

Aromatic Compounds with Planar Tricoordinate Phosphorus

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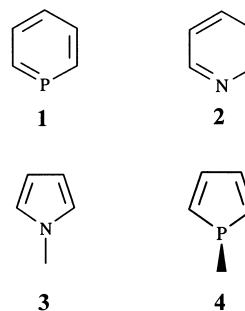
Dedicated to Prof. E. Niecke on the occasion of his 60th birthday

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Abstract—Tricoordinate phosphorus can be planarized, and used as an excellent building block of aromatic compounds. The pyramidality can be reduced by (i) σ donor and π acceptor groups; (ii) steric strain, which increases the bonding angle about phosphorus; (iii) bulky substituent groups; and (iv) delocalization or aromatic stabilization effects. The aromaticity of π systems with planar tricoordinate phosphorus is largest among those rings containing nitrogen or chalcogen heteroatoms. For the flat systems the aromatic stabilization is just compensated by the energy cost of the planarization at phosphorus. Due to this counterbalancing effect a very rich chemistry can be expected for these compounds. © 1999 Elsevier Science Ltd. All rights reserved.

Introduction

Phosphorus in aromatic compounds is dicoordinate (σ^2, λ^3 -phosphorus).¹ Its conjugative ability was shown to be comparable to that of carbon,² and the aromaticity of phosphinine (**1**) is comparable to that of pyridine (**2**) or benzene.³ Tricoordinate (σ^3, λ^3 -) phosphorus is pyramidal, (the barrier to planarization is 35 kcal/mol in case of phosphine PH_3),⁵ thus the lone pair cannot interact with a neighbouring π system. Consequently, while the aromaticity of pyrrole (**3**) is among the largest of the five membered rings, phosphole (**4**) is hardly aromatic at all.⁶ If the tricoordinate phosphorus were planarized, a significant π donor effect would be expected.^{7,8} (According to Schleyer the π donor ability of planar tricoordinate phosphorus rivals that of nitrogen.)⁸ The formation of an aromatic π system was also postulated with planar tricoordinate phosphorus.^{9,10} Recently some new species with planar or nearly planar tricoordinate phosphorus have appeared in the literature. All of these systems were shown to have a high degree of cyclic delocalization according to different aromaticity indices. Some of these structures were predicted computationally, while others could be synthesized. The aim of the present work is to analyse what kind of effects can be used to decrease the pyramidality at the tricoordinate phosphorus, resulting in systems with cyclic electron delocalization. Also, the impact of aromaticity on the chemistry of these systems will be discussed.



Results and Discussion

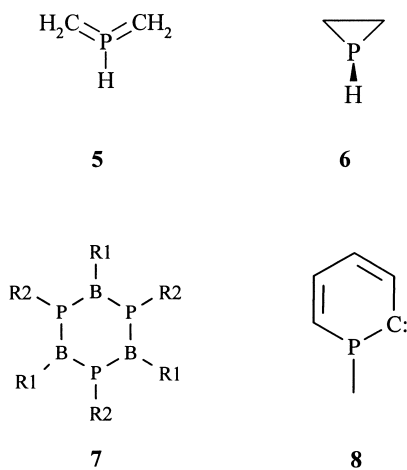
Acyclic compounds with planar tricoordinate phosphorus

The inversion barrier at the tricoordinate phosphorus can obviously be reduced by using bulky substituents. Such effects, however, are more important for cyclic systems, where two bonding directions are somewhat fixed, and will be considered later. It has been discussed by Levin¹¹ that electron donor (σ donor) groups have a planarizing effect on pyramidal systems such as PH_3 . Ab initio calculations show that three PH_3 substituents reduce the inversion barrier of phosphine to 16 kcal/mol.¹² π -Acceptor substituents also play an important role, and are the most effective planarizing groups. Some planar or nearly planar systems with tricoordinate phosphorus (σ^3, λ^3 -phosphorus) are known from the literature. According to ab initio calculations H_2PCH_2^+ ⁸ and H_2PCH^+ ¹³ are planar species. The barrier to planarization in H_2PSiH is 0.4 kcal/mol.⁷ The inversion barrier in boro-phosphines¹⁴ is about 5 kcal/mol¹⁵ and it

