Anellated Heterophospholes and Phospholides and Analogies with Related Non-Phosphorus Systems

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I. Introduction

The subject of this overview is the chemistry of heterocyclic systems having an aromatic heterophosphole ring fused with another five- or six- or in one case seven-membered ring. The heterophosphole ring may be thought of as derived from the classical heteroles such as pyrrole, furan, or thiophene by substituting one ring -CH═ by an sp^2-phosphorus atom (-P═). The two-coordinate phosphorus contributes one π-electron only to the aromatic sextet, but the donation of two π-electrons by an additional heteroatom like N(R), O, or S (Se, Te) furnishes a neutral five-membered 6π system. Furthermore, as in diazoles, oxazoles, thiazoles, or triazoles, there may be one or more two-coordinate nitrogen or even two-coordinate phosphorus in the ring.[1] Likewise, the anellated heterophospholes[2] may be perceived as derived from the classical fused systems[3] such as indole, indolizine, benzofuran, benzothiophene, benzimidazole, benzoxazole, benzothiazole, or azapentalenes. The aromatic anellated phospholide anions that contain no other heteroatom than phosphorus in the five-membered ring are similarly related to pentalenide, indenide, or azulenide anions by a CH/P exchange.[3]

The diagonal relationship between the elements in the periodic table is well documented, but its existence in the carbon−phosphorus pair has been realized only lately.[4−6] The participation of >C═P-[7,8] and -C≡P[9] in the pericyclic reactions is found to be as facile as that of the >C═C< and -C≡C- functionalities. The heterophospholes have been termed as a postscript chapter of the heterocyclic chemistry due to their close resemblance with the related non-phosphorus analogues.[10] The presence of a two-coordinate phosphorus in the heterocyclic ring introduces a functionality in the system that can undergo analogous but also different or additional reactions leading to a wide variety of organophosphorus compounds. Heterocyclic compounds having an anellated five-membered ring constitute a large body of the

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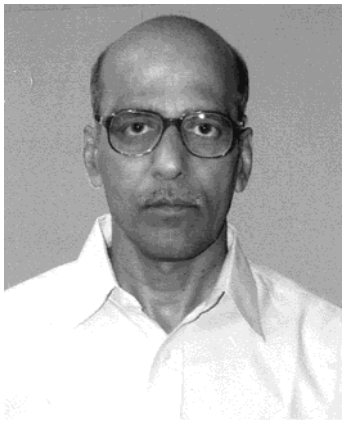


Raj Kumar Bansal was born in Kankhal (North of India) in 1942. After receiving his Ph.D. degree in 1968 from the University of Allahabad under the supervision of the late Professor R. D. Tiwari, he joined the University of Jodhpur as a lecturer. In 1970, he moved to the University of Rajasthan, Jaipur. He was Professor and Head of the Department of Applied Chemistry, MDS University, Ajmer, for some time in 1997–98 but rejoined the University of Rajasthan. As a Fellow of the Alexander von Humboldt Foundation, he visited the Universities of Erlangen and Munich. His main research interests focus on the chemistry of heterocycles containing two-coordinate phosphorus.

Joachim Heinicke was born in Aue/Saxony (Germany) in 1947. He received his Ph.D. degree in 1975 under the supervision of Professor Alfred Tzschach and his Dr.Sc. degree in 1984 from the University of Halle. In 1990, he moved to the University of Greifswald as Lecturer. In 1992, he became Professor and Head of the Institute of Inorganic Chemistry until the Chemistry Institutes amalgamated to the Department of Chemistry and Biochemistry in 1998. His research interest is focused to the chemistry of amino and hydroxy substituted compounds of main group elements, particularly P and Si, with special emphasis on the stabilization of low-coordination by π-bonding to N or O atoms, and, since a few years, their use in coordination chemistry and catalysis.

organic compounds that display distinguished characteristic structural and reactivity patterns that are governed by the type of anellation as well as the relative positions of the heteroatoms. During the past few years, some useful general synthetic methods have been developed for a variety of anellated heterophospholes that are often parallel to those used for their non-phosphorus analogues.[11] In a recent review, this analogy existing between the synthetic methods used for phosphaindolizines and those for indolizines have been highlighted.[12] The difference in the reactivities of 2-phosphaindolizine and indolizine has been explained on the basis of semiempirical calculations.[13] A survey of the literature provides still much more information for illuminating the scope and limits of the analogies of the classical anellated heterocycles to their phosphorus analogues in synthesis, structure, and reactivity and other aspects which can be extrapolated to the hitherto inaccessible anellated heterophospholes.

