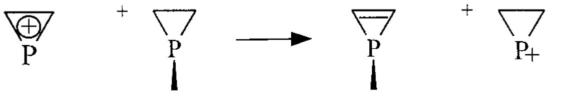
5a



5



5b



(1)

It is also worthy to note that the pentacarbonyltungsten complex of the phosphirenylium cation (**5**) has been recently reported, but no X-ray structure has been obtained.[18] B3LYP/6-311G(d) optimization of the presumed η^1-Cr(CO)$_5$ complex of **5** resulted in an η^3-form (Figure 1) when starting from the η^1-bound chromium complex.[19] Such a structure is in complete accord with a delocalized electronic structure of the cation.

B. Four-Membered Rings

Four-membered rings should be antiaromatic, and they have not been reported in uncomplexed form.

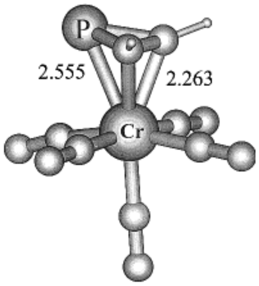


Figure 1. B3LYP/6-311G(d) optimized structure of the Cr(CO)$_5$ complex of the phosphirenium cation.

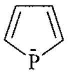
Their discussion will be given in section V.B, together with the four-membered rings containing "**D**"-type phosphorus.

C. Five-Membered Rings

1. Phospholide (*6*) and Polyphospholide Anions

The synthesis, chemistry, and complexing behavior of phospholide (**6**, with **6a**, **6b**, and **6c** resonance structures) and polyphospholide anions have been reviewed recently.[1g,j,20] The $[C_nH_nP_{5-n}]^-$ series with $n = 0-4$ is a complete set of structures with a successive replacement of CH units by the same heteroelement, P. The counterions are alkaline metals (e.g., $P_5^-K^+$, which, together with K_2HP_7, has been obtained from red P in refluxing DMF in a yield of 15%).[21]

6



6a

6b

6c

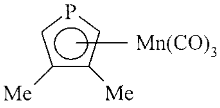
Structural data of phospholide ions themselves are scarce. The lithium salt of the tetramethylphospholide ion,[22] which is in fact an η^5-complex, and the K salt of the 2,4,5-tri-*tert*-butyl-1,3-diphospholide anion[23] have been reported. Also the structure of the Li salt of the 2,5-bis(*tert*-butyl)-1,3,4-triphospholide ion has been obtained[24] In all these structures the bond lengths are equalized (CC, 1.396−1.424 Å; CP, 1.690−1.752 Å).

According to a semiempirical study[25] by Malar, the different polyphospholide anions have 86−101% aromaticities of that of the cyclopentadienide anion. Chesnut and Quin[26] reported on the basis of GIAO NMR calculations using a triple-valence ζ quality basis set that the phospholide anion's aromaticity is 63% that of the cyclopentadienide anion. The aromatic stabilization energy (ASE) obtained by Schleyer et al.[27] from eq 2 ($X = P^-$) was 90% that of the cyclopentadienide anion.

(2)

The NICS(0)[28] values of the polyphospholide anions vary between −12.3 and −15.9 at the HF/6-311+G(d,p)//B3LYP/6-311+G(d,p) level (the "method"//"METHOD" notation means that the property was calculated at the "method" level of the theory at a structure that had been optimized at the "METHOD" level), which is 88−114% that of the cyclopentadienide anion. The NICS$(0)_\pi$[29] values show a gradual decrease from the −20.6 value of cyclopentadienide anion to −17.9 (87%) (P_5H) with an increasing number of phosphorus atoms in the ring.[30] This behavior indicates that the replacement of the CH units by P results in small changes in the conjugative properties not only in the neutral (see section III.C.2.1) but also in the charged systems.

Phospholide ions can form metal complexes with different coordination numbers; η^5-complexation is characteristic for their aromatic behavior. The first η^5-complex with $Mn(CO)_3$ (**7**) was reported in 1976.[31] The ring in some cases (e.g., in **7**)[31] is not strictly planar. In **7**, the P atom is displaced by 0.041 Å from the plane of the carbon atoms. The large number of the different phospholide and polyphospholide ring complexes with different metals can be found in reviews; as a further example, the first pentaphospholide complex (**8**) reported by Scherer et al.[32] is shown, which was a triple decker. The PP bond length obtained by X-ray crystallography varies between 2.15 and 2.21 Å.[1g] The PP distances are shorter in the "normal" double-decker sandwiches and fall between 2.08 and 2.12 Å. In an electron diffraction study of [Fe(η^5-Cp*)(η^5-P_5)], a similar value of 2.117 Å (D_{5h} symmetry) has been reported for the PP distances.[33]



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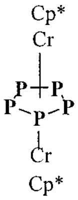
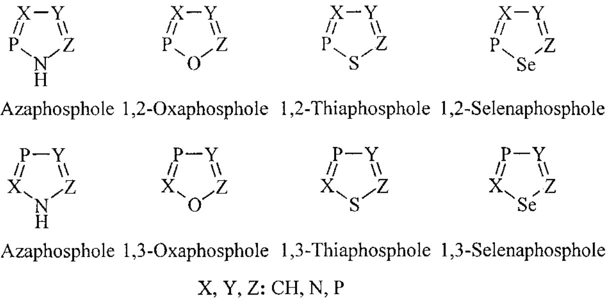


8

2. Heterophospholes

Heterophospholes are five-membered 6π-systems with one or more phosphorus atoms of "**A**"-type bonding. These have been the subject of review papers.[1k,34−36] Here, only those works which are directly related to their aromaticity will be discussed.

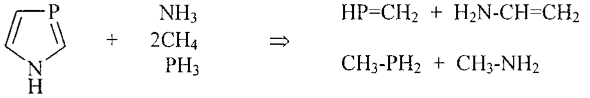
1. Azaphospholes. From the planarity and bond length equalization, a significant delocalization was concluded for the different azaphospholes in reviews.[34,35,37] Equalized bond lengths have also been reported recently for rings with two phosphorus atoms. One example is 1,2,4-azadiphosphole[38] and the other 1,2,3,4-diazadiphosphole. For the latter compound, 1.768 Å was reported[39] for the P−C bond length (X-ray structure), which is between the PC single (1.84 Å)[40] and double (1.64 Å)[40] bond lengths. For the 1,2,4-azadiphosphole, Bird[40] and bond shortening (BDSHRT)[41] indices were calculated from the B3LYP/6-311+G(d,p) optimized structure. All these measures of aromaticity were slightly smaller than those for pyrrole at the same level of the theory.[38] The NICS(0)[28] value (HF/6-311+G(d,p)//B3LYP/6-311+G(d,p)) was −12.8 for 1,2,4-azadiphosphole while −14.7 for pyrrole.[38]



Assessing the aromaticity of 1,3-benzazaphosphole, the ultraviolet photoelectron spectra of some alkylated derivatives have been investigated. The assigned π-bands showed a large splitting with respect to benzene and aminophosphaethene fragments, indicating significant delocalization.[42] The π-bands of the photoelectron spectrum of 1,3-azaphosphole were located at a similar position as those of pyrrole while differing from the imidazole π-band positions.[43] The photoelectron spectra of some of the corresponding five-membered ring arsenic derivatives were also discussed and interpreted—together with their phosphorus analogues—in terms of delocalized and aromatic electronic structures.[44]

Bond separation reaction[45] energies (HF/4-31G(d)) calculated for 1,3-azaphospholes, 1,2,4-diazaphospholes, and 1,2,3,4-triazaphospholes have shown some increasing stabilization with the increasing number of nitrogen atoms in the five-membered ring.[46] The double-bond characters calculated from the respective single- and double-bonded compounds showed significant equalization. In a comparative study, the conjugative effects of the E=C (E = C, N, and P) bonds were investigated. All the known π-ionization energies were taken for related cyclic or open-chained conjugated compounds containing the E=C bond.[47] The correlation between the π-ionization energies of the C=C- and P=C-bonded compounds was linear, with a slope of 0.974, intercept of 0.2 eV, and correlation coefficient of 0.987. This indicates that the P=C bond interacts with the rest of the π-system similarly to a C=C bond, resulting in a similar splitting of the energy levels. (In terms of Koopmans theorem,[48] the ionization energies are negatives of the orbital energies.) The same correlation between the C=C and C=N π-ionization energies has a higher slope (1.094) and a poorer correlation coefficient (0.950). The decrease of the correlation coefficient indicates that the interaction of the C=N π-energy levels (as shown by their splitting) is different from that of the C=C π-orbitals, while more similarity can be found between the P=C and C=C π-bonds.

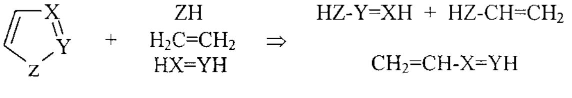
For the complete set of aza-, diaza-, and triazaphospholes and also for **3**, ring fragmentation energies (HF/4-31G(d)) were also investigated to study the stabilization achieved by incorporating an E=C (E = CH, P, and N) double bond into a cyclic delocalized ring.[47] An example of a ring fragmentation reaction for 1*H*-1,3-azaphosphole is shown in eq 3.



