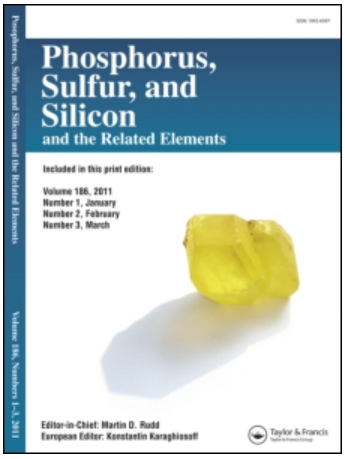

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHETIC ROUTES TO FIVE-MEMBERED AROMATIC PHOSPHORUS HETEROCYCLES

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To cite this Article Schmidpeter, Alfred(1986) 'SYNTHETIC ROUTES TO FIVE-MEMBERED AROMATIC PHOSPHORUS HETEROCYCLES', Phosphorus, Sulfur, and Silicon and the Related Elements, 28: 1, 71 — 89
To link to this Article: DOI: 10.1080/03086648608072799
URL: http://dx.doi.org/10.1080/03086648608072799

Phosphorus and Sulfur, 1986, Vol. 28, pp. 71–89
0308-664X/86/2802–0071/$20.00/0

SYNTHETIC ROUTES TO FIVE-MEMBERED AROMATIC PHOSPHORUS HETEROCYCLES

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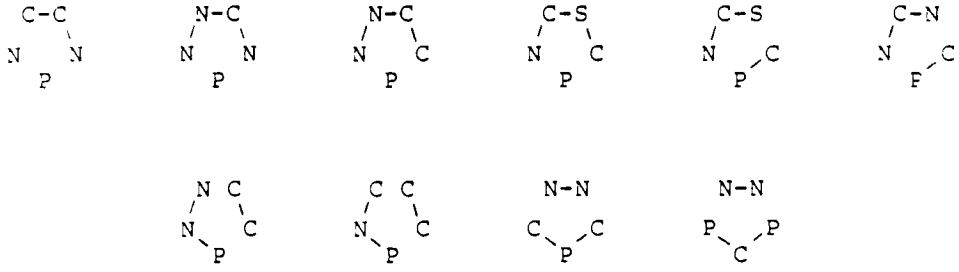
Only late in the development of heterocycles, phosphorus has been recognized as an effective member of aromatic systems. Here, the two-coordinate phosphorus participates much better in cyclic delocalization than the three-coordinate phosphorus. It contributes one electron to the π-system. To constitute a five-membered 6π phosphorus heterocycle, along with N-, CR-, and eventually more P-members, it thus takes one NR- (or S-) member contributing two electrons. This gives rise to the azaphospholes and thiazaphospholes. Since the first representatives were found in 1970 by Melnikov and Shvetsov-Shilovskii in Moscow, the number of known systems has grown to eight including those with annelated rings. They were prepared primarily in the laboratories of Barrans, Malavaud and Majoral in Toulouse, Issleib in Halle, and our own. We can now present ten more new mono- and bicyclic systems.

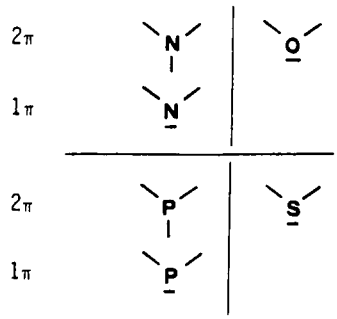
A review is given of the synthetic routes we employed and investigated. They comprise cyclocondensations and cycloadditions and are shown here schematically:



Also, an outline of the chemical behavior of azaphospholes is given, mostly using 1,2,3-diazaphospholes as an example.

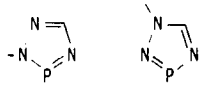
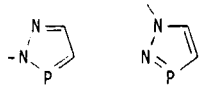
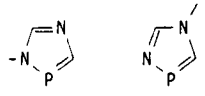
There must be something specific to ring systems that makes us distinguish them from acyclic chemistry. This seems justified where the individual atom as a ring member is so definitely integrated into the cyclic system that it gives up its usual reactivity and that the observed reactions are more characteristic of the ring and not so much of its individual members. The azaphospholes provide good examples of such a full integration of two-coordinate tervalent phosphorus into the five-membered aromatic ring system.

To participate in a 6π ring system, the heteromember must be trigonal planar like the nitrogen in pyrrole or dicoordinate like the nitrogen in pyridine or the oxygen and sulfur in furan and thiophene. Compared to nitrogen and sulfur, phosphorus, which shares the same group with nitrogen and the period with sulfur, is much less known for participating in aromatic heterocycles and in fact it was scarcely 20 years ago that phosphorus was first recognized at all as an effective member in such systems.



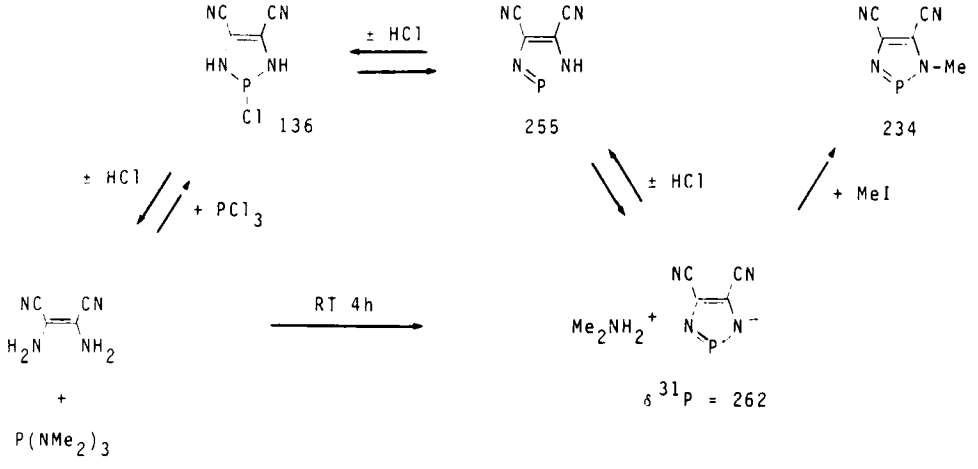
The phospholes, which contain three-coordinate phosphorus and which are analogous to pyrrole, proved much less aromatic than expected, ranging not between pyrrole and thiophene, but only beyond furan. The simple and obvious reason is that three-coordinate phosphorus less easily becomes planar than three-coordinate nitrogen.

Two-coordinate phosphorus on the other hand—as has first been shown in the phosphabenzenes—integrates quite well into 6π systems. It contributes one electron to the system and, to constitute a five-membered 6π heterocycle, it thus takes along with the phosphorus a nitrogen or sulfur member, giving rise to the azaphospholes, thiaphospholes, and thiazaphospholes.[1] I shall try to give you a review of their preparation and their behavior at least as far as we carried out or modified the synthesis.

1981		1,3,2-diazaphospholes	P is introduced by condensation
1976		1,2,4,3-triazaphospholes	
1967 1979		1,2,3-diazaphospholes	
1983		1,3,4-thiazaphospholes	
1984		1,3,4-diazaphospholes	PC is introduced by condensation
1984		1,2-azaphospholes	CC is introduced by cycloaddition
1984		1,2,4-diazaphospholes	
1984		1,2,3,5-diazadiphospholes	NN is introduced by condensation

This is the list of systems I am going to discuss. The somewhat random-looking order has to do with the different synthetic routes. Some of the systems—as the 1,2,3-diazaphospholes first mentioned by Melnikov and Shvetsov-Shilovskii in 1967—are quite old and have been comparatively well investigated in the meantime; some others are very recent. In such cases I may not be able to tell you much more than that the compound exists.

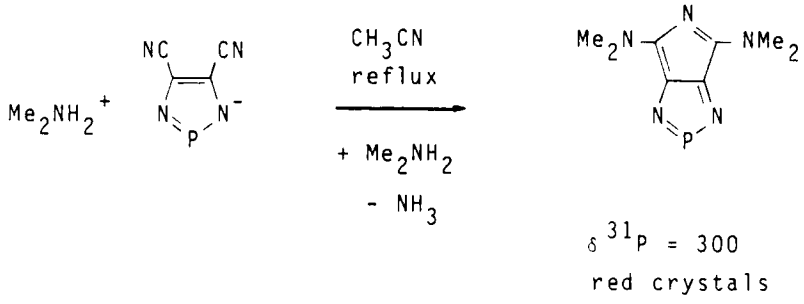
An obvious way to prepare the desired ring systems and in fact the most effective way so far, is to condense tervalent phosphorus—phosphorus trichloride or sometimes better a phosphorus trisamide—to a four-membered chain with e.g. amino end groups. To prepare 1,3,2-diazaphospholes it would take an enediamine.