An earlier comprehensive review on anellated heterophospholes covers the literature up to 1994 and includes a detailed list of these systems.[2] Some further reviews place special emphasis on syntheses of anellated heterophospholes through [4+1]cyclocondensation of 2-substituted cycloiminium salts[11,14] or [3+2]cyclocondensation and [3+2]cycloaddition methods[11] and on analogies between the syntheses of indolizines and phosphaindolizines.[12] The reviews on heterophospholes in general cover anellated derivatives in a limited manner.[1,15,16] Anellated heterophospholes accessible from the reactions of phosphaalkynes are mentioned in reviews dealing primarily with the synthetic uses of these synthons.[9] Similarly, a review[17] devoted to cycloadditions only at the C=P functionality includes those on some anellated heterophospholes. The ^{31}P NMR chemical shifts of a large number of anellated heterophospholes are compiled in two reviews.[2,18]

In the present review, it is intended to highlight the analogy between the syntheses, structures, and reactivities of the anellated heterophospholes with those of the related non-phosphorus systems comprising an up-to-date account (June 2001) of all the heterocycles that have a five-membered ring containing at least one two-coordinate phosphorus anellated to a five-, six-, or seven-membered ring. The latter may be an aromatic ring or it may be partially saturated. As phospholide anions with one or more phosphorus atoms are isoelectronic with heterophospholes and have been found to display interesting coordination behavior[19−22] that should be compared with that of heterophosphol(id)es, the anellated mono- and diphospholide anions are also included.

II. Synthetic Routes

A. General Survey

Two synthetic strategies, formation of one new bond or two new bonds, have been commonly employed for the construction of a five-membered ring.[23] Also, nearly all syntheses of anellated heterophospholes follow these principles. Whereas cycloaddition reactions are much more important for nonanellated than for anellated heterophospholes, the latter profit from the usually much higher stability or even exclusive accessibility of suitable three- and particularly of four-atom fragments for [3+2]- and [4+1]-condensation reactions, for instance 2-amino-, -hydroxy-, or -mercaptoarylphosphines in the latter strategy. Related olefins are not stable. Another route is to build up the anellated ring from reactions of functionally substituted heterophospholes, but due to the high reactivity of P=C or P=N bonds in many heterophospholes, attempts to use this strategy have been made only very rarely.[24−26]

1. One New Bond

The reductive cyclization of *o*-nitrobenzyl ketones involving the formation of a bond between N−C(2)

is a preferred method for preparing indole.[27] A related strategy has been recently developed for 1,3-benzazaphospholes from reductive cyclization of *N*-acyl-2-aminobenzenephosphonic acid esters.[28] Another method for the construction of an anellated pyrrole ring involving formation of one new bond is 1,5-electrocyclization of *N*-allylpyridinium ylides to give indolizines.[29,30] A similar synthesis for 2-phosphaindolizines has been reported from *N*-pyridinium dichlorophosphinomethylides through disproportionation followed by 1,5-electrocyclization.[31]

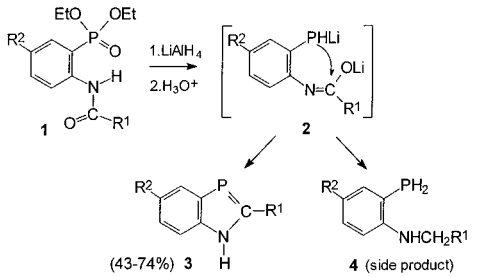
2. Two New Bonds

The second synthetic strategy involving formation of two new bonds is based on [4+1]atom fragments or [3+2]atom fragments. For the construction of an anellated five-membered ring, the four-atom fragment or the three-atom fragment has to be a part of the already existing ring. The [4+1]cyclocondensation of a two-substituted cycloiminium salt with a carboxylic acid anhydride or acyl chloride has been commonly used for the construction of an anellated pyrrole,[30,32] imidazole,[33] pyrazole,[34,35] or even triazole[36] ring. Likewise, a variety of anellated heterophospholes having bridgehead nitrogen have been prepared in this manner using a phosphorus reagent such as PCl_3 or $P(NMe_2)_3$ in place of carboxylic acid derivatives.[11,14] The use of *o*-disubstituted benzenes as the four-atom fragment makes benzo-anellated heterophospholes accessible.[16] The [3+2]atom fragments method may be either [3+2]cyclocondensation or [3+2]cycloaddition. In [3+2]cyclocondensation, α-halocarbonyl compounds have been frequently used as the two carbons fragment which condenses with α-alkyl or alkoxycarbonyl-pyridine[32] or with α-aminopyridines and -diazines[33] to afford the anellated pyrrolo- and imidazolo-ring, respectively. Active methylene esters have also been used as the two carbons fragment in the preparation of indolizines.[37] Chloromethyldichlorophosphine[38,39] has been found as a reagent of choice for furnishing the C−P fragment in the synthesis of anellated diazaphospholes.[40] The [3+2]cycloaddition of *N*-cycloiminium ylides and imines with acetylenic or olefinic 1,3-dipolarophiles has been employed to prepare anellated pyrrole and pyrazole systems.[41−43] Likewise, *tert*-butylphosphaethyne has been found to undergo [3+2]cycloadditions with a variety of *N*-cycloiminium ylides to afford anellated 1,3-azaphospholes.[9]