(3)

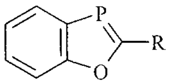
Taking average of the ring fragmentation energies of the C=C-bonded compounds as a reference, 98% has been obtained for the average energy of the C=P-bonded systems while 114% for the C=N-bonded compounds. The correlation between the energies of eq 3 of the different C=E double-bonded systems is poorer than that between the π-ionization energies (this might be attributed to differences of the in-plane lone pair interactions. Evidence for such interactions was found in photoelectron spectroscopic investigations.)[45,49]

In a study of five-membered heteroaromatic systems, semihomodesmotic (SEH) reactions[41] were investigated at the MP2/6-31G(d) level among others for 1,2-azaphospholes (eq 4, X = P, Y = CH, Z = NH) and 1,3-azaphospholes (eq 4, X = CH, Y = P, Z = NH).[41] Although these reactions are not homodesmotic,[50] they include the stabilization already present in the four π-electron units at the right-hand side of the equation. It has also been shown that the average of the double-bond characters (cf. with BDSHRT)[51] correlate with the aromaticity (i.e., with the aromatic stabilization). Both of these measures were similar for the 1,3-azaphosphole and pyrrole (e.g., BDSHRT, 61 for both compounds), while 1,2-azaphosphole exhibited smaller values (BDSHRT, 53).



(4)

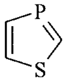
2. Oxaphospholes. Oxaphospholes are much less investigated heterophospholes than their aza analogues,[34] presumably due to their lower stability, which can also be related to their lower aromaticity (see below). The first oxaphosphole reported [52] was a benzocondensed derivative, 1,3-benzoxaphosphole (**9**). The MP2/6-31G(d) semihomodesmotic reaction (eq 4; Z =O) energies and BDSHRT indices for the 1,2- and 1,3-oxaphospholes[41] are of similar values to those obtained for furan (9.25 kcal/mol stabilization).[41] The photoelectron spectrum of 1,3-benzoxaphospholes was similar to that of the corresponding 1,3-benzazaphospholes, although the ionization energies were at higher values.[42] The recently synthesized 1,2,4-oxadiphosphole has been assumed to be aromatic[53] on the basis of the calculated[38] planar structure. The HF/6-311+G(d,p)//B3LYP/6-311+G(d,p)



9 (R: tBu)

NICS(0) value (−11.0) is lower than that for the corresponding azadiphosphole (−12.8; see section III.C.2.1), similar to the differences in the furan and pyrrole NICS values (−12.3 and −14.7, respectively, at the same level of theory).[38] The high reactivity of the oxadiphosphole in cycloaddition reactions[53] is in accord with its low aromaticity.

3. Thia- and Selenaphospholes. While substituted derivatives of 1,3-thiaphosphole are known (the first benzocondensed 1,3-thiaphosphole derivative was reported by Issleib and Vollmer),[54] the unsubstituted parent compound (**10**) has been synthesized only recently.[55] On the basis of its reactivity, it has been stated that **10** is a "highly activated aromatic ring".[55] The ^{1}H NMR shift for the proton in the 5 position is at 7.41 ppm,[55] which is close to the ^{1}H NMR signal of the α-proton of thiophene (7.35 ppm).[56] The photoelectron spectrum of an alkylated 1,3-thiaphosphole derivative exhibited π-bands at similar positions to the corresponding thiophene derivative.[57] The bond separation and semihomodesmotic reaction (see eq 4, X = P, Y = CH, Z = S) energies were close to the thiophene values at the MP2/6-31G(d) level.[41] The BDSHRT index for 1,3-thiaphosphole (63) was also close to the thiophene value (63).[41] The 1,2-thiaphosphole exhibits smaller values than the 1,3-derivative, similar to the azaphospholes.[41] It is worth mentioning that very recently the unsubstituted 1,2- and 1,3-thiaarsoles were also reported.[58]



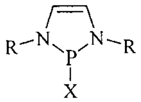
10

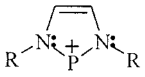
Among thiadiphospholes, the 1,2,4- and 1,3,4-thiadiphospholes were reported recently by reacting ^{t}BuCP with CS_2 (or with an ylidic derivative of carbon disulfide).[59] The HF/6-311+G(d,p)//B3LYP/6-311+G(d,p) NICS(0) values for the 1,2,4- and 1,3,4-thiadiphospholes were −12.4 and −12.7, respectively, matching favorably with the −13.2 value obtained for thiophene.

Selenaphospholes exhibited similar photoelectron spectra and SHE stabilization energies to the thiaphospholes.[57] The recently synthesized 1,2,4-selena- and 1,2,4-telluradiphosphole rings were complexed (η^1 at the 2 position by $Cr(CO)_5$ and $W(CO)_5$) and the structure of these compounds was obtained by X-ray crystallography.[60] The planar structures showed equalized CP bond lengths (1.69−1.77 Å for the selenaphosphole and 1.70−1.79 Å for the telluraphosphole). The structure of the Se derivative was in good agreement with the calculated MP2/6-31G(d) geometry[41] for the uncomplexed ring. B3LYP/6-311G(d)//B3LYP/3-21G(d) relative energies of the two possible η^1-chromium complexes were also obtained for the unsubstituted ring. It has been shown that the η^1-complexation on phosphorus has a minor effect on the structure only.[60]

4. 1,3,2-Diazaphospholium Cation (11). Although different diazaphospholes have been known for a longer amount of time (section III.C.2.1), the research of 1,3,2-diazaphospholium cation (**11**) and its possible aromaticity became more intense after the appearance of Arduengo's carbene (**12**, E = C)[61] and Denk's silylene (**10**, E = Si).[62] (Note that P^+ is isoelectronic with Si.) Denk et al. reported[63] that the chloride of **11**, which was insoluble in hexane, should be considered as an ion pair, which is stabilized by the aromaticity of the cationic system. This view was also supported by the long PCl bond (Table 1) observed in the X-ray structure.[63] Cowley et al.[64] synthesized **11** (R = ^{t}Bu) and its arsenic analogue and reported the X-ray structures as well.[64] The delocalization was concluded from the lengthening of the P^+−N bond with respect to other N−P^+−N systems, while the 1.330 Å C═C bond length is indicative of a localized double bond. The aromatic stabilization energy for **11** has been obtained from an isodesmic reaction, which considers the hydrogenation energy differences of **11** and its σ^4,λ^5-P-derivative of 22.97 kcal/mol (MP4/6-31G(d)//HF/6-31G(d) level).[65] Other quantum chemical investigations have also shown that **11** has a considerable aromatic character,[65−67] similar to **12**.[68] Gudat pointed out by using experimental (X-ray structures, NMR investigations) as well as theoretical means that the donation of the nitrogen lone pairs together with the σ-effects plays a more important role in the stabilization of **11** than the aromaticity.[67a] He also showed that the behavior of P-halogeno-1,3,2-diazaphospholenes can be well understood by considering the hyperconjugative interaction of the −N−C═C−N− unit with the P−Hal σ*-bond.[67b] Also, the PH bond has been found to be longer than usual in the hydride of **11** (Table 1).[67c] With substituents on the chloride of **11** other than R = ^{t}Bu, the PCl bond is becoming much shorter[67b] than that in the study of Denk et al.[63] (R = ^{t}Bu on the chloride of **11**). Important structural data of **11** and its chloride are given in Table 1.

Table 1. Selected Bond Lengths (in Å) for 11 and Some of Its Derivatives As Obtained from X-ray Structures

	PN	NC	C═C	P−X	ref
X = -$^+$; R = ^{t}Bu	1.66(1)	1.376	1.330	-	64
X = Cl; R = ^{t}Bu	1.66(0)	1.37(9)	1.347	2.759	63
	1.66(2)	1.38(9)			
X = Cl; R = Mes	1.67(3)	1.40(6)	1.338	2.324	67b
	1.67(5)	1.40(2)			
X = H; R =: Mes	1.70(9)	1.40(7)	1.327	1.51	67c
	1.72(2)	1.41(0)			



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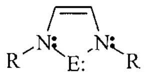

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D. Six-Membered Rings

1. Phosphinine (3)

The first phosphinine derivative was synthesized by Märkl in 1966,[3] and the parent unsubstituted phosphinine itself was first reported by Ashe.[69] The

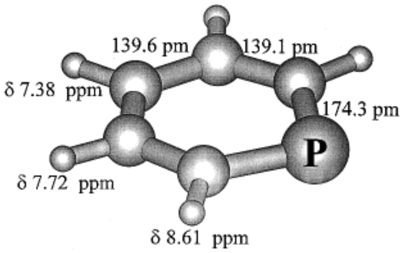
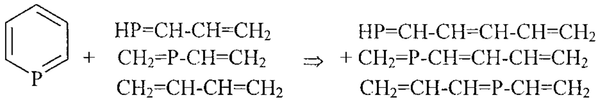


Figure 2. B3LYP-6-311+G(d,p) structure of phosphinine (**3**), with calculated bond lengths and experimental ^{1}H NMR chemical shifts.