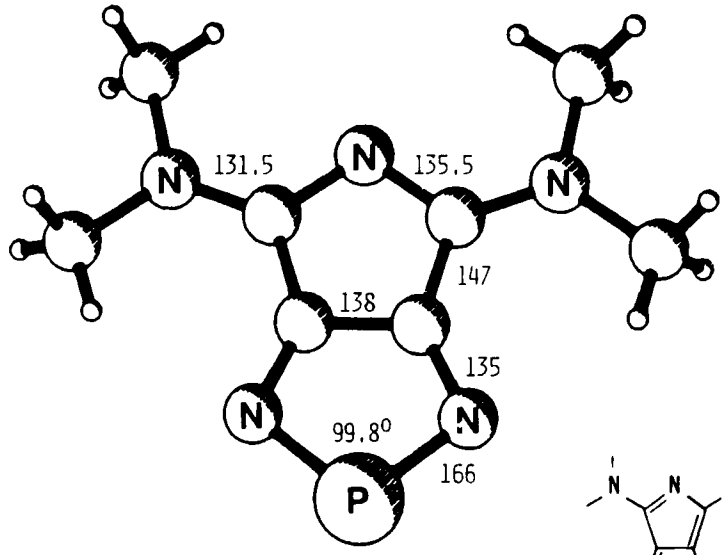
Diaminomaleonitrile provides a good example. At room temperature it reacts with tris(dimethylamino)phosphine to give a crystalline colorless product which proves to be the dimethylammonium salt of the dicyano-diazaphosphole anion.[2] We might of course write formulas with some other electron distribution for the anion, e.g. with the negative charge on the phosphorus. But when it comes to methylation or protonation, we find the methyl group and the proton always at the nitrogen, never at the phosphorus. In comparable acyclic systems clearly the opposite would be true. This demonstrates nicely the interdependency of phosphorus two-coordination and its ability to take part in the aromatic system. The typical behavior of tervalent phosphorus is thus strongly modified by the cyclic system.

That the phosphorus has remained two-coordinate in the neutral derivatives is immediately shown by its characteristic low field chemical shift. More hydrogen chloride adds to the PN bond and the now three-coordinate phosphorus gives a signal more than 100 ppm upfield. This addition of a polar partner to the PN (or PC) double bond is of course expected and constitutes the main reactivity of the azaphospholes. What is remarkable is the ease with which this addition is reversed to reform the aromatic system. Excess HCl finally splits the phosphorus from the diamine. Boiling it with phosphorus trichloride for 12 h in acetonitrile gives the ring again.

At higher temperatures and longer reaction times, the yield of the diazaphosphole salt decreases.



A bicyclic diazaphosphole—a phosphapentalene—is formed instead, obtained in deep red crystals.[3] It is somewhat surprising that an 8π antiaromatic system forms under rough conditions. Certainly the amino groups help to stabilize the system.



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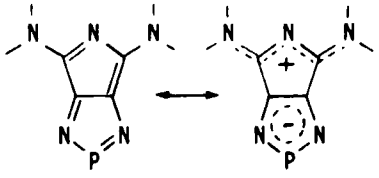
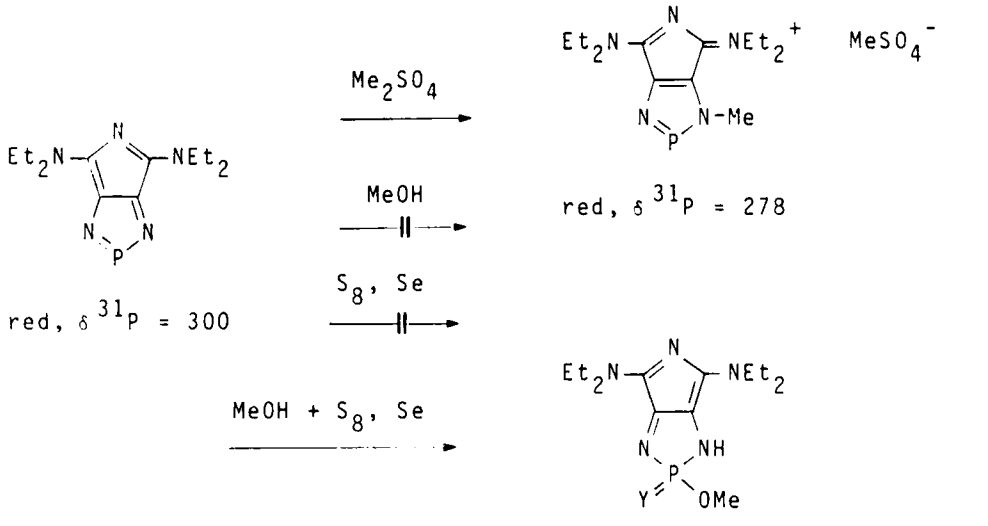
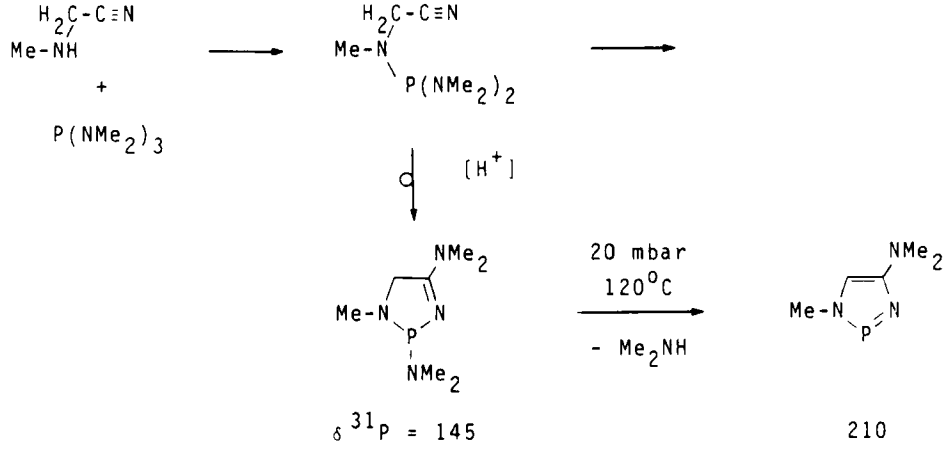


This is well demonstrated by the molecular structure. Its most important features are the CC bonds of 147 pm length. They indicate that the molecule in fact consists of two conjugated systems, the cationic azaallylic part and the anionic diazaphosphole part.



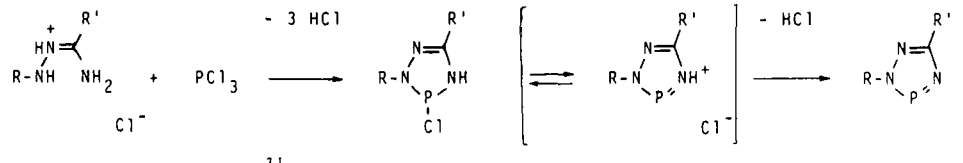
Methylation consequently occurs at the azaphosphole nitrogen. Methanol does not add to the PN double bond and sulfur or selenium does not oxidize the phosphorus. Together, however, they add easily and completely. Presumably methanol gives an adduct concentration too small to be detected, but sufficient to give a normal phosphine reaction with the chalcogen. This synergetic combination of 1,2-addition and oxidation is frequently found in azaphosphole chemistry.



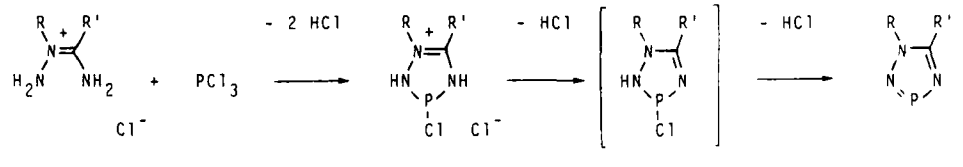
As enediamines are rare, the synthesis shown can not be made a general one. The nitriles of α-amino acids (sarcosine nitrile in this case) also provide a four-membered unsaturated chain with two nitrogen ends. Its initial reaction with phosphorus

trisamide will be a transamination. Further steps lead to a variety of products unless a rearrangement of the primary product is induced by acid catalysis. It involves an intramolecular PN addition to the CN triple bond and gives a dihydrodiazaphosphole. Heating it under reduced pressure causes a 1,4-elimination of dimethylamine and gives the diazaphosphole as a light yellow liquid. Unfortunately, the synthesis could not be made more general because in the case of other aminonitriles the cyclization does not compete effectively enough with alternative reactions.