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shows a gradual decrease with increasing number of BH₂ groups. At the HF/6-31G* level (BH₂)₃P is planar,¹⁶ however, the MP2/6-31+G* structure is pyramidal.¹² Nevertheless, even in the non-planar H₂BPH₂ the bond order was 1.35.¹⁴ Also the HOMO was not a pure phosphorus lone pair, but it had a significant contribution on boron as well. For (Mes₂B)₂PPh a planar X-ray structure was reported by Power.¹⁵ Bis-methylene-phosphorane (**5**) type compounds (X=P(H)=Y; X: CH₂, NH, PH, O, S, Se and Y: CH₂, NH, PH, O, S, Se) also contain planar tricoordinate phosphorus (which is often classified as σ³,λ⁵-phosphorus).¹ Their electronic structure—discussed in detail by Schoeller¹⁷—was shown to be similar to that of the allyl anion,¹⁷ and as an important characteristic the phosphorus lone pair was shown to be delocalized over the three centres.¹⁸ Due to the allylic structure the terminal atoms have negative, while the central phosphorus a positive, partial charge, and as a result phosphorus serves as a π electron donor. There is no need to invoke d orbitals to describe the bonding here. These systems are often prone to isomerize to a three membered cycle (bis-methylene-phosphorane (**5**)→phosphirane (**6**)) where phosphorus is pyramidal.¹⁷ As is seen from the above examples, the most effective planarization of the tricoordinate phosphorus can be achieved by using π electron acceptor substituents. Further stabilizing effect can be expected by cyclic electron delocalization.



Cyclic compounds with planarized tricoordinate phosphorus. The first known cyclic compounds with planar tricoordinate phosphorus were the six membered cyclic boro-phosphines (**7**), synthesized in the Power group (R1: Mesityl; R2: Phenyl).¹⁹ **7** is planar according to the calculations even with R1=R2: H.²⁰ The aromaticity of **7** (R1=R2: H) was shown to be about 60–70% that of benzene by different research groups, using homodesmotic reaction energies^{20a,b} and 80% (–8.7 ppm) according to the NICS aromaticity criterion.^{20c} The six membered phosphinocarbene ring (**8**)²¹ was also shown computationally as a planar minimum on the potential energy hypersurface. It is, however, by 57 kcal/mol less stable than its isomer (**1**), and is not stable against dimerization. The aromatic stabilization according to a homodesmotic reaction energy was 60% that of benzene.²¹

While the planarization of the tricoordinate phosphorus was aided both in **7** and in **8** by the π electron acceptor groups,

Table 1. Different aromaticity measures²² for pyrrole and phosphole (the calculations²³ were carried out at the B3LYP/6-311+G** level. See also Ref. 18)

	NICS ²²	BI ²²	BDSHRT ²²	SHE ²²
4	–5.0	46	50	0.0
3	–14.7	55	55	8.1
4pl	–17.4	87	64	26.0

phosphole (**4**)—which could be the prototype of an aromatic system with tricoordinate phosphorus—is non-planar, and consequently was shown to have low aromaticity according to various aromaticity indices.²² In contrast, the planar form—**4pl** a first order saddle point—is highly aromatic (Table 1).^{6,8} While all aromaticity measures of phosphole are significantly smaller than those for pyrrole, the planar phosphole is even more aromatic than pyrrole. The phosphorus inversion barrier—as a consequence of the aromatic stabilization in the planar form, as was first noted by Mislow⁹—is 18 kcal/mol at the B3LYP/6-311+G** level,¹⁸ significantly smaller than for phosphine.