spectroscopic and physicochemical investigations of the parent compound clearly indicated aromaticity.[70] The structure of phosphinine has been determined by a combined electron diffraction−microwave study and has been proven to be planar.[71] The CC bond length alternation was small ($C_\alpha C_\beta = 1.413$ Å, $C_\beta C_\gamma = 1.384$ Å) but larger than in the case of the arsenic analogue ($C_\alpha C_\beta = 1.390$ Å, $C_\beta C_\gamma = 1.401$ Å).[72] Computationally obtained structures at different levels[43,46,73−80] show that the CC bond length alternation is less than 0.01 Å. Frenking,[75] on the basis of a series of calculations, has challenged the experimentally obtained structure, suggesting the following bond lengths: $PC_\alpha = 1.737$ Å, $C_\alpha C_\beta = 1.396$ Å, $C_\beta C_\gamma = 1.398$ Å (MP2/6-311G(d)) (see also Figure 2).[75] The CC bond lengths are very close to the benzene values, indicating a similar aromaticity. Also, the BDSHRT index is 62, close to the value obtained for benzene.[81] The Bird aromaticity index calculated from experimentally available structures (of substituted derivatives) varies between 74 and 79[82] (benzene 100). Computationally, a much higher Bird index (96) has been obtained, showing again similar aromaticity to benzene.[81]



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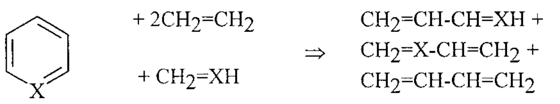
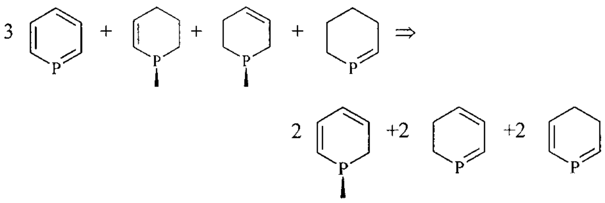


(6)

The energetic measures also indicate that the aromaticity is similar to that of benzene. According to the superhomodesmotic reaction[83] (eq 5), the (HF/3-21G(*)) stabilization is 20.9 kcal/mol (88% of the benzene value) while the homodesmotic reaction (eq 6, X = P) gives 27.2 kcal/mol (MP2/6-31G*)[79] stabilization (97% of the benzene value) (24.0 kcal/mol; 97% of the benzene value at HF/6-31G(d)).[74] These reactions do not correct for the ring strain (which should obviously have some contribution due to the narrow bonding angle about phosphorus). In eq 7, which should partly compensate for ring strain, a 91.7 kcal/mol stabilization has been obtained for the three phosphinines.[84] The stabilization for one phosphinine unit is thus 30.6 kcal/mol (B3LYP/6-311+G**), a somewhat larger value than from eq 6. For benzene, the corresponding reaction (eq 8; X = CH) provides 34.9 kcal/mol stabilization. The homomolecular reaction of Chesnut and Davis at the BLYP/6-311G(d,p) level resulted in 36.6 kcal/mol stabilization (benzene 39.3 kcal/mol).[85] Also, the magnetic properties of phosphinine are clear, indicative of its aromaticity. The NICS(0)$_{tot}$ value is −8.1,[81] while the NICS(0)$_\pi$ is −19.1 at the HF/6-311+G**//B3LYP/6-311+G** level of the theory (84% and 93% of the benzene value, respectively).[81] The NICS(1)$_{tot}$ value is −10.8 (−11.3 for benzene). The NICS(0)$_{tot}$ values are more influenced by the σ contributions than NICS(1)$_{tot}$; thus, the latter is considered to be more characteristic for the aromaticity of the π-system. The ^{1}H NMR shifts are downfield from the benzene values; the largest difference (1.2 ppm) is seen in case of the α protons (8.61 ppm)[86] and is significantly smaller in the case of the β and γ protons (7.72 and 7.38 ppm, respectively, see Figure 2).[86] The downfield shift should be mainly accounted for by the magnetic anisotropy effect of the heteroatom. Correcting for this effect,[70] a residual 7.0 ppm shift has been obtained that is at somewhat higher field than that for benzene. The signal of the γ proton matches by 0.01 ppm that of the benzene protons.



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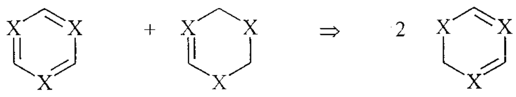

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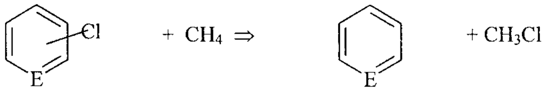
From the investigation of all these data it is clear that the aromaticity of phosphinine is nearly equal to that of benzene. Their chemical reactivity, however, is different.[1k,l,7] Most important is the effect of the in-plane phosphorus lone pair, which (i) is able to form a complex and (ii) can be attacked by electrophiles to form λ^5-phosphinines. Thus, electrophilic substitution reaction on the ring carbon is impossible. In Diels−Alder reactions, phosphinines behave as dienes, providing similar products to benzene but under less forcing condition (the reaction with bis(trifluoromethyl)acetylene takes place at 100 °C with **3**, while for benzene 200 °C is required).[87]

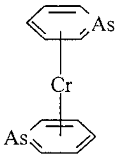
The substituent effect on the aromaticity of phosphinines has not been investigated in great detail, with the exception of the chloro group, which has been studied by photoelectron spectroscopy and quantum chemical methods.[76] Inspection of the ionization energies of some substituted phosphinines revealed that the π-ionization energies nearly match those of the corresponding benzene derivatives. Also, the chlorine separation isodesmic, eq 9, energies were of similar values with the chloro groups in different positions on phosphinine (E = P) pyridine (E = N) or benzene (E = CH).[76]

While phosphinine is easily complexed η^1-bound at the phosphorus, resulting in σ complexes, π-complex-



(9)

es bound η^6 are also known, provided that the phosphorus lone pair is shielded by substituents at the 2 and 6 positions.[1g,j,l] Accordingly, while bis(η^6-arsinine)chromium (**13**) has been formed by co-condensation of arsinine with chromium atoms, the corresponding phosphinine has not been obtained.[88] From 2,4,6-triphenylphosphinine, however, the Cr(CO)$_3$ complex (**14**) has been reported as the first η^6-phosphinine derivative.[89]



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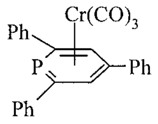

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2. Azaphosphinines

Among azaphosphinines, the 1,4-derivative was reported first—although only in solution—by Märkl and Matthes.[90] The first derivative stable enough for isolation was 1,3-azaphosphinine.[91] For the 1,2-aza- and 1,3,2-diazaphosphinines, an efficient synthesis has been designed recently.[92] The relative aromaticities of the 1,2- and 1,3-azaphosphinines as well as that of the 1,3,2- and 1,3,5-diazaphosphinines has been investigated subsequently computationally.[80] All structures are planar and exhibit averaged bond lengths. Some bond length contraction was also observed (with respect to the average of the single and double bonds), but no BDSHRT has been reported. On this basis, azaphosphinines were considered somewhat less aromatic than pyridine or phosphinine. Inspection of the NICS(0.5) values has also shown that the gradual replacement of the CH units by N somewhat reduces the aromaticity (HF/6-31+G(d)//B3LYP/6-31+G(d) values are −11.5, −10.2, −8.9, −9.3, −7.5, and −8.4 for benzene, phosphinine, 1,2-azaphosphinine 1,3-azaphosphinine, 1,3,2-diazaphosphinine, and 1,3,5-diazaphosphinine, respectively). The thermodynamic stability differs from the NICS(0.5) aromaticity ordering (the 1,2-azaphosphinine, e.g., being more stable than the 1,3-isomer).

3. Di- and Triphosphinines

Among 1,4-diphosphinines, the 2,3,5,6-tetrakis(trifluoromethyl) derivative has been synthesized,[93] a compound unstable even in solution. ^{t}Bu derivatives of the 1,3-diphosphinine[94] and the symmetric triphosphinine[95] have been reported more recently. The crystal structure of the triphosphinine has been published,[96] showing that the molecule is planar and all bond lengths are equal. The 1.727 Å value is between the usual single- and double-bond length range. Photoelectron spectroscopic investigation of the two rings has also been carried out. From inspection of their assigned first π-ionization energies (8.2 eV for the 1,3,5-tri-*tert*-butyl-2,4,6-triphosphinine and 8.5 eV for 2,4-di-*tert*-butyl-1,3-diphosphinine), it turns out that they are very close to those observed for the 1,3,5-tri-*tert*-butylbenzene and 1,3-di-*tert*-butylbenzene (8.19 and 8.43 eV, respectively).[97] This indicates that the successive replacement of C=C by P=C bond does not result in a significant change of the π-orbital energies.