Of the triazaphospholes three isomeric forms may be distinguished, depending on the position of the *N*-substituent. The 1- and 2-isomers are known.



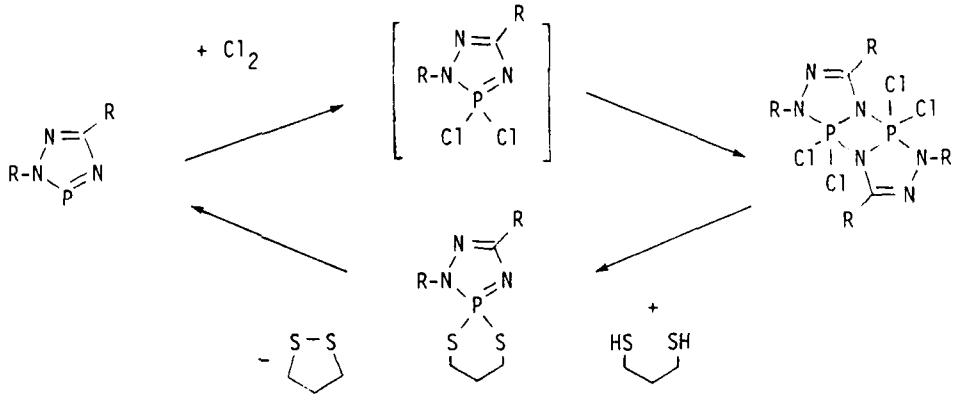
$\delta^{31}P$, R'= Ph: 154 254



$\delta^{31}P$, R'= Me: 107 257

Amidrazones or better their hydrochlorides provide the necessary four-membered chain.[4] They condense readily with phosphorus trichloride to give the chloro-dihydrotriazaphospholes or their hydrochlorides, from which a tertiary amine takes the last HCl to give the triazaphosphole.

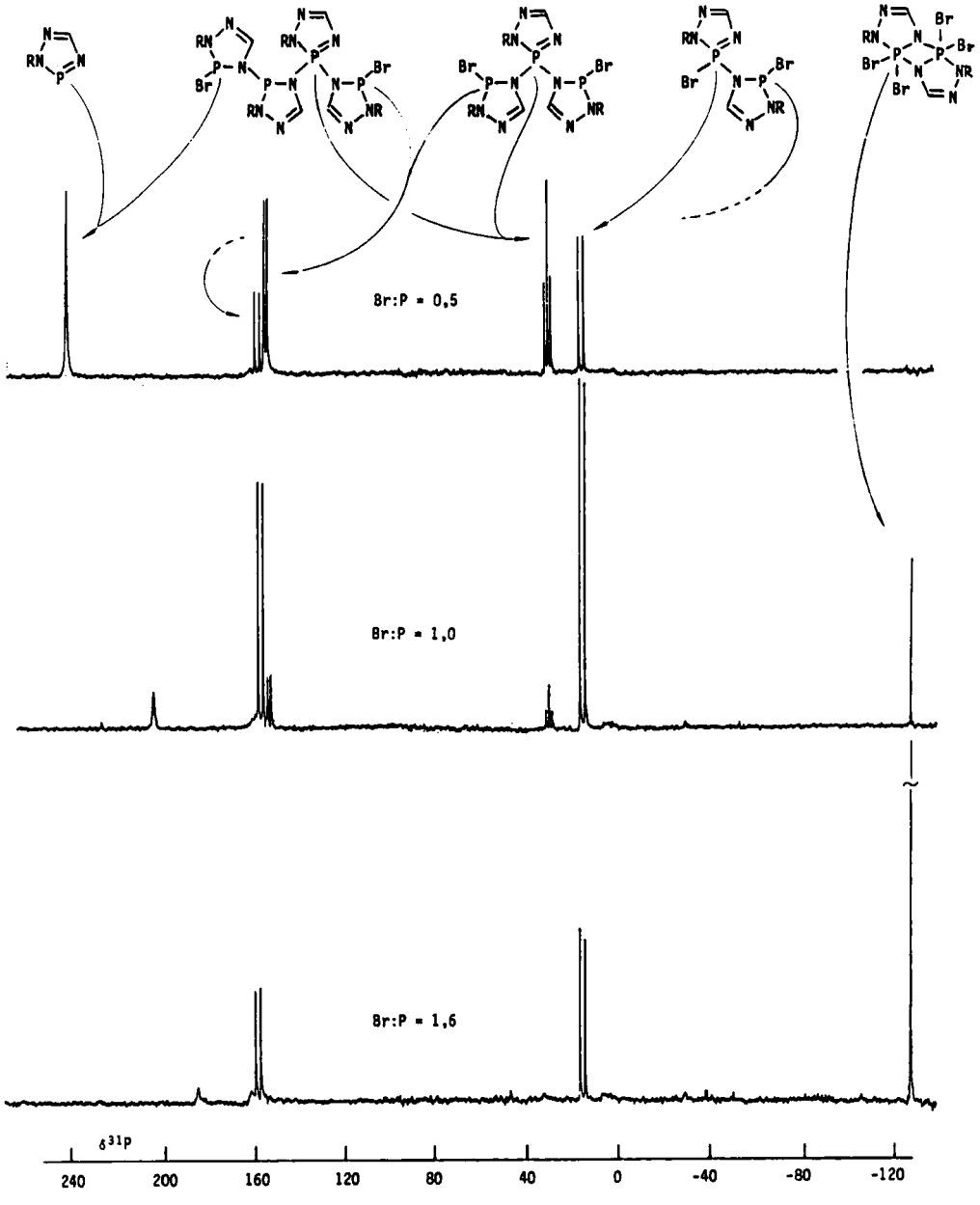
As in the diazaphospholes—and as is true in all the aromatic phosphorus heterocycles—the tervalent phosphorus here again has lost most of its otherwise characteristic reactivity against electrophiles and oxidants. It will not methylate and will not take up sulfur to form a sulfide. In the case of the triazaphospholes it may at least be halogenated.

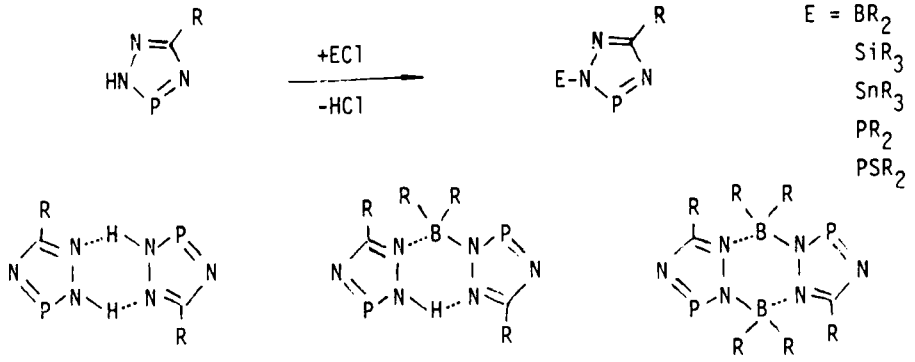


$\delta^{31}P$ 253 83 - 63 (Me, Ph)

With chlorine a 1 : 1 product is obtained. It proves to be the dimer of the expected dichloride.[5] Substituting the chlorine with a dithiol results in a spontaneous reductive disulfide elimination and leads back to the triazaphosphole. This is the first reductive elimination from tetracoordinate phosphorus reported!

Consistent with the low reductive power of the triazaphosphole, iodine gives no stable adduct but bromine does and it shows how complex in detail such a simple looking reaction may be. There are at least four products with a different bromine : phosphorus ratio which may be detected in ^{31}P-NMR.