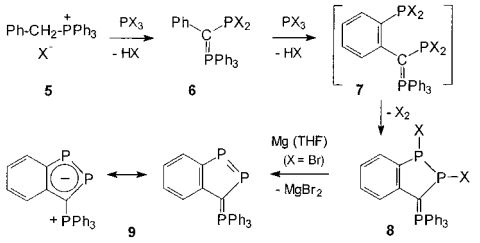
3. Anellation of Heterophospholes

This method has been only rarely used. First examples were pyrrolo-anellated 1,3,2-diazaphospholes formed by the reaction of dimethylammonium 4,5-dicyano-1,3,2-diazaphospholide with secondary amines.[24,25] Other interesting examples are the syntheses of phospha-analogous nucleobases with phosphorus replacing one of the N atoms of the five-membered ring by fusion reactions of functionally substituted 1,3-azaphospholes with formamidinium acetate, formamide, or urea affording 1,3-azaphospholo-pyrimidines.[26]

Scheme 1



Scheme 2



B. Synthesis by Formation of One New Bond

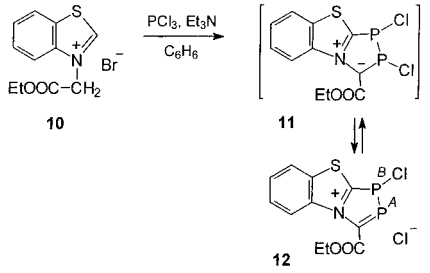
1. Reductive Cyclization

N-Secondary 2-acylamidobenzenephosphonic acid esters **1**, obtainable from the reaction of 2-bromo-*N*-acylanilides with triethyl phosphite, on reduction with excess $LiAlH_4$ followed by hydrolysis give 1*H*-1,3-benzazaphospholes **3** as the main product (Scheme 1). Small amounts of *N*-secondary 2-phosphinoanilines **4** are also formed. It is assumed that the reaction proceeds via primary reduction at phosphorus followed by intramolecular attack of the resulting phosphido group at the C=N bond of the metalated amido group in **2** yielding a benzazaphospholide anion that is hydrolyzed to give **3**.[28] The cyclization step may be compared with the base-catalyzed Madelung cyclization of *N*-acyl-*o*-toluidide.[44] *N*-Alkyl derivatives of **1**, e.g., with a NMe group, are unable to undergo reductive cyclization.[28]

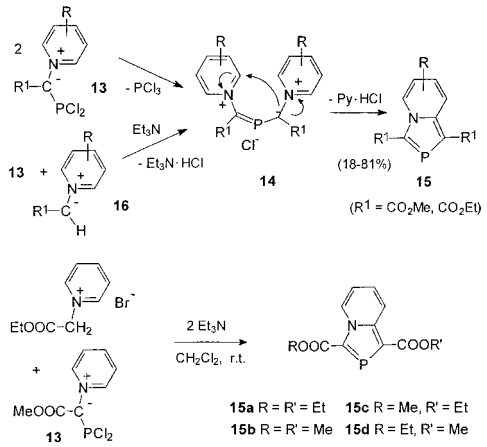
An interesting example of the reductive cyclization resulting in the formation of a P−P bond has recently been reported. Benzyltriphenylphosphonium bromide **5** reacts with phosphorus trichloride or tribromide in the presence of triethylamine to give 1,2-dihalo-3-triphenylphosphoranediyl-1,2-diphosphaindane **8** through a self-reductive cyclization of the intermediate **7** through loss of a halogen molecule. The corresponding reaction of (3-methylbenzyl)triphenylphosphonium bromide yields a mixture of two regioisomers. The bromide derivative **8** (X = Br) could be reduced with magnesium in THF to give the 3-triphenylphosphonio-1,2-diphosphaindenide **9** (Scheme 2).[45] The formation of **9** is also observed besides other products in the sulfide-initiated disproportionation of the primary product **6**.[46]