The homodesmotic reaction (eq 10 with X = P) energy calculated for 1,3,5-triphosphinine is 26.0 kcal/mol at the MP2/6-31G(d) level.[79]

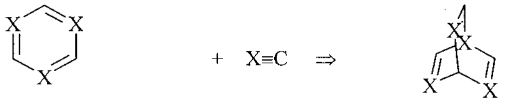
$$C_3H_3X_3 + 3CH_2{=}XH \Rightarrow 3CH_2{=}X{-}CH{=}XH \quad (10)$$

This is just slightly smaller than for benzene (28.2 kcal/mol) or for phosphinine (27.2 kcal/mol).[79] Bachrach and Magdalinos[98] noted the planarity (D_{3h} symmetry) of $C_3H_3P_3$. By comparing the MP2/6-31G* bond length (1.739 Å) with that of the PC bond length in phosphinine, it has also been assumed that triphosphinine is aromatic.[98]

Schleyer et al. very recently[99] also investigated the stabilization and NICS of triphosphinine. For the symmetric triphosphinine and for 1,3-diphosphinine, the (HF/6-31+G(d)) NICS(0) is −5.9 and −7.2, respectively. The HF/6-311+G(d,p) NICS(1) values are −9.6 and −10.3, matching favorably with the −10.8 and −11.3 values for phosphinine and benzene, respectively.[84] This behavior indicates the rather large influence of the PC σ contributions, which die out above the ring plane. Schleyer et al. also observed that with reference to the homodesmotic eq 10, for benzene (X = CH) the variation is 2−4 kcal/mol if a CH unit is replaced by phosphorus.[99]

Recently the stability of diphosphinine isomers has been investigated.[100] The three diphosphinines are the most stable among the possible isomers investigated by at least 20 kcal/mol. Also, from a comparison of the 1,3-diphosphinine ring isomers (including carbene and allene), the diphosphinine was the most stable isomer (in the case of the parent compounds having hydrogens on the carbon atoms).[101] Remarkably, due to the steric repulsion of four ^{t}Bu groups on the 1,3-diphosphinine, the structure of the ring is nonplanar and the stability of the six-membered ring allene becomes similar to that of the aromatic diphosphinine.[101]

Investigating the high Diels−Alder reactivity of phosphinines (eq 11), the transition-state energy was much smaller for X = P than for X = CH (17.8 vs 44.6 kcal/mol—MP4/6-31G*//MP2/6-31G*). Bachrach and Magdalinos[98] attributed the lowering of the activation energy to the reduction of the resonance stabilization. They also noted that in Diels−Alder reactions about 10 kcal/mol reduction of the activation barriers have been observed when a CH unit has been replaced by P. (Note that the Diels−Alder reaction of bis(trifluoromethyl)acetylene with phosphinine (**4**) proceeded by 100 °C lower temperature than for benzene[87]—see section III.D.1). Since the aromaticity criteria show only a small decrease between benzene and triphosphinine, the increased



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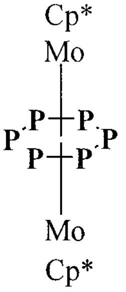
Diels−Alder reactivity of the PC-bonded compounds can rather be attributed to the diminished strength of the PC bond as compared to the hydrocarbon bonding than to the decrease of the cyclic delocalization by a P=C vs C=C replacement.

4. Hexaphosphinine (P_6)

The P_6 hexagonal ring is not a minimum, and it is far from being the most stable P_6 structure.[102] According to Janoschek,[103] in the homodesmotic reaction in eq 5 (when all X and CH units are replaced by P), + 8.5 kcal/mol destabilization has been obtained. P_6 is more stable, however, than $3P_2$.[104] The calculated B3LYP/6-311+G(d,p) bond length was 2.133 Å[29] (2.095 Å HF/6-31G(d)), which falls between the usual value of the PP single and double bonds. The NICS-(0.5) and NICS(0.5)π values are −15.8 and −14.7, respectively, indicating a significant ring current. The destabilization in the homodesmotic reaction in eq 5 has been attributed to ring strain, which was estimated[103,104] to be 17−22 kcal/mol, resulting in a resonance stabilization of 9−14 kcal/mol. Although P_6 has not been isolated, it has been reported in η^6-complexed form. The first P_6 complex (**15**) reported was a triple decker.[105] The PP bond length for that P_6 complex varied between 2.167 and 2.175 Å).



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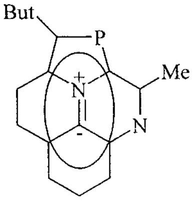
E. Azaphosphaullazine (4,9*b*-Diaza-2-phosphacyclopenta[*c,d*]phenalene) (16)

While some condensed aromatic rings containing phosphorus in “**A**”-type bonding are known (e.g., dibenzo[*b,e*]phosphinine[106]), perhaps as a curiosity also phosphaullazine (**16**) should be mentioned.[107] This compound contains the P=C bond in a 14π-electron perimeter ring, showing the capability of the P=C bond to delocalize in an annulene. The delocalized structure was concluded from the ^1H NMR signals (7.0−7.9 ppm for the ring protons), which were in the range of the phosphorus free analogue, and the mass spectrum, which exhibited a paucity of fragments as is typical for stable aromatic systems.



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While the π-conjugation ability of phosphorus compounds does not seem to depend on the size of the system, it must be mentioned that the small bond angles typical for phosphorus will result in large ring strain, particularly for large planar ring systems. Thus, for large planar rings containing phosphorus, even more serious stability problems can be expected than for their carbon analogues.

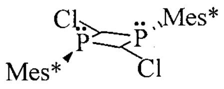
IV. “B”- and “C”-Type Bonding, Phosphorus Lone Pair in Delocalized Aromatic Systems

Structure “**C**” is usually written with a pentavalent phosphorus;[108] this description, however, should merely denote that the phosphorus lone pair is delocalized and no allenic bond with two perpendicular π-systems has been formed. $H_2C{=}P(H){=}CH_2$, a typical representative of structure “**C**” phosphorus, can be described by an allyl-like π-system,[30,109,110] with the “p”-type lone pair of a planar tricoordinate phosphorus participating in the 4-electron-3-center π-bonding, without invoking d-orbital participation.[111] Thus, the “**C**”-type bonding of phosphorus involves tricoordination, with a planar bonding environment, whereby the lone pair is available for π-bonding.

As a result of the allylic bonding, the terminal carbons are negatively polarized while the central phosphorus is positively charged, in agreement with the resonance structure $CH_2^{-}{-}P^{+}(H){=}CH_2$. Although there were some earlier indications of the good donor property of the planar phosphorus lone pair,[9,112] Schleyer has concluded “The π-donor ability of planar tricoordinate phosphorus rivals to that of nitrogen”.[113] Tricoordinate phosphorus, however, is not planar; the lone pair has a significant “s” orbital character (the bond angles are 90−95°; the sum of bond angles (**SBA**) is, thus, about 280−290°); therefore, it is unable to overlap with a neighboring π-system. The barrier to planarization is 35 kcal/mol in PH_3,[8] and this energy has to be invested before a conjugated π-system involving phosphorus lone pairs can form. Substituent effects on inversion barriers of ER_3 molecules (such as PH_3) are well studied;[114] σ-donors and π-acceptors are planarizing. Among them, π-acceptor $-C^{+}R_2$,[113] −CR (carbene),[115] or BR_2[116] groups should have the strongest effect. The minimization of steric strain, including the use of bulky groups on phosphorus, is also a planarizing factor. The conjugation and especially cyclic conjugation also stabilizes the planar structure.[9,10] In the following section, the known aromatic or potentially aromatic systems with tricoordinate “**B**”- or “**C**”-type phosphorus will be discussed.

A. Four-Membered Rings

Niecke et al.[118] reported the synthesis of the first stable 1,3-diphosphete-1,3-diyl ring (**15**) (with substituents attached to phosphorus) in 1995. The ring is planar with a CP bond length of 1.750 Å, which is close to the CP bond length in **3** (1.737 Å, see section III.C.1). The phosphorus atom is pyramidal. However, **SBA** about phosphorus is 337.9° in **17**, indicating a significant planarization of the phosphorus atom. The supermesityl (Mes*) residue on the P atom reduces the pyramidalization, as it is obvious from the comparison of the (MP2/6-31G(d,p)) calculated structure of the parent $C_2P_2H_4$[117] with the X-ray structure of **17**. The MP2/6-31G(d,p) optimized PC bond length for the parent ring $C_2P_2H_4$[117] is 1.821 Å. This is far longer than in **17**, which has less pyramidalized phosphorus. $C_2P_2H_4$ has a considerable biradicaloid character.[117] The stabilization of the singlet can be achieved in this system by planarization of the tricoordinate phosphorus, resulting in a "perfect cyclic π-conjugation as in disulfur-dinitride".[117] Calculated (HF/6-311+G(d,p)//B3LYP/6-311+G(d,p)) magnetic susceptibility exaltations between the nonplanar (−41.1 ppm) and planar $C_2P_2H_4$ amounts to 7.3 ppm[84] and indicate the increase of the cyclic delocalization with the flattening of tricoordinate phosphorus. More recently, the Niecke group reported the anionic four-membered ring structure **18**.[118] This compound can be considered as a 6π-diphosphacarbene anion with the phosphorus atoms being substantially flattened (**SBA** 336° and 343°). The NBO analysis carried out for $C_2P_2(CH_3)_2(SiH_3)^-$ gave a π population of 1.02 electrons on the formally empty p orbital of the carbenic carbon atom, indicative of extended electron delocalization.