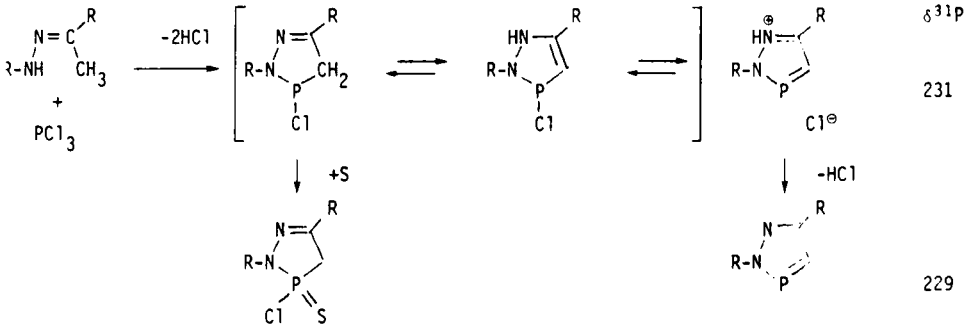




The N-unsubstituted triazaphosphole (R = NMe_2) again demonstrates the persistence of phosphorus two-coordination:[6] the hydrogen and all the substituents introduced in its place bond to the nitrogen, none to the phosphorus—as contrasted with acyclic aminophosphines, which typically react at the phosphorus. Whereas the parent compound, obviously due to hydrogen bonding, is a glassy, though volatile material, the substitution products generally are mobile liquids.

The boryl derivatives are crystalline solids. They are dimeric with four-coordinate boron. Nitrogen only, not phosphorus, is involved in the coordination. A corresponding oligomeric hydrogen-bonded structure might describe the parent compound also. Consequently also a half-borylated triazaphosphole can be prepared. All this behavior resembles very much that of pyrazoles and triazoles. Especially the last mentioned compound is a perfect analogue to the pyrazolylborate which has become famous as a chelating ligand.

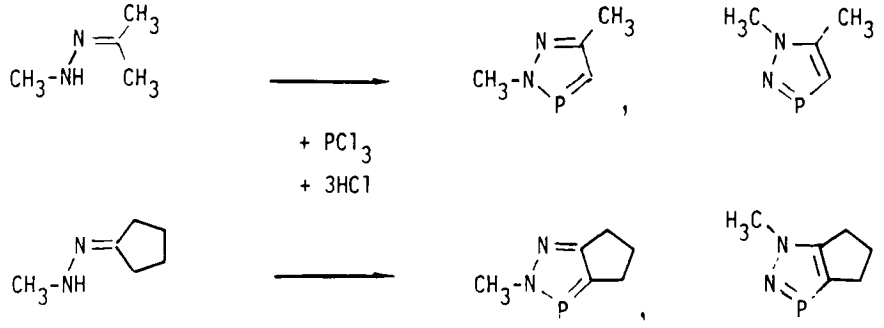
Two isomers are again feasible for the 1,2,3-diazaphosphole.



The dimethyldiazaphosphole can be prepared simply from acetone methylhydrazone and phosphorus trichloride. The hydrogen chloride comes off just by boiling in benzene. In boiling methylene chloride only two HCl are lost. The intermediate is a crystalline, sublimable substance and we should of course expect for it this cyclic chlorophosphine structure or its enamine form. Instead it is ionic with the phosphorus already dicoordinate, as shown by the characteristic phosphorus NMR shift to low field.[7] This is in fact the first spontaneous dissociation of a chlorophosphine and immediately shows that there must be a considerable benefit in the phosphorus dicoordination for the ring. For otherwise comparable acyclic or saturated cyclic

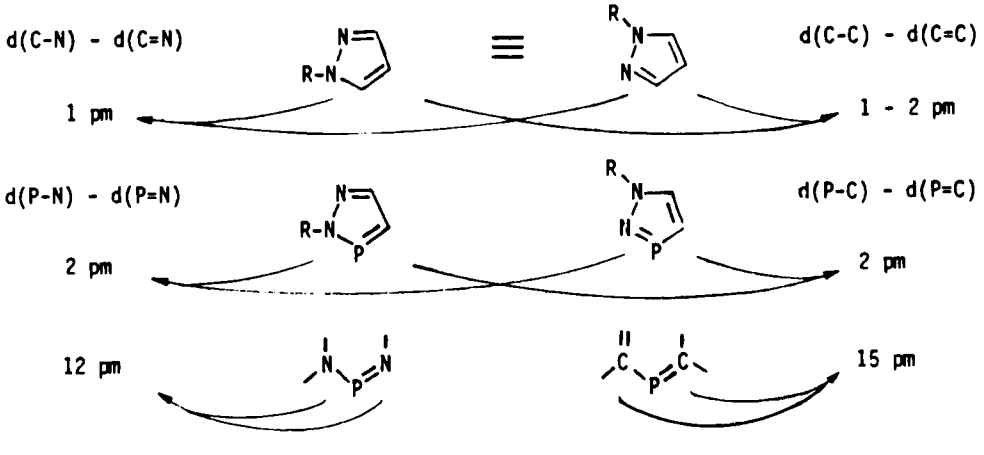
chlorophosphines, it takes a strong Lewis acid such as aluminum chloride to abstract the chloride ion and to stabilize the phosphenium ion. The equilibrium participation of the covalent form is only indicated by the reaction with sulfur; the azaphosphole phosphorus does not react with sulfur. The equilibrium is sensitive to substituent influence: with phenyl instead of methyl at the nitrogen, the equilibrium is at the covalent side.

Quite unexpectedly we isolated from the reactions of methylhydrazones with phosphorus trichloride not only the 2- but also the 1-methyl derivatives.[8]



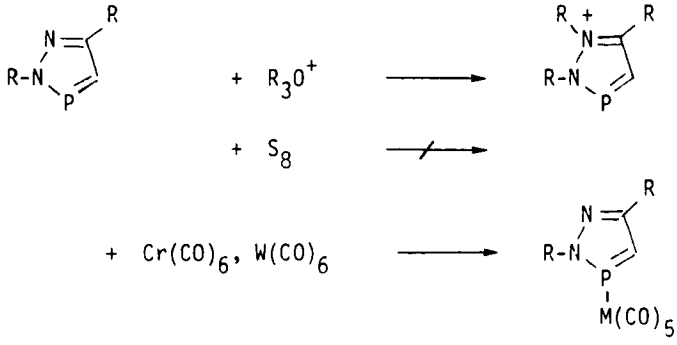
It is not completely clear how this isomerization proceeds, but its result is very welcome. It probably occurs at a stage when the ring has not yet closed. The diazaphospholes themselves isomerize only in the opposite direction, i.e. from the 1- to the 2-methyl derivatives.

From a structural comparison of the two isomers, we might learn about the azaphosphole delocalization. With localized double bonds they would be methylene and imino phosphines, respectively, and should correspondingly differ quite a bit in structure. If, on the other hand, the diazaphospholes are good phospha-pyrazoles with the two-coordinate phosphorus not disturbing the delocalized system, the differences should diminish. As expected, the single bond PN distance is longer than the double-bond distance and the same is true for the PC distances. The differences are positive in both cases. But they are small, just 2.2 and 2.1 pm. They are in fact nearly as small as the single and double bond CN and CC differences in pyrazole and they thus indicate a delocalization to the same extent.



In acyclic compounds of dicoordinate phosphorus, on the other hand, the corresponding differences between formal single and double bonds are much larger both from PN and PC!