A similar reaction takes place when 3-(ethoxycarbonyl)methylbenzothiazolium bromide **10** is treated with one equivalent of PCl_3 in the presence of two equivalents of Et_3N. The ^{31}P NMR spectrum reveals the formation of **12** ($\delta_A = 275.75$, $\delta_B = 134.68$, $J_{PP} = 424.8$ Hz), which exists in a dissociation equilibrium with the ylide **11** (Scheme 3). It could however not

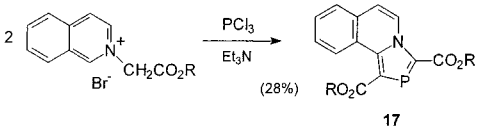
Scheme 3



Scheme 4



Scheme 5



be separated from the ammonium salt.[47] The benzothiazolium methylide formed in the reaction acts possibly as the reducing agent by taking up a halogen molecule leading to the P−P bond.

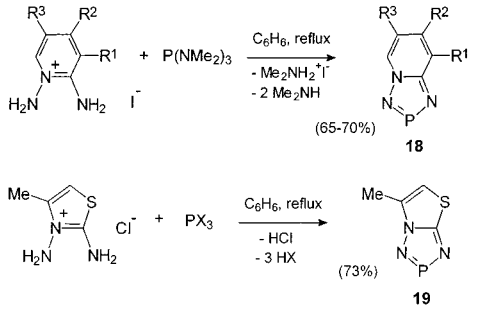
2. 1,5-Electrocyclization

Pyridinium dichlorophosphinomethylides **13**, generated from the reaction of PCl_3 with *N*-alkylpyridinium bromides in the presence of Et_3N,[48] undergo dismutation followed by 1,5-electrocyclization to give 2-phosphaindolizines **15**.[31] The formation of the intermediate 1,5-dipolar species, bis(pyridinium ylidyl)phosphenium chloride **14**, which could also be generated from the reaction of **13** with pyridinium methylide **16** (Scheme 4), is proved by carrying out a crossed reaction using **13** ($R^1 = CO_2Me$) and a precursor of **16** ($R^1 = CO_2Et$) yielding the expected four products **15a**−**15d** including the two cross-products **15c** and **15d** with different R^1. Formation of the phosphonium analogue of **14**, bis(triphenylphosphonium ylidyl)phosphenium halide, from disproportionation of the corresponding triphenylphosphonium dihalophosphinomethylides[49] has been reported.

The above method has been extended to the synthesis of 1,3-azaphospholo[5,1-*a*]isoquinolines **17** (R = Me, Et) as well (Scheme 5).[50]

Attempts to generate a bis(*N*-dichlorophosphinoiminopyridinium ylidyl) phosphenium chloride, an analogue of **14** with N=P−N$^-$ in place of C(R^1)=P−C(R^1)$^-$, from disproportionation of the *N*-dichlorophosphinoiminopyridinium ylide failed.[51] The corresponding carbon analogues, however, are available and have been used in the synthesis of 3-azaindolizines from 1,5-electrocyclization of *N*-vinyliminopyridinium ylides.[29,52,53]

Scheme 6



Some further cyclocondensation reactions of acyliminium salts with PCl_3 have been reported where intermediates could be isolated which with excess base undergo intramolecular condensation at acyl-activated CH_2-groups. These reactions are presented in the next section since normally excess base is already used in the initial step so that intermediates are not observed.

C. Synthesis by Formation of Two New Bonds

1. [4+1]Cyclocondensation

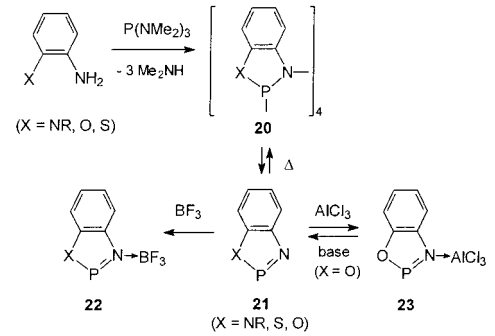
This strategy comprises two approaches. In the first, the one-atom fragment being phosphorus, either an electrophilic phosphorus reagent such as $P(NR_2)_3$, $P(OPh)_3$, and PCl_3 or a nucleophilic reagent like phosphines, alkaliphosphides, or silylphosphines, condenses with a four-atom fragment, which in part belongs to the already existing ring, to form an anellated heterophosphole. In the second approach, phosphorus is a substituent of the ring which acts as a four-atom fragment and will be anellated after ring closure with a non-phosphorus one-atom fragment, in the known cases, a carbon electrophile.