The obvious question is, if there is any possibility of further reducing the pyramidalicity at the tricoordinate phosphorus of **4**, by applying proper substituents. The idea of using π electron acceptor groups at the different ring atoms proved to be fruitful again, and the inversion barrier at the phosphorus atom of **4** has been considerably decreased by using BH₂ groups.^{10b} With the boro group attached to phosphorus the barrier has decreased to 1.5 kcal/mol. BH₂ groups at the α carbon atoms were less effective than at the 1 position, nevertheless, they caused a reduction of the inversion barrier from 18 kcal/mol in **4** to 8 kcal/mol in case of C₄H₇B₂P. The SiH₃ substituent has a smaller effect than boron. The inversion barrier of 2,5-disilylphosphole is 14 kcal/mol. The electron acceptor PPh₃⁺ group has been shown (first by Schmidpeter) to planarize phospholes as well.²⁴

Quin and Keglevich have used a quite different approach, by using sterically demanding groups attached at the phosphorus atom.²⁵ As a result of the increasing steric bulk, the bond angle sum about phosphorus increases from 290 to 330°.²⁶ The aromaticity indices also show a continuous increase with the bond angle sum.²⁶ The phosphorus lone pair ionization energy of 1-(4,6-ditertiary-butyl-tolyl)-3-methyl-phosphole measured by photoelectron spectroscopy was larger than that of the corresponding phospholane (the saturated analogue of phosphole).^{25c} This increase of the lone pair ionization energy is typical for other five membered heterocycles (furan-tellurophene), and indicates aromatic stabilization.^{25c} Such an effect has never been observed in the spectra of phospholes substituted by less bulky groups. 1-(2,4,6-Tri-tertiary-butyl-phenyl)-3-methyl-phosphole even undergoes electrophilic substitution.^{25d}

Not only the substituents can be varied on the phosphole ring, but also the CH groups can be replaced by other moieties. While the CH to N exchange has only a small effect,^{10b} the replacement of CH groups by P has a significant impact on the planarity and aromaticity of the rings.^{18,27} The bond inversion barrier about the tricoordinate phosphorus shows a gradual decrease^{18,27a} while the bond angle sum

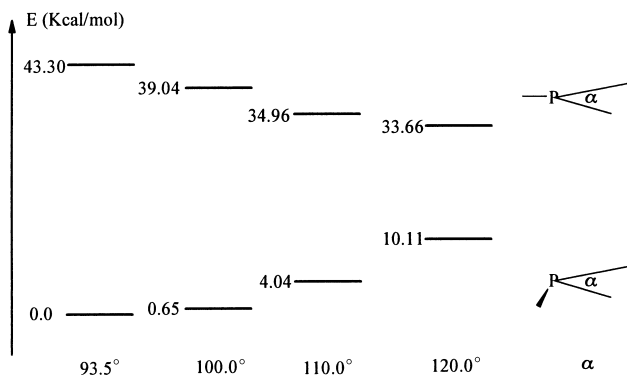
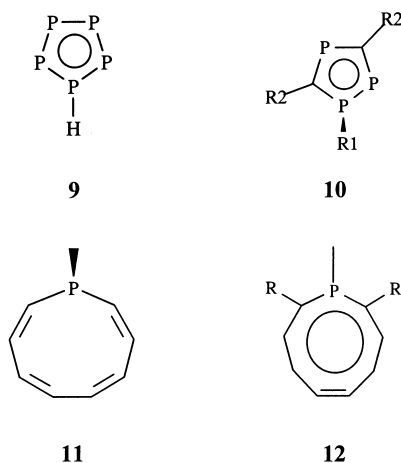


Figure 1. B3LYP/6-311+G** relative energies of phosphine calculated with fixed HPH angles (α) in planar and non-planar form.

about the tricoordinate phosphorus increases¹⁷ with the increasing number of the dicoordinate phosphorus built into the ring. Pentaphosphole P_5H (**9**) is a planar species.^{12,18,27^b,28} However, its dimer is more stable than two monomers by 35 kcal/mol.^{27^b} Since there is no possibility of using bulky groups to prevent dimerization (and any subsequent polymerization), it is unlikely that pentaphosphole could be synthesized.²⁹ Di-^{24c} and triphospholes,^{30,31} however, are known. 1,2,4-triphospholes—synthesized first by the Nixon group³⁰—(**10**) have been extensively investigated.