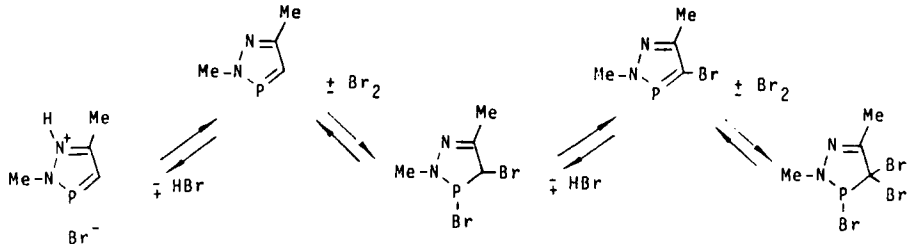
In the chemical behavior of the diazaphospholes, consequently, heterocyclic reactivity predominates over typical phosphorus reactivity.[9] They are therefore not easily methylated and not at the phosphorus but at the nitrogen; and they do not react with sulfur. At least they form phosphorus bonded metal complexes.[10-12]



In the pentacarbonyl complexes the metal is coplanar with the ring and the phosphorus is thus in a trigonal coordination state but it is very unsymmetrically surrounded because the endocyclic angle on coordination has just slightly opened (from 91° to 93°). From the spectral data one may also conclude that rather little charge has been transferred to the metal.[10]

Bromine invariably oxidizes tervalent phosphorus to pentavalent phosphorus. And this is still true in cases where the tervalent phosphorus is part of cyclic 6π systems such as phosphabenzene or—as we have seen—triazaphosphole. The dimethyldiazaphosphole also reacts smoothly with bromine even at temperatures as low as −80°C. But what is isolated in good yield is not the product of oxidation or 1,1-addition to the phosphorus but the result of substitution at the carbon adjacent to the phosphorus. It is a distillable liquid with a phosphorus chemical shift close to the starting diazaphosphole.[13]

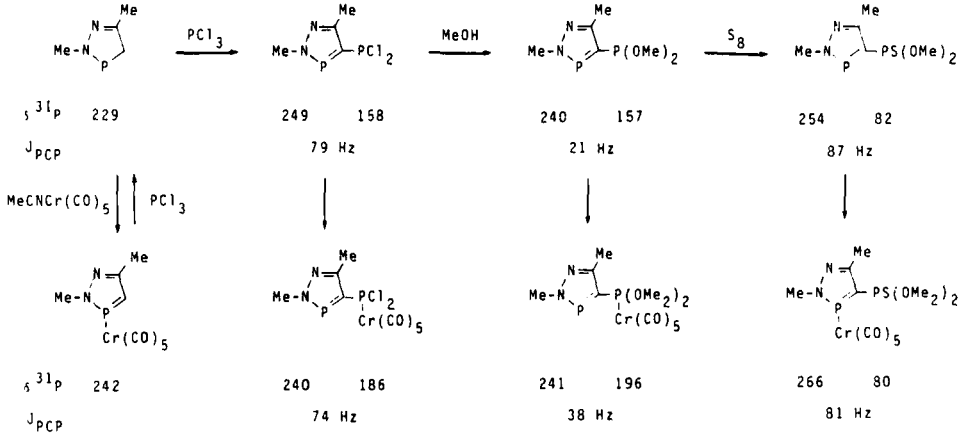
At first sight the bromination looks like an electrophilic aromatic substitution, not involving the phosphorus. On the other hand, the bromo derivative is prepared in even better yield in the presence of triethylamine to take on the hydrogen bromide.



$\delta^{31}P$	232	231	120	217	129
$\delta^{13}C$-4	136	135	55	128	64
J_{PC}	47 Hz	35 Hz	35 Hz	52 Hz	61 Hz

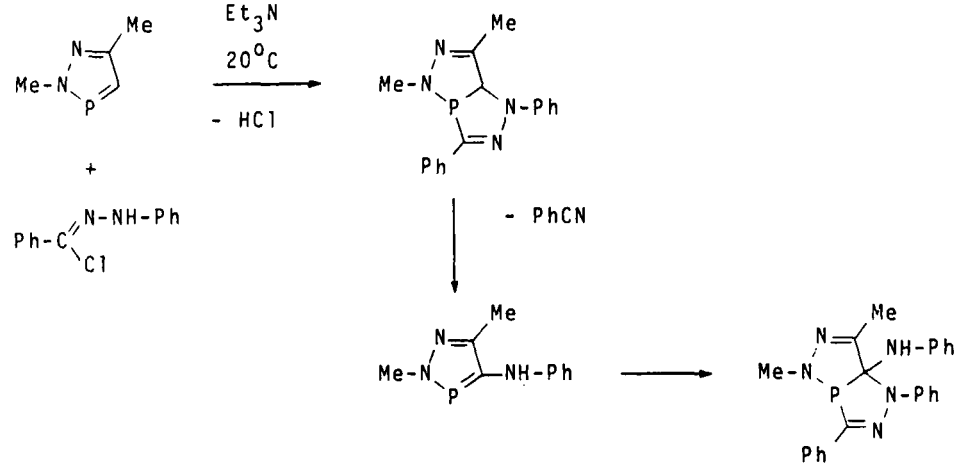
The ^{31}P-NMR at −60°C reveals that the addition of an equimolar amount of Br_2 to the diazaphosphole establishes an equilibrium with these four species participating. They are all connected to each other and to the starting compound by 1,2 additions to and eliminations from the PC bond. Addition of the first Br_2 gives a dibromodihydrodiazaphosphole with a ^{31}P chemical shift characteristic for a three-coordinate phosphorus. It loses HBr reforming the phosphole system. This hydrogen bromide adds to some more diazaphosphole. The left-over bromine adds to the bromodiazaphosphole once again in a 1,2 way to the PC bond and not 1,1 to the phosphorus.

By the reaction of the diazaphosphole with chlorophosphines or phosphorus trichloride, phosphino derivatives can be prepared and we assume that these substitutions too occur by an addition/elimination mechanism.[9]

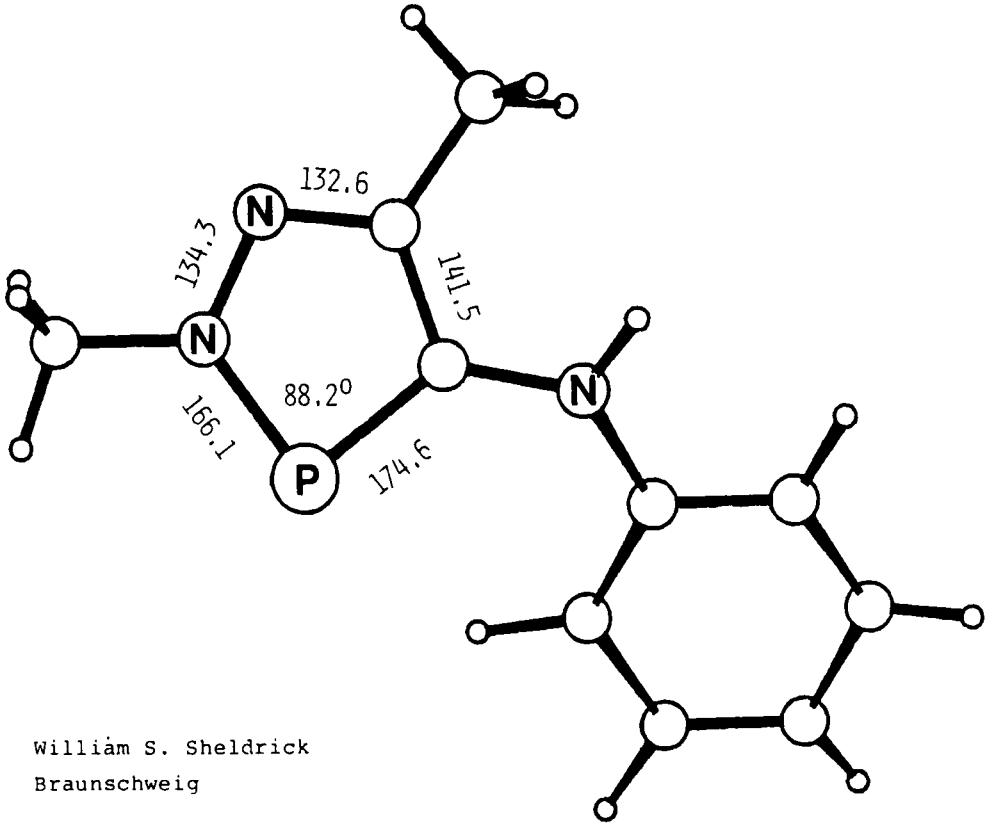


These derivatives allow an intramolecular comparison of complex stability. We find the metal always prefers the exocyclic phosphorus over the heterocyclic. Only when it is oxidized will the ring phosphorus coordinate, but it is replaced easily e.g. by phosphorus trichloride.

Finally I'd like to mention two cycloadditions to the diazaphosphole system:



Nitrilimines, as generated from hydrazide chlorides, add to the PC bond, but not in the direction we had expected originally.[14] The most interesting feature of the adduct is its thermal lability. Above 60°, e.g. on attempted distillation it loses benzonitrile, to reinstate (by a 1,2 proton shift) the 6π system.