1.1. [4+1]Cyclocondensation Using Electrophilic Phosphorus Reagents. This strategy uses carbo- or heterocyclic compounds containing four-membered chains terminated at both ends by an amino, hydroxy, mercapto, phosphino, or active methylene group or a tautomer thereof as a four-atom fragment.

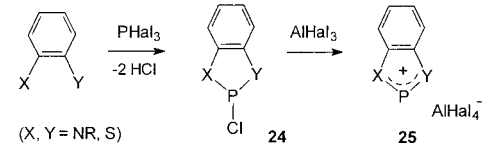
NNCN + P. 1,2-Diaminopyridinium iodides[54,55] condense with $P(NMe_2)_3$ on refluxing in benzene to give 1,2,4,3-triazaphospholo[1,5-*a*]pyridines, i.e., 1,3-diaza-2-phosphaindolizines **18** (Scheme 6), in high yields.[56] 1-Amino-2-imino-1,2-dihydropyridines have also been used in place of the pyridinium salts.[57] 1,2,4,3-Triazaphospholo[5,1-*b*]thiazole **19** has been obtained in a similar manner. In the latter case, the reaction has been carried out also with PCl_3 in place of $P(NMe_2)_3$ as the electrophile.[57] The method can be possibly extended to other diaminocycloiminium salts.[58]

NCCN + P, O/SCCN+P and SCCS +P. The condensations of a phosphorus reagent, $P(NMe_2)_3$ or $PHal_3$, with NCCN, OCCN, SCCN, or SCCS proceed

Scheme 7



Scheme 8

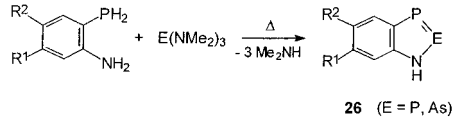


in a similar manner. *N*-Monoalkyl-*o*-phenylenediamines when refluxed with $P(NMe_2)_3$ form oligomers **20** of 1,3,2-benzodiazaphospholes. The monomer benzodiazaphospholes **21** (X = NR) are less stable than the similarly synthesized pyrido- or thiazolo-anellated triazaphospholes **18** or **19** but exist in equilibrium with the oligomers **20** at elevated temperatures and could be trapped by the Lewis acid BF_3 as stable adduct **22** (X = NR) (Scheme 7).[59] The N-phenyl derivative also preferably forms the oligomeric product.[60] The monomer, however, could be stabilized by complexation with $AlCl_3$.[60] **20** could also be produced from condensation of an iminophosphorane generated from 2-(dimethylamino)-1,3,2-dithiaphospholane and phenyl azide through reductive disulfide elimination.[61] *o*-Aminophenol and -thiophenol behave analogously affording oligomers which on treatment with BF_3 (X = S) or $AlCl_3$ (X = O) give stable adducts **22** (X = S) or **23** of the monomers. **23** on reacting with a base generates free benzoxazaphosphole that oligomerizes again after some time.[59b] Formation of anellated 1,3,2-diazaphospholes has also been claimed from the condensation of diaminopyrimidine and -pyridine with triphenyl phosphite although physical properties indicate their oligomeric nature.[62]

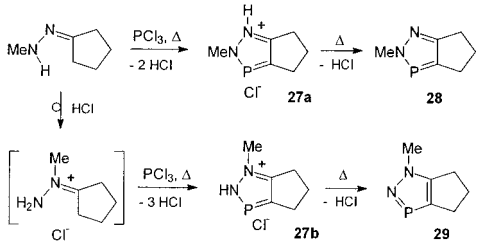
This ring closure principle is analogous to the preparation of benzimidazoles,[63] benzoxazoles,[64] or benzothiazole[65] from the condensation of *o*-phenylenediamines, *o*-aminophenols, or *o*-aminothiophenol with carboxylic acids or their derivatives, but the presence of a two-coordinate phosphorus in the above systems induces oligomerization due to the higher polarity of the bonds within the X−P═N (X = O, S) structural unit and the electron donor character of nitrogen on the one and the rather electrophilic behavior of two-coordinate phosphorus on the other side.