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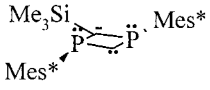

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B. Five-Membered Rings

1. Phosphole (4)

The potential aromaticity of phosphole was discussed after its first practically applicable synthesis[119] was reported in the 1960s. From the different observations it emerged until the early 1980s, as discussed in reviews as well,[1b,d,120−121] that phosphole is basically not aromatic. The reason of the nonaromatic behavior of phosphole, however, is not an inherent insufficient overlap between the phosphorus lone pair and the rest of the π-system but the nonplanarity at the tricoordinate phosphorus, which can immediately be recognized on the first X-ray structure published.[122] Aromatic delocalization stabilization is obviously insufficient to overcome the significant planarization barrier of 35 kcal/mol (see above). Mislow compared the inversion barriers (obtained by dynamic NMR spectroscopy) of a phosphole (16 kcal/mol) with a saturated counterpart (phospholane, 36 kcal/mol) and attributed the ca. 20 kcal/mol lowering to the aromatic stabilization in the planar form of the unsaturated derivative.[9] The aromaticity of the planar structure was also investigated by CNDO calculations.[123]

The lack of aromatic delocalization of phosphole can clearly be seen in the low (12−18 kcal/mol) bond separation, eq 12, energies.[43,46,73] Superhomodesmotic reaction (eq 13) energies are more informative, giving a stabilization of (−1.5 kcal/mol HF/3-21G(*)).[73] The ASE obtainable from eq 2 (X = PH) was 7 kcal/mol[124] (MP2/6-31G(d)), a rather moderate value. In the SEH eq 14, +0.43 kcal/mol has been obtained (MP2/6-31G-(d)).[125] The NICS(0) value has also been quite low for phosphole (HF/6-31G(d)//MP2/6-31G(d), −5.3;[28] HF/6-311+G(d,p)//B3LYP//6-311+G(d,p), −5.0[30]) The NICS(0)π value (−13.2) is just slightly higher than that for cyclopentadiene (−12.1).[30] The Bird aromaticity index calculated from the reported X-ray structure was 36.[82,122] This value is again marginally higher than that for cyclopentadiene. The fact that aromaticity measures for phosphole are somewhat larger than for cyclopentadiene can be explained by the hyperconjugative involvement of the σ_{PR} orbital (R = alkyl, H), as suggested by Schweig et al.[126] on the basis of the analysis of the photoelectron spectra of alkyl−phospholes.

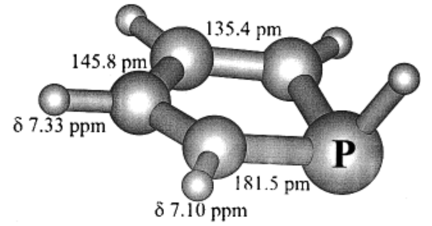


Figure 3. B3LYP-6-311+G(d,p) structure of phosphole (**4**), with calculated bond lengths and experimental ^{1}H NMR chemical shifts.

$$\mathbf{4} + PH_3 + 4CH_4 \rightarrow 2CH_3PH_2 + CH_3{-}CH_3 + 2CH_2{=}CH_2 \quad (12)$$

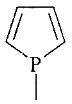
$$\mathbf{4} + 2H_2P{-}CH{=}CH_2 + H_2C{=}CH{-}CH{=}CH_2 \rightarrow 2H_2P{-}CH{=}CH{-}CH{=}CH_2 + H_2C{=}CH{-}PH{-}CH{=}CH_2 \quad (13)$$

$$\mathbf{4} + PH_3 + 2CH_2{=}CH_2 \rightarrow 2CH_2{=}CH{-}PH_2 + CH_2{=}CH{-}CH{=}CH_2 \quad (14)$$

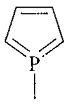
The B3LYP/6-311+G(d,p) calculated structure (from the parent **4**, no experimental structure is available since it could only be detected in solution) and the measured NMR data[127] of **4** are given in Figure 3.

The planar form of phosphole is a first-order saddle point on the potential energy surface, 16−24 kcal/mol above the minimum (at different levels of the theory).[26,30,128−129] (The calculated barriers are the highest at the HF level, which underestimates aromatic stabilization of the planar saddle point, while the MP2 results are at the low end.) It has been demonstrated by calculation of the NMR properties,[26] structural parameters,[30,129] and geometric aromaticity indices as the Bird index[30] and the BDSHRT,[30] as well as the stabilization energies (with planarized phosphorus in the reference structures)[30,125,129] and NICS values[30] that the planar form of phosphole has an even larger aromaticity than pyrrole or thiophene.

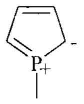
The planarity of the tricoordinate phosphorus and thus the aromaticity of **4** can be influenced by substituents. It turns out from ab initio calculations that π-acceptor groups either at phosphorus[129] or at the neighboring carbon have a planarizing effect. The barrier to planarity decreases to 1.56 kcal/mol (MP2/6-31G(d)) as a result of $-BH_2$ substitution at phosphorus. The bond length alternation in the planar form of this substituted derivative increases in the ring, indicating a decrease of the aromaticity (structure **4a***pl*).[129,130] Also, the NICS(0) value decreases.[130]



4a*pl*



4b*pl*



4c*pl*

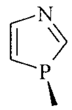
Apparently the lone pair of phosphorus is conjugated with the boron empty orbital and cannot effectively be involved in the cyclic conjugation, as demonstrated by the decrease of the NICS value.[131] Two $-BH_2$ groups at the carbons at the 2 and 5 positions of the ring are also planarizing (8.42 kcal/mol at MP2/6-31G(d)), although to a lesser extent than at phosphorus.[130] The effect of AlH_2 and SiH groups was similar to that of the BH_2 substituent. π-Donors at the 2 and 5 positions of the ring shorten the PC distances considerably. The structural data more closely resemble **4b***pl*,[130] which is formally written with a pentavalent phosphorus. Schmidpeter was first to consider such a **4b***pl*-type structure for a benzocondensed phosphole[131] on the basis of NMR data. Although it turned out later that instead of **19** a different compound must have been in the reaction mixture,[132] similar structural characteristics were reported for a 1,2-diphosphole with an unambiguous X-ray structure[133] (see section IV.B.3). The common feature in these compounds is the presence of the electron-withdrawing R_3P^+ substituent at the carbon attached to phosphorus.

While **4b***pl*-type structures can be considered as resonance structures, **4c***pl* is also an alternative. The importance of structure **4c***pl* is supported by the fact that the negative charge at the carbon atoms in the 2 and 5 positions is indeed larger than at the 3 and 4 positions.[30] The common feature in all **4a***pl*-, **4b***pl*-, and **4c***pl*-type structures is that the lone pair of the planar tricoordinate phosphorus is fully delocalized, resulting in an enhanced bond order about the tricoordinate planar phosphorus. The d-orbital participation at phosphorus is insignificant in **4**, either in the planar or nonplanar form.[30]

A further alternative to flatten phosphole was to use bulky substituents at phosphorus. The idea came from Quin and was fully exploited in a series of works with Keglevich. The di-*tert*-butyltolyl group at the phosphorus in phosphole did not have a large impact on the chemistry of the phosphole.[134] The photoelectron spectrum, however, indicated a small stabilization of the phosphorus lone pair with respect to the saturated counterpart of the phospholane as a sign of cyclic conjugation.[135] The supermesityl (tri-*tert*-butylphenyl) substituent has shown a considerably larger flattening effect at phosphorus.[136] The **SBA** in 1-(2,4,6-tri-*tert*-butylphenyl)-3-methylphosphole (**19**) was 331.7°, which is much larger than that in 1-benzylphosphole (**SBA** 302.7°) according to the X-ray structure.[136] As a remarkable indicator of its aromatic behavior, **19** has shown S_E reactivity.[136,137] The Bird aromaticity index (57) exceeded that of furan and approached the pyrrole value.[136] The theoretical and photoelectron spectroscopic investigation of a series of phospholes with increasing steric bulk at the phosphorus has shown the gradual increase of the Bird and BDSHRT aromaticity indices with a decrease of the phosphorus lone pair ionization energy.[138] Also, the propensity in taking part in Diels–Alder reactions is diminishing with the increasing steric bulk on the phosphorus substituent, in accordance with the increasing aromatic stabilization, although this effect can at least partly be attributed to the protecting effect of the substituent too.[139] To date, the complete flattening of the phosphole ring (**4**) could not be achieved.