While the bond angle sum about the tricoordinate phosphorus in 1-bis(trimethylsilyl)-methyl-3,5-di-tertiary-butyl-1,2,4-triphosphole is 342°,³⁰ 1-bis(trimethylsilyl)-methyl-3,5-bis-trimethylsilyl-1,2,4-triphosphole is the first planar phosphole reported.³¹ However, even the non-planar 1-bis(trimethylsilyl)-methyl-3,5-di-tertiary-butyl-1,2,4-triphosphole has formed an η^5 complex with $Cr(CO)_3$, $Mo(CO)_3$ and $W(CO)_3$.³² Such a complexation mode is characteristic for aromatic compounds only.³³ Also, the aromaticity indices of the polyphosphaphospholes¹⁸ as well as those of the phospholes²⁶ were shown to increase gradually with the increasing bond angle sum at the tricoordinate phosphorus atom. Thus, aromaticity and aromatic chemical behaviour is possible even in the case of non-planar species (note also the S_N reactivity of the supermesityl-phosphole—as discussed above). It seems that at a bond angle sum of about 330–340° the interaction between the phosphorus lone pair and the system is getting large enough to provide a significant stabilization and thus exert

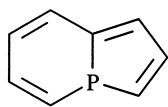
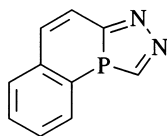
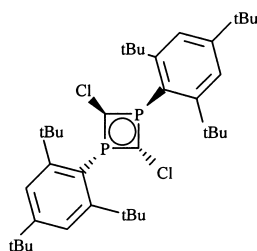
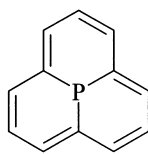
an influence on the chemistry too. The aromaticity measures for the planar phospholes (irrespective of whether they were minima or saddle points on the potential energy hypersurface) were of similar values to those for the planar form of phosphole **4pl**. These values were the largest among the five membered heteroaromatic systems.¹⁸ Undoubtedly, aromaticity plays an important role when stabilizing the planar form of phospholes.

In analysing the factors reducing the pyramidity about the tricoordinate phosphorus of polyphosphaphospholes, two effects were considered. One of these is the influence of electron donor groups which is known to decrease the inversion barrier of phosphine or related pyramidal species.^{11,12} A different explanation was that the dicoordinate (σ^2, λ^3) phosphorus has a small bond angle (ca. 95°) compared to the sp^2 carbon (120°).^{27^a} As a consequence, the bond angle at the tricoordinate phosphorus should open up as the number of dicoordinate phosphorus in the ring increases. The increasing bond angle results in a decrease of the inversion barrier. From calculating the relative energies of PH_3 (at the B3LYP6-311+G** level) with one fixed HPH angle both in the planar and the non-planar forms Fig. 1 has been obtained. The opening of one HPH bonding angle from about 95 to 120° results in a decrease of the inversion barrier by up to 20 kcal/mol. Comparing this value with the 18 kcal/mol inversion barrier of phosphole (and taking into account the electron donor effect of phosphorus) the planarity of pentaphosphole is understandable.

Since bond angles are opened up in large rings, we have investigated the planarity of the nine membered ring **11**, which is the next neutral Hückel aromatic ring after phosphole (**4**). **11** is not-planar, but the inversion barrier is only 8.9 kcal/mol (cf. with the 18 kcal/mol in case of phosphole). Introduction of a triple bond into the ring increases the strain further, and gives **12** (R:H), which has an inversion barrier of 1.9 kcal/mol only. The NICS value of **12** (R: H) at the ring centre is -15.4 ppm.³⁴