In the reaction of *N*,*N*′-dimethyl-*o*-phenylenediamine with PCl_3, the 2-chloro-benzodiazaphosphole **24** (X = Y = NMe) could be obtained.[66] Halide abstraction with $AlCl_3$ furnished the diaminophosphonium tetrachloroaluminate **25** (X = Y = NMe)[67] (Scheme 8), which is an analogue of the recently reported benzimidazoline-2-ylidenes, the first representatives of an isolable anellated cyclic diaminocarbene.[68] Analogous condensation reactions of *o*-aminothiophenol with PCl_3 or PBr_3[69] and of *o*-phenylenedithiols with PCl_3[70] and the halide abstraction with $AlCl_3$ or $AlBr_3$ to give the carbene-analogous 1,3,2-benzothiazaphospholium **25** (X = NH, Y = S)[69] and benzodithiaphospholium salts **25** (X = Y = S),[71−73] respectively, have also been reported. The 1,3-diselena-analogue of **25** (X = Y = Se) has been mentioned as an unpublished compound.[69]

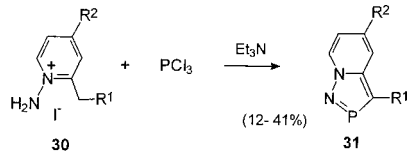
Scheme 9



Scheme 10



Scheme 11

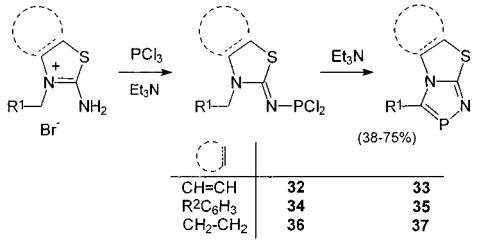


NCCP + P. 1,2,3-Benzazadiphospholes **26** (E = P) have been obtained from the condensation of *o*-aminophenylphosphines with $P(NMe_2)_3$ (Scheme 9).[74,75] Reaction with $As(NMe_2)_3$ makes the 2-arsa derivative **26** (E = As) accessible, whereas with $Sb(NMe_2)_3$ a dimer of the less stable 2-stiba heterocycle was formed.[75] Attempts to synthesize a related 1,2,3-benzoxadiphosphole from di-*tert*-butyl-2-phosphinophenol and $P(NMe_2)_3$ failed and led instead to a P−P bridged bis(dihydrobenzoxadiphosphole) and a cyclic phosphinidene-phosphorane.[76]

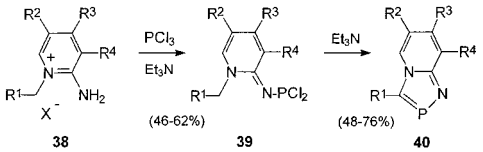
NNCC + P. The hydrazones of cyclic ketones provide a four-membered chain with a methylene group at the carbon end, activated by the α-imino function. The cyclocondensation of cyclopentanone methylhydrazone with PCl_3 leads to two isomeric diazaphospholes **28** and **29** through the intermediate salts **27a**,**b** (Scheme 10).[77] The latter have been isolated and characterized.[78] Their formation is understood in terms of an acid mediated isomerization of the hydrazone to an $H_2N-NMe^+=CR_2\ Cl^-$ species prior to the attack of PCl_3. A cyclohexane-anellated 1,2,3-diazaphosphole has been prepared in a similar manner.[79]

In analogy to the synthesis of pyrazolo[1,5-*a*]-pyridines from the condensation of 2-alkyl-1-aminopyridinium iodides **30** with acyl halides,[34] 1,2,3-diazaphospholo[1,5-*a*]pyridines, i.e., 3-aza-2-phosphaindolizines **31**, have been obtained from **30** and PCl_3 in the presence of Et_3N (Scheme 11).[80] The reaction of 1-amino-2-methylpyridinium iodide **30** ($R^1 = R^2 =$

Scheme 12



Scheme 13



H) with 2 equivalents of PCl_3 under these conditions affords the 1-dichlorophosphino derivative **31** (R^1 = PCl_2, R^2 = H).[80] It should be possible to extend this method to other *N*-aminocycloiminium salts.[58]