2. 3H-1,3-Azaphospholes

Azaphospholes substituted at phosphorus have different characteristics than those substituted at nitrogen (which were discussed in sections III.C.2.1 and III.C.2.4). The structural comparison of 1*H*-1,3-azaphosphole (section III.C.2.1) with 3*H*-1,3-azaphosphole **20** reveals their difference. 3*H*-1,3-Azaphosphole is a nonplanar compound, characterized by low bond separation reaction energies similar to those in phosphole.[43,46] The equalization of the bond lengths is small and speaks against cyclic conjugation.[44] The BDSHRT index[41] is also much smaller in **20** (51) than in 1*H*-1,3-azaphosphole (62).[140] The photoelectron spectrum of alkyl-substituted 3*H*-1,3-benzazaphospholes showed closely spaced ionization energies, indicating that the energy levels were not split as observed for 1*H*-1,3-benzazaphospholes, where a conjugative interaction was shown to be important.[44,141]



20

Planarization of the P-substituted azaphospholes results in structures with similar aromaticity to the planar phosphole. Replacement of the CH units by N in these rings has some effect on the barrier to planarization. The MP2/6-31G(d) barrier of 2*H*-1,3,2-diazaphosphole was 17.6, while that of 3*H*-1,5,3-diazaphosphole was 13.5 kcal/mol (phosphole 17.2 kcal/mol at the same level).[129]

3. Polyphospholes

In polyphospholes, the CH units of phosphole are replaced by one or more “P” units (i.e., phosphorus with “**A**”-type bonding). It has been shown that with the gradual increase of the number of the phosphorus atoms, the inversion barrier of the tricoordinate phosphorus is decreasing.[30,125] The planarizing effect of the “**A**”-type phosphorus atoms can partly be attributed to the +I effect[30,142] and partly to the release of the ring strain due to the narrow bonding angle about the dicoordinate “**A**”-type phosphorus.[30,125] Pentaphosphole, P_5H, turned out to be planar computationally according to two independent studies.[142,143] Analysis of the wave function showed close resemblance to that of thiophene. The NICS(0) value (−17.2 at HF/6-311+G(d,p)//B3LYP/6-311+G(d,p)) and other aromaticity criteria including geom-

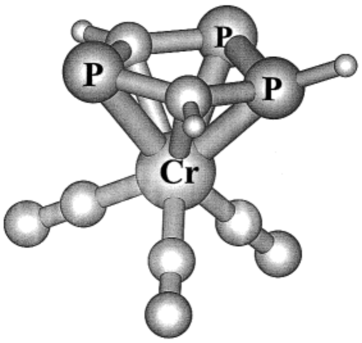


Figure 4. B3LYP/LANL1DZ structure of the $Cr(CO)_3$ complex of 1,2,4-triphosphole.

etry indices and exaltation of the magnetic susceptibility were close to those of the phospholide and polyphospholide anions.[30] Furthermore, all these measures of aromaticity are of similar values for the planar phosphole and planar polyphospholes, being larger than for the other five-membered heterocycles (thiophene, pyrrole).[30] P_5H, however, has been shown to be unstable against dimerization (and subsequent polymerization) by about 30 kcal/mol (HF/6-31G(d)).[143] This computational result is in agreement with experimental observations of Baudler et al.,[144] who obtained no pentaphosphole but a polymer while reacting the pentaphospholide anion with alkylhalide.

Not only the planar polyphospholes are aromatic, but the aromaticity of the nonplanar structures, which are minima on the potential energy surface, is also becoming significant with the enhancing planarity of the tricoordinate phosphorus (e.g., in triphospholes). In the MOs of the 1,2,5-triphosphole, contrary to phosphole itself, the lone pair and the π-system show considerable mixing.[125] Also, the NICS(0), NICS(0)π, and geometry aromaticity indices are getting larger with the increasing number of "**A**"-type phosphorus atoms in the ring.[30] 1-(bis(trimethylsilyl)methyl)-3,5-di-*tert*-butyl-1,2,4-triphosphole (**SBA**: 342°) has equalized bond lengths as concluded from its X-ray structure.[145] More interestingly, it forms an η^5-complex with $Cr(CO)_3$ (for the calculated structure of 1,2,4-triphosphole with $Cr(CO)_3$ see Figure 4), $Mo(CO)_3$, and $W(CO)_3$.[146] The complexation results in an increased planarity at the tricoordinate phosphorus, and the ring bond lengths are further equalized, as can be concluded from the comparison of the X-ray structures of the parent system[145] with that of the complex.[145] A further example for a ring system with significantly flattened tricoordinate phosphorus comes from Schmidpeter et al.;[133] 1-methyl-4-phenyl-3,5-diphosphonio-1,2-diphosphole has a **SBA** of 339°, leading the authors to the conclusion that the cyclic 6π-system has been preserved contrary to phospholes. The planarizing effects in this compound should be attributed to the "**A**"-type phosphorus in the ring as well as to the $-P^+Ph_3$ π-electron acceptor substituents (see section IV.B.1).

Triphospholes can even be planarized fully by using proper substituents. 1-(Bis(trimethylsilyl)methyl)-3,5-bis(trimethylsilyl)-1,2,4-triphosphole **21** (see Figure 5) was the first planar phosphole reported.[147] Its Bird aromaticity index is 84, BDSHRT 60.[147] All these values are larger than for thiophene, in agreement with the computational results obtained for the planar saddle points of the polyphosphaphospholes.[30] Apart from the weak π-acceptor trimethylsilyl groups (the planarizing effect of π-acceptors on phosphole[129] has been discussed in section IV.B.1), the bulky bis(trimethylsilyl)methyl group also has an impact on the planarity of the system. It has also been shown computationally that 1-supermesityl-1,2,4-triphosphole is planar and aromatic (NICS(0) −14.7 cf. with pyrrole −15.1, all HF/3-21G(*); Bird index 83).[148]

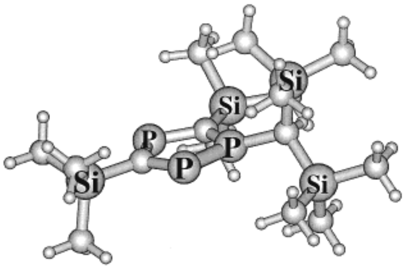
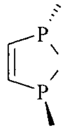


Figure 5. B3LYP/3-21G(d) structure of 1-(bistrimethylsilylmethyl)-3,5-bis-(trimethylsilyl)-1,2,4-triphosphole **21**.

A further possible aromatic five-membered ring would be the phosphorus analogue of imidazol-2-ylidene (**22**), an isomer of 1*H*-1,3-diphosphole. Schoeller[149] recently calculated the singlet−triplet gap of **22**, which was somewhat higher than that for acyclic phosphanylcarbenes. From the shortening of the PC(carbene) bonds with respect to other phosphanylcarbenes, some cyclic delocalization has been concluded.[149] **22** is not planar, although the sum of bond angles (**SBA**) about phosphorus is 333.6° (B3LYP/6-311+G(d,p)),[19] a sign of some delocalization in agreement with Schoeller's conclusion.[149]



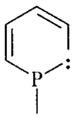
22

The NICS(0) value of −10.4 (HF/6-31G(d))[19] is also indicative of a somewhat delocalized structure for **22**. Even more interesting is that the planar form of **22**, which is a second-order transition structure, is by only 8.91 kcal/mol less stable than the minimum, despite the two tricoordinate phosphorus atoms (for the planarization of each 35 kcal/mol can be estimated). The planar **22** is highly aromatic, as can be judged from the −19.5 NICS(0) value (HF/6-31G(d)//B3LYP/6-31G(d)) and the 1.384 Å C=C distance (B3LYP/6-31G(d)), which is close to the benzene value.[19] Supermesityl rests on phosphorus atoms and is planarizing, in accordance with the expectations, resulting in **SBA** of 350.8° (B3LYP/6-31G(d)) about P and a NICS value of −15.8[19] (HF/6-31G(d)//B3LYP/6-31G(d)). It is likely that this carbene with the proper substituents will be synthesized in the future.

C. Six-Membered Rings

1. Cyclic Phosphinocarbenes

The vacant p orbital on a carbene center is an excellent π-acceptor and as such is planarizing on the tricoordinate phosphorus. The resulting phosphinocarbene unit then can be incorporated into a six-membered ring, forming a 6 π-system, phosphinine-2-ylidene (**23**). It has been shown computationally that **23** is planar,[78] has a singlet ground state, and exhibits equalized bonds (CC bond lengths vary between 1.378 and 1.419 Å at MP2/6-31G(d)). In the homodesmotic reaction (analogous to eq 6), 16.5 kcal/mol stabilization has been obtained (27.1 kcal/mol for phosphinine (**3**)).[78] **23**, however, is less stable than **3** by 74.6 kcal/mol and is unstable against dimerization by $\Delta G = -82.4$ kcal/mol (B3LYP76-311+G(2d));[150] thus, it is an unlikely synthetic target. Planarizing groups at phosphorus, however, might lower the dimerization energy, making **23** a possibly synthesizable molecule. **23**, similar to some other phosphorus compounds such as pentaphosphole P_5H, provides an example for a system which is unstable chemically despite its aromatic electronic structure.