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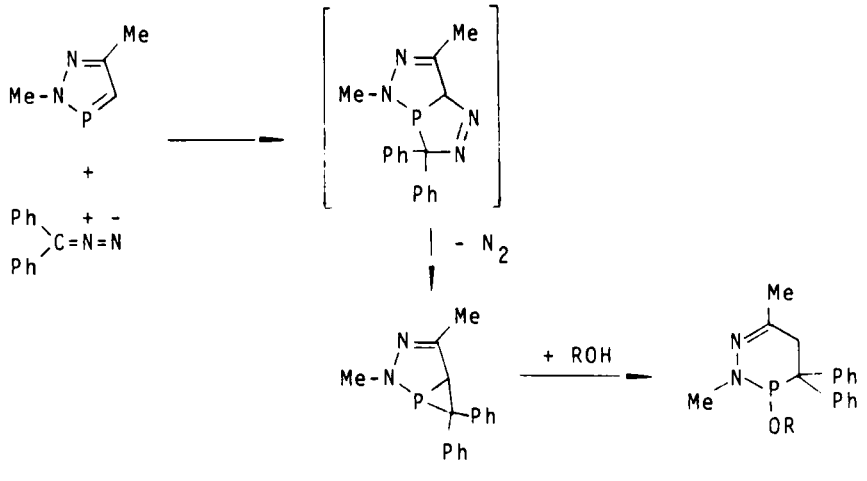
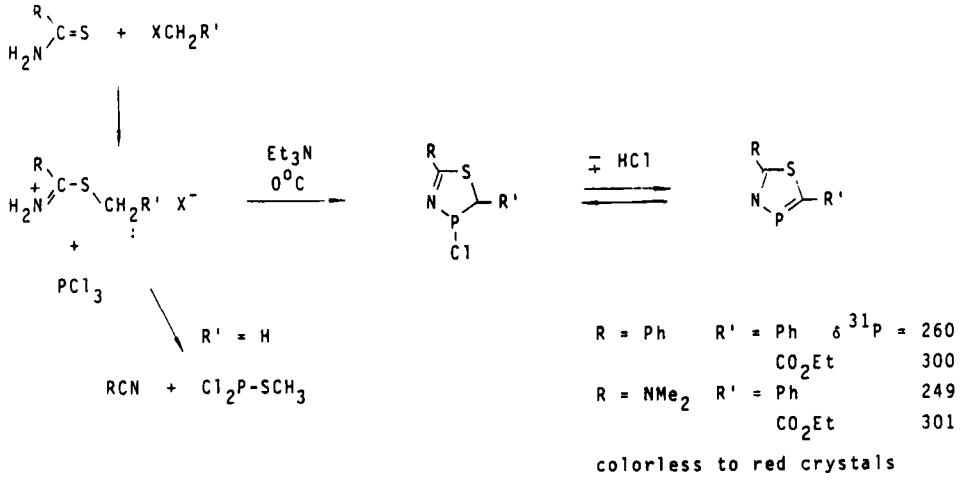
Braunschweig

Its structure shows again the small endocyclic angle. The PC bond is significantly longer than in the 4-unsubstituted diazaphosphole, obviously affected by the electron release from the anilino group.

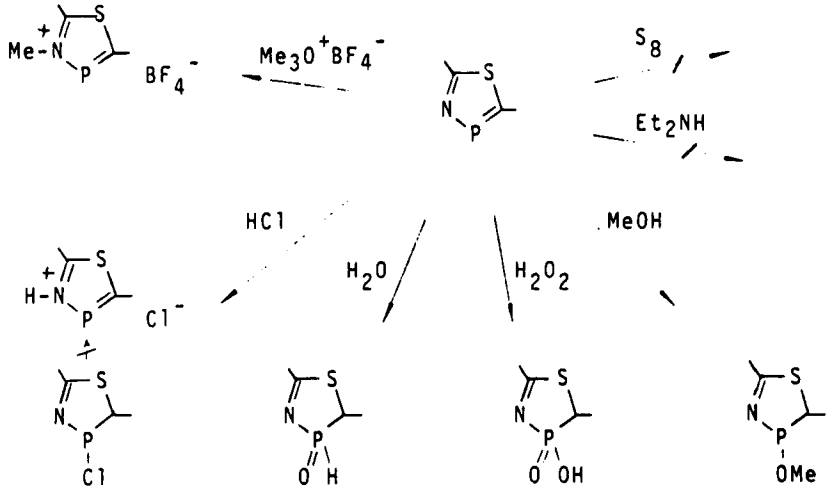


The sequence of nitrilimine addition and benzonitrile elimination may be compared to the reaction of the diazaphosphole with diphenyl diazomethane investigated in cooperation by Arbusov and Dianova in Kazan. The very slow reaction leads presumably in an analogous manner at first to a [3 + 2]-cycloadduct which on loss of N_2 yields this bicyclic product. The diazaphosphole system does not recover in this case and the PC bond in common to the two rings is easily split by an alcohol.

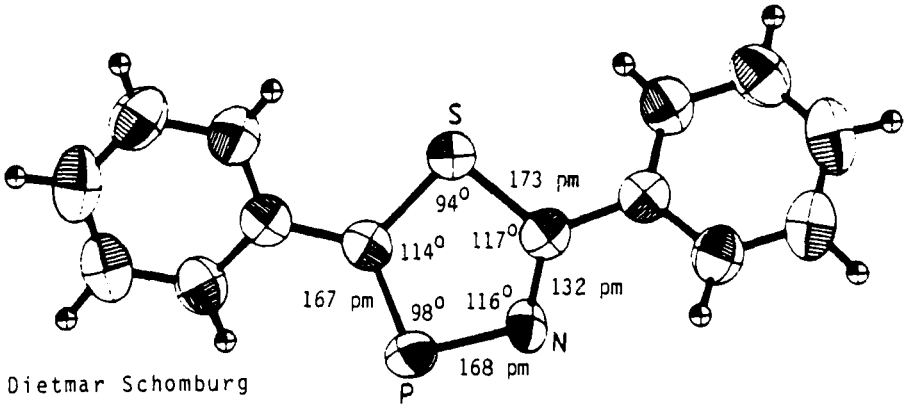
In the diazaphosphole synthesis, the hydrazones provided a chain with an amino group at one end and a reactive methylene group at the other. On a similar basis we tried to prepare 1,3,4-thiazaphospholes.[15]



A thioamide or thiourea is alkylated e.g. by benzyl bromide to give the four-membered chain with the amine group and the reactive methylene group at its ends, which can in fact be condensed with phosphorus trichloride to give the desired thiazaphospholes.



They show the reactivity already known from the diazaphospholes: reversible addition of HCl to a product which is not ionic in this case, addition of methanol, water, hydrogen peroxide to the PC bond, no reaction with sulfur and methylation only at the nitrogen.

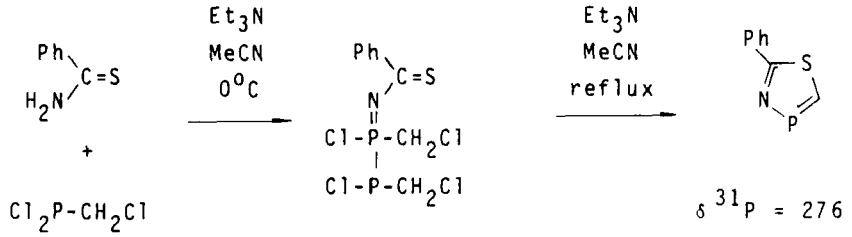


Dietmar Schomburg

Braunschweig

Due to the sulfur as another larger member in the ring, the strain on phosphorus is reduced and the endocyclic angle opens to 98°. The structure allows a most interesting comparison to the thiadiazole, the symmetric analogue with another nitrogen in place of the phosphorus. Compared to it the CS bond in the phosphorus-containing heterocycle is shorter (173/177 pm) and the CN bond is longer (132/126 pm), which implies that in the thiazaphosphole there is a better equalization between formal single and double bonds, a better delocalization than in the classical heterocycle.