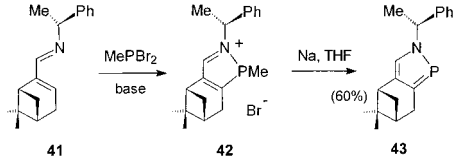
NCNC+P. 3-Alkyl-2-aminothiazolium and -benzothiazolium bromides condense with PCl_3 in the presence of Et_3N to give thiazolo[3,2-*d*][1,4,2]diazaphospholes **33** and the benzoanellated derivatives **35**, respectively. Likewise, 3-alkyl-2-aminodihydrothiazolium bromides give 5,6-dihydrothiazolo[3,2-*d*][1,4,2]-diazaphospholes **37** under these conditions (Scheme 12).[81] The reaction occurs through the intermediate 2-(3-alkyl)-2,3-dihydrothiazolylidenamino-dichlorophosphine **32**, **34**, and **36**, respectively, which could be isolated under mild conditions.[82,83] The latter can be cyclized intramolecularly to the respective anellated diazaphospholes on reacting with additional Et_3N, provided the *N*-methylene group is sufficiently activated. The non-phosphorus analogues of **33**, imidazo[2,1-*b*]thiazoles, have been prepared through [3+2]-cyclocondensation of 2-aminothiazoles and α-bromoketones or bromoacetic acid or intramolecular [5+0]cyclocondensation of the *N*-phenacyl intermediates.[84] In a [4+1]cyclocondensation approach, 2-acetaminothiazole was used.[84]

The above reaction has been extended to 1-alkyl-2-aminopyridinium halides **38** (X = Cl, Br; R^1 = COOEt), which give 1,4,2-diazaphospholo[4,5-*a*]pyridines, i.e., 1-aza-2-phosphaindolizines **40**, under these conditions. In this case also, the intermediate 2-(1-alkyl)-1,2-dihydropyridinylidenamino-dichlorophosphines **39** could be isolated which on reaction with Et_3N were converted to **40** (Scheme 13).[85] The *N*-methylene group should again be sufficiently activated, otherwise the reaction stops at the stage of **39** and cyclization does not take place even on prolonged heating.

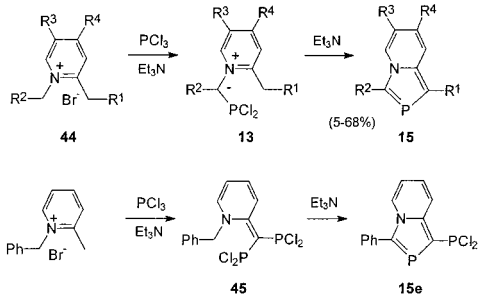
The above procedure is analogous to the synthesis of imidazo[1,2-*a*]pyridines from 1-alkyl-2-aminopyridinium salts.[33]

NCCC + P. Recently, a chiral anellated 1,2-azaphosphole **43** has been prepared from the condensation of the Schiff base **41** with $MePBr_2$ in the presence of a base followed by reduction of the resulting salt **42** with sodium in THF (Scheme 14).[86] Reduction of **42** with Mg proceeds differently with

Scheme 14



Scheme 15

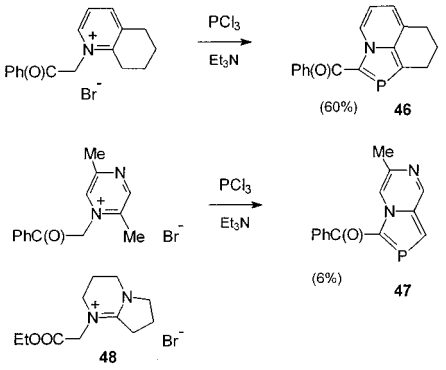


C−C coupling (adjacent to nitrogen) and gives a dimer useful in the Ni-catalyzed asymmetric hydrovinylation of styrene.[87] Attempts to utilize **43** in catalysis have not been mentioned. **41** was prepared from the reaction of (−)-(*R*)-myrtenal with (+)−(*R*)-phenylethylamine.[86]