23

Carbocations have similar electronic structures to carbenes. The P-protonated derivative of phosphinine should also be similar to **23**. Indeed, while investigating the proton affinity of **3**, the most preferred protonation site was phosphorus and not carbon, whereby the cyclic π system would be interrupted.[151]

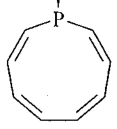
2. Cyclic Phosphinoboranes

Similar to carbenes, BH_2 groups are also good π-acceptors, due to the vacant p orbital on boron. In phosphinoboranes the inversion barrier about phosphorus is quite low (about 5 kcal/mol), and the PB bond has some double-bond character due to the π-donor bonding.[152] The phosphorus analogue of borazene can be built up from the PB units. The Power group has reported the synthesis of several B_3P_3 rings, the first one $(MesBPCy)_3$ in 1987.[153] Those six-membered PB rings substituted with organic groups at boron are planar and have equalized bond lengths. The ^{1}H NMR signals of the *o*-methyl groups of the mesityl substituents, which occupy a perpendicular position to the ring, are by 0.4−0.7 ppm shifted from those of the *p*-methyl groups[154] in agreement with a ring current effect exerted by the π-system of the B_3P_3 ring.[155] $(MesBP^tBu)_3$ was reported to form an η^6-complex with $Cr(CO)_3$.[156] Quantum chemical calculations were also carried out to estimate the aromaticity of the parent $B_3P_3H_6$.[155] The calculated structure is nonplanar in the absence of the bulky protecting groups. From the homodesmotic reaction in eq 15, 12.7 kcal/mol stabilization (HF/6-31G(d)) has been obtained (cf. with the 22.1 kcal/mol stabilization for benzene at the same level in the analogous reaction 6, X: CH).[157] The NICS(0)π value was −15.0 (cf. with −20.7 for benzene).[29] The decrease of the aromaticity of $B_3P_3H_6$ in comparison with benzene was attributed to the electronegativity difference of the heteroatoms.[157]

$$B_3P_3H_6 + 3H_2PBH_2 \rightarrow 3H_2P(H)B(H)PBH_2 \qquad (15)$$

D. Nine-Membered Rings

It has been shown that the opening of the bonding angle at the tricoordinate phosphorus is favorable for the planar structure[10] (cf. with the stabilization of the planar forms of polyphospholes, section IV.B.3). It is thus likely that with increasing ring size, tricoordinate phosphorus will be planarized. Indeed, phosphonin C_8H_9P (**24**) has a barrier to inversion of 8.9 kcal/mol (B3LYP/6-311+G(d,p)), which is much smaller than that for phosphole (18 kcal/mol at the same level of the theory).[10] The planar phosphonin (**24**) exhibits equalized bond lengths and thus should be aromatic.[158] **25**, the diboro derivative of phosphonindiyl, is planar at the B3LYP/6-311+G(d,p) level and exhibits a NICS(0) value of −15.4 (HF/6-311+G(d,p)//B3LYP/6-311+G(d,p)).[10]



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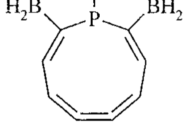
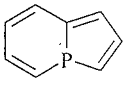


25

E. Fused Systems

Phosphindolizine (**26**), a condensed ring system with bridgehead phosphorus, has recently been investigated[81] by ab initio calculations following the synthesis of a benzoanellated (**27**).[159] **26** is not planar, but the barrier to planarity is only 3.5 kcal/mol at the B3LYP/6-311+G(d,p) level. Even the nonplanar system shows equalized bond lengths (the Bird index is 75 for the six and 66 for the five-membered ring).[81] The NICS(0)$_\pi$ value is −17.8 for the five-membered ring and −13.4 for the six-membered ring. For the planar structure, the NICS(0)$_\pi$ value is −23.5 and −19.1 for the five- and six-membered rings, respectively,[81] indicating a significant delocalization. To estimate the aromatic stabilization, the planarization barriers of **26** and **28** have been compared. The 40 kcal/mol difference in the planarization barriers is about twice the value obtained for the aromatic stabilization of the planar phosphole.[81] It has been expected by analogy to the polyphosphaphospholes[30,125] that replacing CH units by P in the five-membered ring favors the planar structure.[81] **29** was calculated to be planar and exhibited large aromaticity measures in both the six-membered and five-membered rings (e.g., NICS(0)π was −19.8 and −18.9 for the five- and six-membered rings, respectively).[81]



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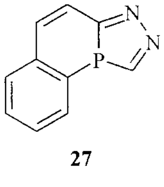

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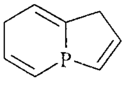

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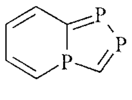

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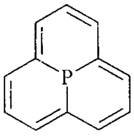
Incorporation of tricoordinate phosphorus to three delocalized systems resulted in **30**, a planar compound (B3LYP/6-311+G(d,p)) exhibiting equalized bond lengths.[10] Detailed investigation of its aromaticity is in progress.[84]



30

V. "D"-Type Bonding

A. Comparison of the Bondings in $H_3P{=}CH_2$ and $HP{=}CH_2$

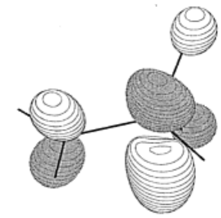
The bonding characteristics of phosphorus ylides is a matter of continuos discussion in the literature. This bonding[1h] is most frequently referred to as ylide,[160] while sometimes the ylene description is also used (Scheme 2). Some characteristics of the λ^5-P=C bond (e.g., the PC bond length, ellipticity, electron density at the critical point) are similar to those of the λ^3-P=C bond (with "**A**"-type phosphorus). The polarization of the electron distribution increases somewhat in H_3PCH_2 with respect to $HPCH_2$, however, by far less than one electron.[161] Using a simple MO scheme, the bonding characteristics in H_3PCH_2 can easily be compared to those in $HP{=}CH_2$.[161] The two hydrogens (or other substituents) on phosphorus form a 3-center-4-electron bond by using the phosphorus lone pair. From the three MOs obtained, a doubly occupied one has an appropriate symmetry to overlap with the π-orbitals. Thus, an allyl-like π-system forms in which the contribution of the central phosphorus atom is small. As a consequence, phosphorus is positively charged while the terminal centers, including the carbon atom, are getting negative.[161] The allyl-like π-type MOs of H_3PCH_2 are shown in Figure 6. The bonding characteristics of "**D**"-type phosphorus can thus be related to those of the "**A**"-type phosphorus as a double bond to an allyl system, without invoking any valence shell expansion or artificial charge separation. The rotational barrier about the PC bond is very low, since the three substituents on phosphorus provide orbitals of proper symmetry to interact with the p orbital of the $-CH_2$ group at any torsion angle (negative hyperconjugation).[162] Thus, it can be expected that the extended π-systems of "**D**"-type phosphorus can be stabilized by conjugative interactions, including aromaticity.

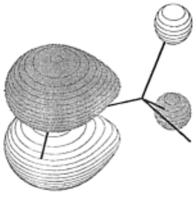
Scheme 2

$H3P^{+}\text{-}C^{-}H2$ $\quad$ $H3P{=}CH2$

B. Four-Membered Rings

The four-membered rings are generally considered to be antiaromatic according to Hückel's rule. How large is the perturbation of the antiaromaticity if a CH unit is replaced by P or PR_2 groups? The antiaromatic character of $1\lambda^3,3\lambda^3$-diphosphacyclobutadiene is well preserved with unequal bond lengths.[79,163] Diphosphacyclobutadienes themselves could only be isolated as ligands of a transition metal (e.g., **31**);[164] however, they have been considered as intermediates in many reactions resulting in cage compounds.[165]





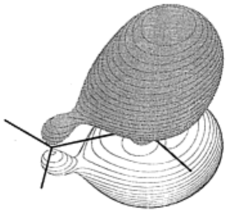
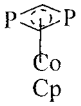
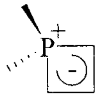


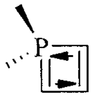
Figure 6. HF/6-31+G(d)//MP2/6-31+G(d) a"-type MOs of $H_3P{=}CH_2$ in its planar form.