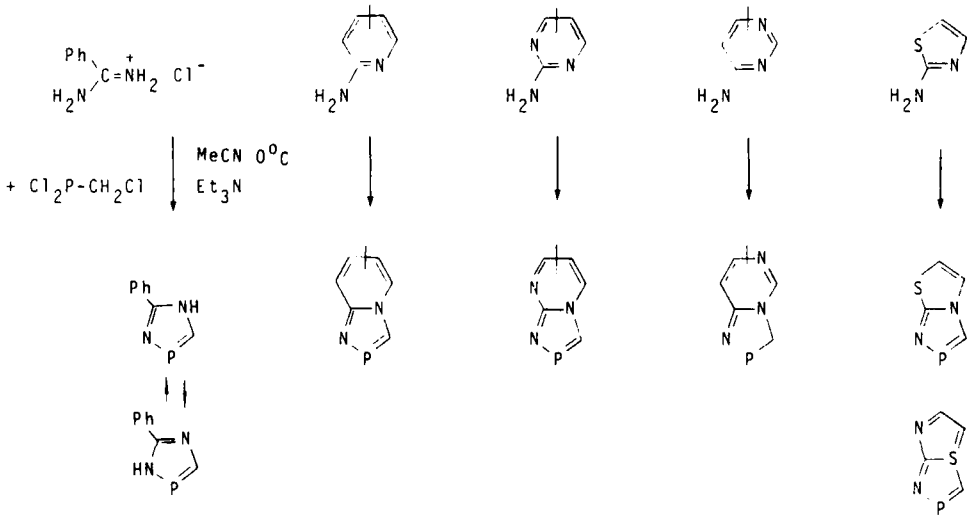
As shown, thiazaphospholes with hydrogen at the carbon adjacent to the phosphorus (R′ = H) may not be prepared that way. In this case phosphorus trichloride takes over the methylthio group and thus converts the thiomide to the nitrile. We therefore had to look for a different synthetic principle. Here we try to introduce the phosphorus and the adjacent carbon at the same time using chloromethylphosphorus dichloride. As a reaction partner a thioamide will do.



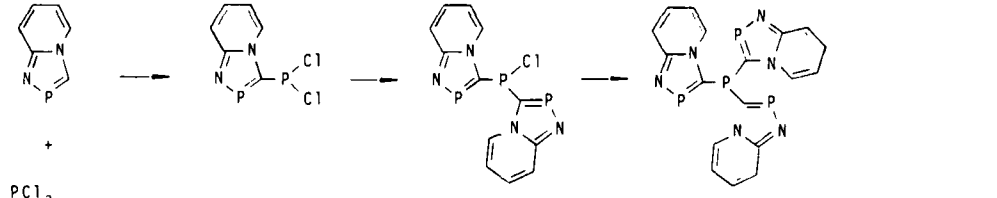
$\delta^{31}P$ = -43, 136 (273 Hz)

-15, 137 (231 Hz)

At low temperature the reaction takes an entirely different direction and results in a diphosphine monimine as 2 : 1 condensation product. At reflux temperature it converts, however, into the desired thiazaphosphole. This condensation now opens the way also to another type of diazaphospholes: the 1,3,4-diazaphospholes. In place of the thioamides, amidines (or their hydrochlorides) are used as reaction partners.

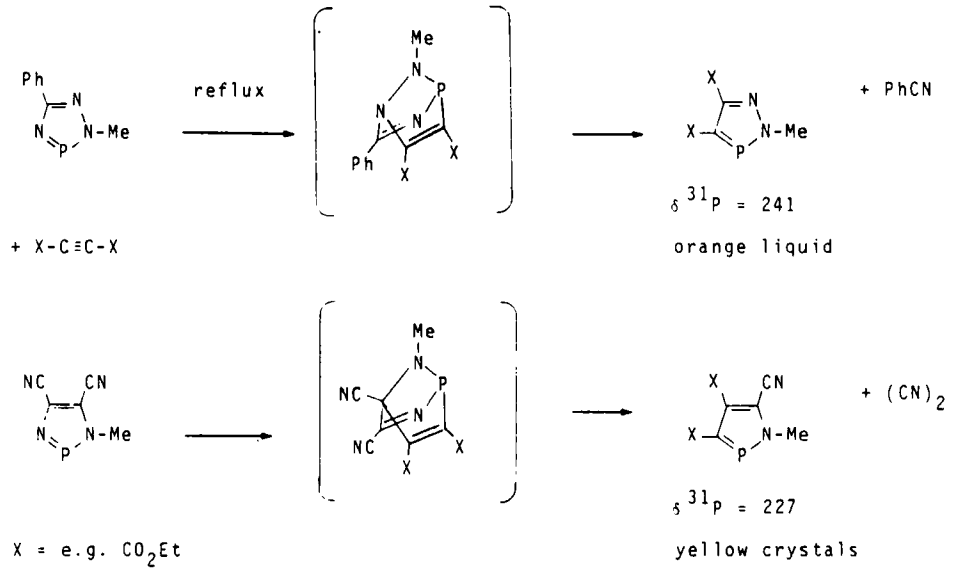


The synthesis also gives excellent results when applied to *o*-aminopyridines, aminopyrimidines and aminothiazole, which also contain the amidine system. A number of bicyclic 10π phosphorus heterocycles have thus become available as stable crystalline substances. In their reactivity they resemble the azaphospholes mentioned before. Remarkable again is the easy substitution of the CH group adjacent to the phosphorus. All three substitution steps of phosphorus trichloride can be obtained. Oxidation of the final product occurs only at the central, exocyclic phosphorus.



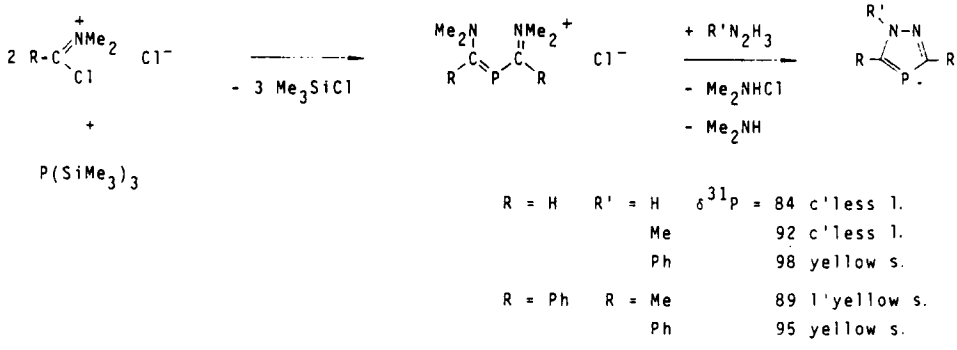
			O	S	Se	
$\delta^{31}P$ =	243.5	237.5	236.2	242.8	240.7	239.7
	123.0	25.1	- 74.7	- 1.9	- 3.2	- 26.3
J_{PCP} =	169.0	62.9	8.3	43.1	40.3	36.7 Hz

The next azaphosphole synthesis is rather a conversion of one azaphosphole into another. The new azaphosphole contains one nitrogen less in the ring, as a CN unit is exchanged for a CC unit.

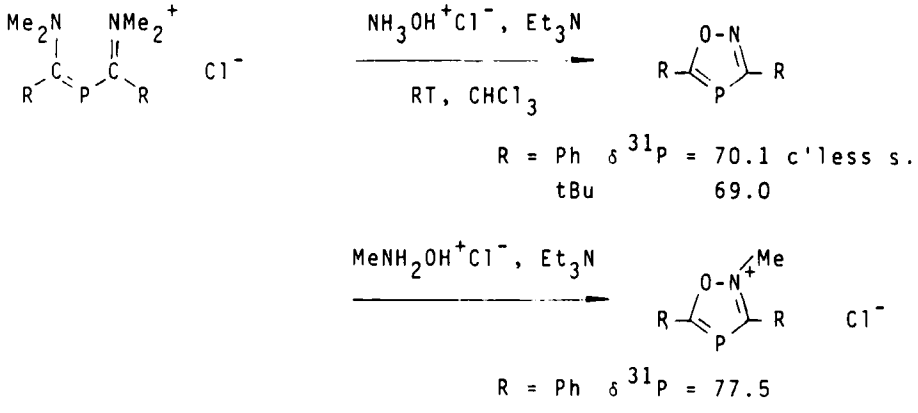


This is achieved by the reaction of a 1,2,4,3-triazaphosphole or a 1,3,2-diazaphosphole with an electron-poor acetylene, acetylene dicarbonic ester in this case.[16] Most probably the reaction proceeds via a [4 + 2]-cycloaddition and a subsequent elimination of a nitrile. Starting from the 1,3,2-diazaphosphole, this conversion provides us with the first monoazaphospole.