Since aromaticity definitely plays a role in the stabilization of the planar rings, it is likely that this effect will increase by placing the tricoordinate phosphorus in two rings simultaneously. Phosphaindolizine (**13**) is such a compound, with an inversion barrier of only 3.5 kcal/mol, according to B3LYP/6-311+G** calculations.³⁵ A derivative of phosphindolizine has been synthesized in the Regitz group (**14**),

its chemistry will be explored.³⁵ All the aromaticity measures again indicated sizeable cyclic delocalization even in the non-planar form. The aromatic stabilization itself was estimated by comparing the inversion barrier of **13** with that of its least possible saturated derivative.³⁵ This energy difference was 40 kcal/mol,³⁵ twice as much as in the case of phosphole (**4**), in good agreement with the aromatic stabilizations in two rings.

**13****14****15****16**

15, a peculiar 6π electron compound which has been synthesized in the Niecke group, has a bond angle sum at the tricoordinate phosphorus of 337.9° .³⁶ It has been shown by the calculations of Schoeller³⁶ that aromaticity plays a role in this system, while the flattening effect of the supermesityl groups should apparently also be important.³⁷

In all the above examples the participation of the phosphorus lone pair in aromatic systems was clearly shown. The stabilization accompanied with the formation of the cyclic conjugated system is the largest among the common heteroatoms bearing lone pairs (N, S, O).

Combined planarizing effects

The (a) influence of the π acceptor substituents, (b) different steric strain effects and (c) conjugative/aromatic stabilization of the planar structure can be combined, and these effects turned out to be additive. In case of 1-bis(trimethylsilyl)-methyl-3,5-bis-trimethylsilyl-1,2,4-triphosphole the impact of all these combined effects was shown to be important for the planarization of the tricoordinate phosphorus. The comparison of the non-planar *t*Bu³⁰ and the planar SiMe₃³¹ substituted systems clearly shows the influence of the weak π acceptor silyl substituent. It was also shown computationally that with the bis-silyl-methyl substituent in the 1 position the 3,5-disilyl substituted 1,2,4-triphosphole is non-planar, indicating the importance of the bulkiness of the trimethylsilyl groups on the phosphorus substituent.

The combination of the above effects results in several possibilities for the prediction of systems with planar tricoordinate phosphorus. These ideas were checked computationally, and the following systems were obtained as stable minima on the potential energy hypersurface:

In **16**, aromatic stabilization can be achieved in three rings. This compound was shown to be flat according to our preliminary calculations.³⁸ 1-(2,4,6-Tri-tertiary-butyl-phenyl)-3,5-di-tertiary-butyl-1,2,4-triphosphole was shown to be planar, computationally.³⁹ The nine membered ring **12**, substituted with the π acceptor R:BH₂ groups, is planar.⁴⁰ Substituting two CH groups of the five membered ring part of phosphindolizine by P units also results in a flat ring system.³⁵ Thus the combination of the effects planarizing the tricoordinate phosphorus is effective.

Concluding remark

It is shown that rather large aromatic stabilization can be achieved in the case of compounds containing tricoordinate planar phosphorus. The obvious question is, how large an impact does this aromaticity have on the chemical reactivity of these compounds. Aromatic systems are generally considered as inert in chemical reactions due to their inherent stabilization which is a consequence of their electronic structure. On the basis of their rather large aromaticity, compounds with planar tricoordinate phosphorus are expected not to be reactive. However, this is not always the case. 1,2,4-Triphosphole, for example, has been shown to rearrange at room temperature (under the influence of light) to its isomer, 1,3,5-triphosphabicyclo[2,1,0]pent-2-ene.⁴¹ The reason for this instability is the energy cost of the planarization of the tricoordinate phosphorus that counterbalances the stabilization achieved by aromaticity. If—as a result of a chemical reaction—a non-planar tricoordinate phosphorus can form, energy can be gained during the repyramidalization. Thus, although aromaticity stabilizes the planar structures, repyramidalization (if possible) stabilizes the non-aromatic products. As a result of these counteracting effects the chemistry of systems with planar, aromatic tricoordinate phosphorus should be very rich and can give unforeseeable results.

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