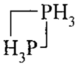
31

On the contrary, $1\lambda^5,3\lambda^5$-diphosphacyclobutadienes could be synthesized as stable species.[166] The X-ray structure of 1,1,3,3-tetrakis(dimethylamino)-$1\lambda^5,3\lambda^5$-diphosphacyclobutadiene obtained by Fluck et al.[166] exhibited equal PC bond lengths and a planar structure. The planar structure of the parent $1\lambda^5,3\lambda^5$-diphosphacyclobutadiene is slightly (by 0.4 kcal/mol at MP2/6-31G(d)) above the nonplanar minimum, where the Hs are out of plane.[79] Considering the equal bond lengths alone (Bird index, 100) and the rather short PC distance (1.736 Å at MP2/6-31G(d), similar to the PC distance in phosphinine (**3**)), high aromaticity can be surmised for these four-membered rings. This presumption was not only in contrast with the expectations, but also with other experimental results as well. By comparing the photoelectron spectra of 1,1,3,3-tetrakis(dimethylamino)-$1\lambda^5,3\lambda^5$-diphosphacyclobutadiene with that of 1,1,3,3,5,5-hexakis(dimethylamino)-$1\lambda^5,3\lambda^5,5\lambda^5$-triphosphinine,[167] a great similarity has been found which is completely unexpected if a six-membered system is compared to a four-membered one.[168] Rationalization of these observations could be given by using the island model of Dewar et al.;[169] however, that model invokes explicitly the d-orbital participation in the bonding that has been shown[111] to be of little importance according to ab initio calculations. In recent ab initio works, two different models have been used to describe the bonding. The interrupted cyclic delocalization model considers that the pentavalent phosphorus has no available p orbitals for the π-system; thus, the compounds are zwitterionic with a delocalized negative charge (see structure **32a**).[170] This model is discussed in recent reviews as well.[1h,171] (**33a** was considered as a system "escaping" from antiaromaticity.) An alternative model (represented as **32b**),[79] which is an expansion of the bonding model developed for the λ^5-P=C bond,[161] also accounts for the alternating charge distribution. The substituents at the pentavalent phosphorus of the λ^5-P=C bond form an additional π-center with two π-electrons (as discussed in section V.A), resulting in an allyl-like π-system (Figure 6) similar to that of vinylamine. As a result, the carbon center acts as a π-electron donor while the tetracoordinate phosphorus acts as a π-electron acceptor. Thus, the conjugation is of donor−acceptor type or in other words "one-way conjugation" (**32b**).[79] The electronic structure of the resulting four-membered ring, which is built up from two π-donors (carbon) and two π-acceptors (phosphorus), will be similar to the "electron delocalized-type cyclobutadienes (e.g. 1,3-diamino-cyclobutadiene—that's π-system is built up from two vinyl-amine units)".[171] This four-membered unsaturated ring has equal bond lengths and cannot be considered as an antiaromatic species. Accordingly, the homodesmotic reaction in eq 16 (X = PH$_2$) resulted in a destabilization of −10.2 kcal/mol (MP2/6-31G(d)) for the ring with pentavalent phosphorus, a value which was significantly less than for the analogue with tricoordinate phosphorus (X = P) at the same level (−40.0 kcal/mol). Obviously ring strain has a significant destabilizing effect, which was estimated at 20 kcal/mol on the basis of eq 17. Thus, the net *stabilizing* effect in the four-membered 1λ^5,3λ^5-diphosphabutadiene ring is about 10 kcal/mol.[79]


32a


32b

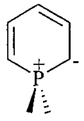
$$+ 2\ CH_2{=}XH \Rightarrow 2\ CH_2{=}X\text{-}CH{=}XH \qquad (16)$$

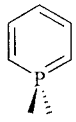


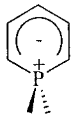
$$+ PH_3 + CH_4 \Rightarrow 4\ CH_3\text{-}PH_4 \qquad (17)$$

C. λ^5-Phosphinine (33), 1λ^5,3λ^5,5λ^5-Triphosphinine

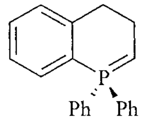
The generally accepted view about the aromaticity of λ^5-phosphinines as summarized in the recent book is that "λ^5-phosphinines are not aromatic but they clearly are highly stable substances exhibiting very little ylidic character".[1h] In accordance with the description used for the four-membered ring phosphetes and diphosphetes, the resonance structures **33a**−**c** are usually considered to describe the electronic structure.[1h]


33a

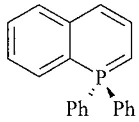

33b


33c

Märkl,[172] who synthesized **34**, has noticed that it behaves like normal ylides (reacting, e.g., in Wittig reaction). Its unsaturated counterpart **35**, however, was more stable and did not undergo the Wittig reaction. The homodesmotic reaction in eq 6 (X = PH$_2$) shows a significant 20.6 kcal/mol stabilization at the MP2/6-31G(d) level for **33**, a value which is somewhat less than obtainable from eq 6 for phosphinine (X = P) at the same level of theory (27.2 kcal/mol).[79] Also, the lengths of the bonds as well as their alternation is similar for λ^3- and λ^5-phosphinines (Table 2).[79] Bird indexes of λ^5- and λ^3-phosphinines were also reported to be similar, albeit the values for the λ^5-phosphinines are slightly smaller than for their λ^3-phosphorus-containing counterparts.[82] The low ionization energy from the photoelectron spectrum[173] was interpreted[79] by the MO model, which derives the electronic structure of **33** from that of **3** by a perturbation at the phosphorus center; thus, there is no need to consider[161] that the delocalization itself is interrupted at the phosphorus atom. (Recalling the above mentioned analogy between the λ^5-P=C bond and vinylamine, the π-systems of λ^3- and λ^5-phosphinines are related to each other as those of benzene and aniline, as it can be seen on the lowering of the corresponding ionization energies as well.) The π-MOs of λ^3- and λ^5-phosphinine are shown in Figure 7 for comparison, showing the perturbing effect of the substituting group on phosphorus while leaving the cyclic delocalization basically intact.[79]



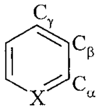
34



35

It is worth mentioning at this point that the formation of a σ^4-phosphorus from σ^2-phosphorus resulted in "σ-aromatic"[174] compounds in the case of the 1*H*-phosphirenium cation as well. Disubstitution at the phosphorus in 1*H*-phosphirenium cation (**5**) resulted in the preservation of aromaticity with proper substituents (fluorine) in **36**, as a result of the interaction with PF$_2$ σ*-orbitals,[174] as indicated by isodesmic reactions. A similar phenomenon has been observed also for 1,1-difluorocyclopropene,[175] 1,1-bissilylcyclopentadiene, and 1,1-bisstannylcyclopentadiene. In the latter case, the phenomenon has been called "hyperconjugate aromaticity".[176] The effect of

Table 2. MP2/6-31G(d) Bond Lengths (in Å) for λ^3- and λ^5-Phosphinine[79]

 	PC	C$_\alpha$C$_\beta$	C$_\beta$C$_\gamma$
X = P	1.739	1.393	1.396
X = PH$_2$	1.732	1.390	1.395

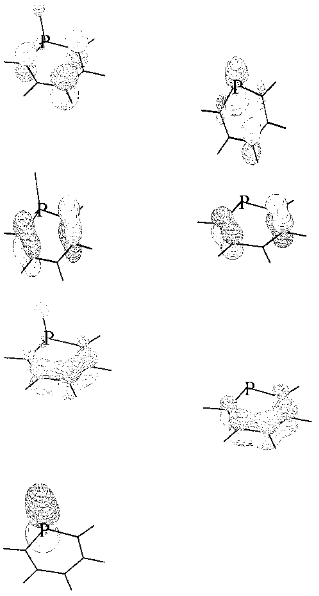


Figure 7. HF/6-31+G(d)//MP2/6-31+G(d) occupied π-MOs of λ^3- and λ^5-phosphinine.

difluoro substitution on the phosphorus of λ^5-phosphinines (**33**) is to increase the aromaticity.[177]

36

$1\lambda^5,3\lambda^5,5\lambda^5$-Triphosphinines were also investigated. In the homodesmotic reaction in eq 10 ($X = PH_2$), 21.8 kcal/mol stabilization has been obtained at the MP2/6-31G(d) level (cf. with the 26.0 kcal/mol value for $1\lambda^3,3\lambda^3,5\lambda^3$-triphosphinine at the same level of the theory).[79] This stabilization is in agreement with the cyclic delocalization stabilization resulting from donor−acceptor-type interactions discussed in section V.B.[79] The 1.707 Å bond length (MP2/6-31G(d)) is somewhat shorter than that for the λ^3- analogue. However, the calculated structure is not entirely planar;[79] the hydrogens on the carbon atoms move somewhat out from the plane. The X-ray structure of the heavily substituted 1,1,3,3,5,5-hexakis(dimethylamino)-$1\lambda^5,3\lambda^5,5\lambda^5$-triphosphinine was planar.[167] In all cases the PC bond lengths were equal and in the range of the aromatic PC bonds (1.687 Å from the X-ray structure).[167] It is worth noting that no NICS data has been reported for λ^5-phosphinines as yet.

VI. Outlook

Carbon and nitrogen are the most common elements from the first row of the periodic table to form aromatic compounds, characterized by cyclic electron delocalization. The bonding of these elements in the conjugated systems shows a large variety. Carbon can be a divalent (carbene),[68] sp^2 carbon with one π-electron, but also sp^3 carbon can be part of hyperconjugate aromatic systems, provided that it is properly substituted.[176] The pyrrole- and pyridine-type nitrogens also allow the formation of cyclic electron delocalization in a large variety of aromatic systems.

Among the second-row elements, phosphorus, which is below nitrogen and has a diagonal relationship to carbon, has a similarly important role. Phosphorus is able to be a building block of cyclic conjugated systems in several bonding environments either in σ^2-, λ^3- (with planarized phosphorus), or σ^4 form ("**A**"-, "**B**"-, or "**C**"-type or "**D**"-type bonding, respectively). While the electronic structure of these phosphorus systems shows high aromaticity and the stabilization energy with respect to the unsaturated analogues is also large, the overall stability of some of these phosphaaromatics is much lower than that of the carbon-containing systems.

The reason for this behavior in the case of the double-bonded structures ("**A**"-type phosphorus) is the easy dimerization of the P═C bond. Tricoordinate planar (or nearly planar) phosphorus ("**B**"- and "**C**"-type bonding) can be stabilized by repyramidalization when the cyclic electron delocalization is disturbed or lost (e.g., in a chemical reaction). The fine balance between these energetic effects cannot easily be predicted by using analogies or other simple models. Such predictions, however, can be made by using the sophisticated methods of computational chemistry, leaving the field of the chemistry of the aromatic phosphorus compounds an interesting research area with unexpected results in the future.

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