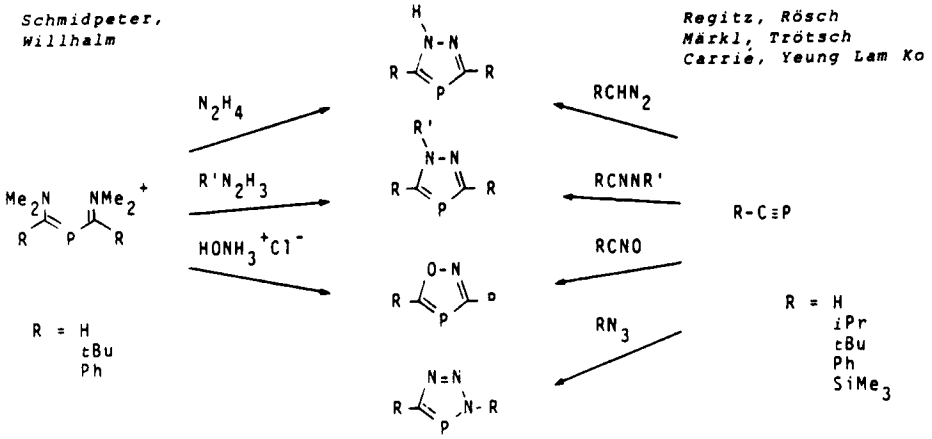
The missing 1,2,4-diazaphospholes would have no PN, just PC bonds and should therefore necessitate a completely different route for their synthesis.



It starts with imido chlorides which react 2 : 1 with tris(trimethylsilyl)phosphine. The result is phosphaallylic cations, presumably the least reactive acyclic derivatives of dicoordinate phosphorus. As they are rather unreactive at the phosphorus, they can be subjected to a transamination at the carbon. Using for this a hydrazine we end up with the wanted 1,2,4-diazaphospholes.[17] They are similar to the other diazaphospholes as again the phosphorus is not to be alkylated or oxidized. They are different in respect to their hydrolytic stability even in acidic or basic media. Bases convert the compounds R′ = H to the diazaphosphole anions.

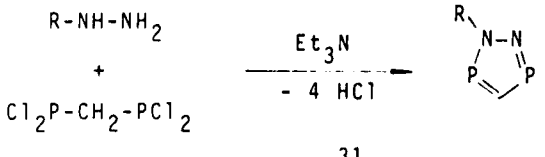


By the same route with hydroxylamines instead of hydrazines, oxazaphospholes and oxazaphospholium salts are obtained.



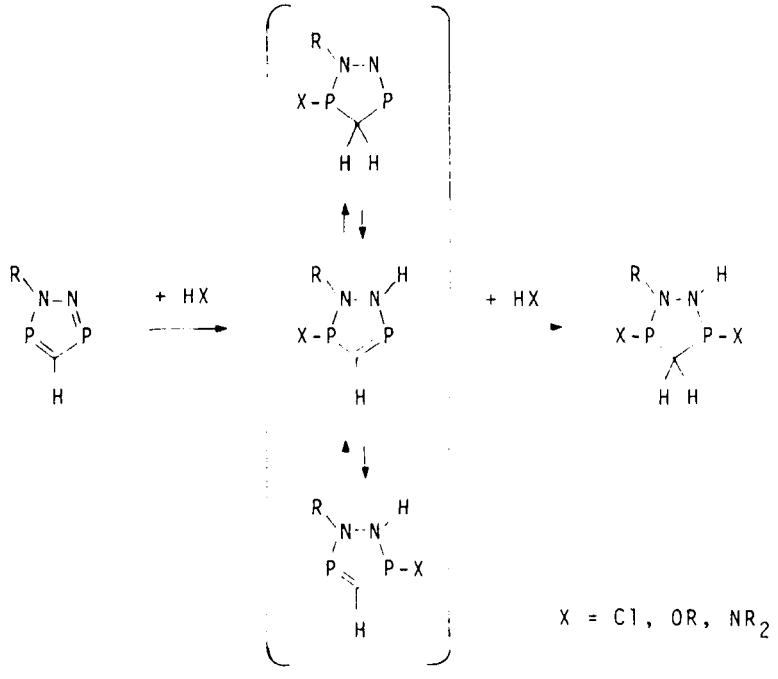
1,2,4-diazaphospholes and 1,2,4-oxazaphospholes have been prepared last year also by three other groups in Kaiserslautern,[18] Regensburg[19] and Rennes[20] in a [3 + 2]-cycloaddition starting from a phosphaalkyne or its precursor and its reaction with a diazoalkane, a nitrile imine or a nitrile oxide. With azides the cycloaddition gives a new triazaphosphole, the 1,2,3,4-triazaphosphole, which cannot be obtained by condensation methods.

The last azaphosphole heterocycle to be mentioned, the 1,2,3,5-diazadiphosphole, contains two dicoordinate phosphorus atoms in the ring. Its synthesis resembles that of the 1,2,4-diazaphospholes with phosphorus and carbon having interchanged their roles.



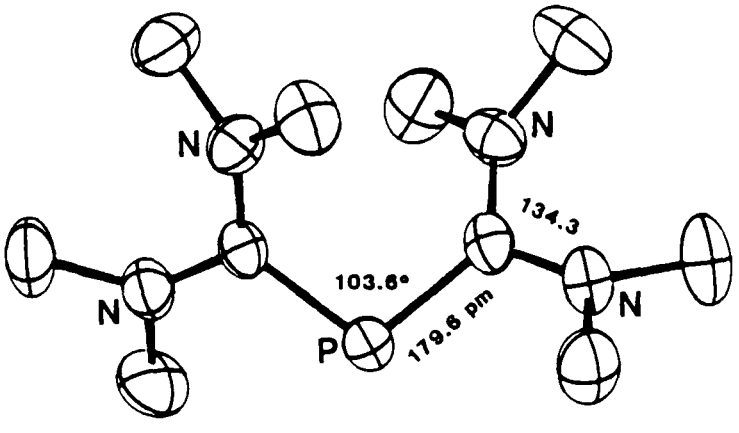
R = Me $\delta^{31}P$ = 278, 266 J_{PCH} = 44, 30 Hz
Ph 275, 265 45, 29 Hz
25 Hz

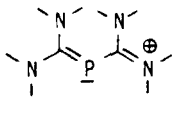
Condensation of the tetrachlorodiphosphinomethane and an alkyl or aryl hydrazine gives the diazadiphospholes as distillable liquids.[21] The two phosphorus members are very much alike as seen from the similarity of their chemical shifts.



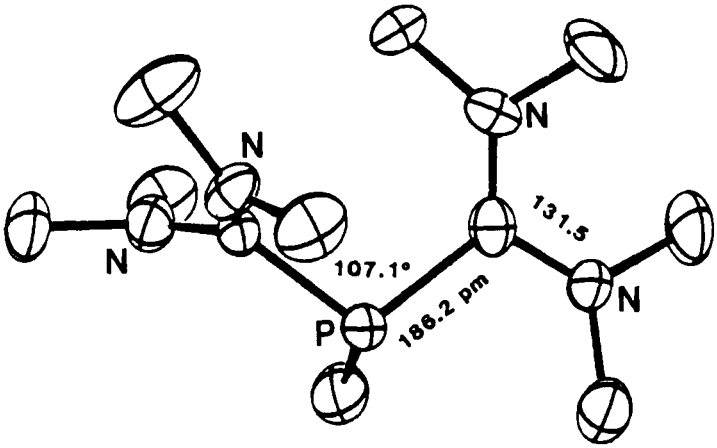
Their addition behavior is of special interest. The two dicoordinate phosphorus atoms should allow two addition steps. As the first one will destroy the aromatic system, we may anticipate the second to be more favored than the first. In fact we observed just the 2 : 1-addition.

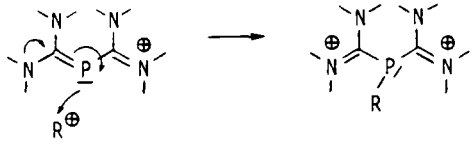
During this lecture I pointed several times to the interdependency of phosphorus two-coordination and the 6π ring system. I suggested it to be the reason for the lack of phosphorus nucleophilicity in the azaphospholes and I postulated that alkylation of the phosphorus would ruin the heterocyclic delocalization. I cannot prove this, simply because the rings will not alkylate at the phosphorus, but I can show it in the case of an acyclic conjugated system, the aforementioned 2-phosphaallylic cations.[22]





The structure, obtained by Bob Holmes and his group, shows PC bonds definitely shortened below the single bond length and two CN_2 groups as coplanar as possible.





After methylation the phosphorus coordination is as in ordinary phosphines, the PC bonds are normal single bonds and the two CN_2 groups obviously have become independent. Methylation of the phosphorus has thus destroyed conjugation.

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