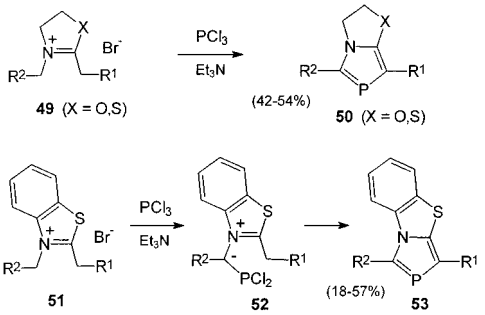
CNCC + P. 1,2-Dialkylpyridinium bromides condense with PCl_3 in the presence of Et_3N to give 1,3-azaphospholo[1,5-*a*]pyridines, i.e., 2-phosphaindolizines **15**.[13,88,89] Depending on the relative activation, the reaction may start either at the *N*-methylene group or the 2-methylene group. In the case of 2-ethyl-1-(ethoxycarbonylmethyl)pyridinium bromide **44**, R^1 = Me, R^2 = COOEt, and R^3 = R^4 = H, bearing a mildly activated *N*-methylene group, an intermediate pyridinium dichlorophosphinomethylide **13** could be isolated under mild conditions using toluene as the solvent. It underwent ring closure to 2-phosphaindolizine on heating with additional Et_3N.[13] But in other cases, such as **44** with R^2 = C(O)*t*Bu, C(O)-Ph, CN, 4-$O_2NC_6H_4$, the corresponding ylide could not be isolated though its formation was revealed by ^{31}P NMR ($\delta \approx 140$). Thus, the pyridinium salt bearing an activated *N*-methylene group first changes into the pyridinium ylide which subsequently reacts with PCl_3 to generate **13**. In the case of *N*-benzyl-2-methylpyridinium bromide **44** ($R^{1,3,4}$ = H, R^2 = Ph), the reaction starts at the 2-Me group as indicated by the isolation of **45**, which in the presence of more Et_3N undergoes cyclization to 1-dichlorophosphino-3-phenyl-2-phosphaindolizine **15e** (Scheme 15).[48]

The reaction may be extended to anellated pyridinium salts as shown for the condensation of 5,6,7,8-tetrahydro-1-phenacylquinolium bromide with PCl_3 to give **46**.[13] Introduction of a second nitrogen atom into the six-membered ring seems to disfavor the process. 2,5-Dimethyl-1-phenacylpyrazinium bromide gives 1,3-azaphospholo[1,5-*a*]pyrazine **47** under these conditions only in low yield (Scheme 16).[13] The behavior of the related pyridazinium and pyrimidinium salts toward PCl_3 and Et_3N has not been investigated so far. The bicyclic amidinium salt **48** did not undergo cyclocondensation with PCl_3 and Et_3N.[90]

Scheme 16



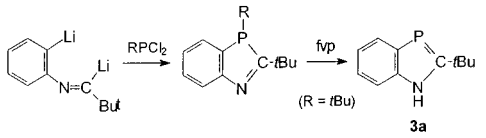
Scheme 17



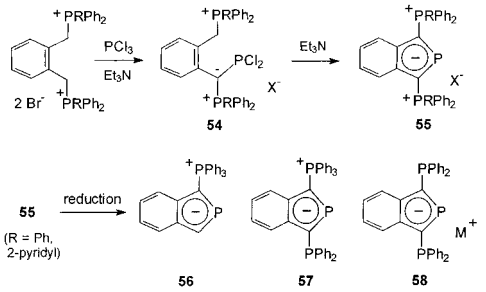
1,2-Dialkylcycloiminium ether and thioether **49** (X = O, R^1 = Me, R^2 = PhCO; X = S, R^1 = H, R^2 = COOEt) as well as *N*-alkyl iminium salts of π-excessive benzothiazoles **51**, with the N-alkyl groups activated each by an α-carbonyl substituent, condense however in reasonable yields with PCl_3 in the presence of Et_3N and provide the corresponding 1,3-azaphospholo[5,1-*b*]oxazoline,[91] -thiazoline,[92] and -benzothiazole[92] derivatives **50** and **53**, respectively (Scheme 17). Like in **44** (R^1 = H), mentioned above (Scheme 15), the methyl substituent in **49** (X = S, R^1 = H, R^2 = COOEt) is preferably attacked and leads to the 1-dichlorophosphino-substituted derivative **50** (X = S, R^1 = PCl_2, R^2 = COOEt) instead of the product with R^1 = H, even when only one equivalent of PCl_3 is used.[92] In the reaction of **51** (R^1 = Me, R^2 = 4-$O_2NC_6H_4$, CN), the intermediate benzothiazolium dichlorophosphinomethylides **52** could be isolated.[92] The non-phosphorus P → C analogues of **50** (X = S), the pyrrolo[2,1-*b*]thiazoles, have been prepared by different routes, namely, through [5+0] or [3+2]cyclocondensations.[93−95]

In the above examples, the activation of the carbon ends of the CNCC fragments was accomplished by electron withdrawal, by an α-carbonyl and the iminium function. Activation by metalation was used up to now only in the synthesis of heterophosphole precursors. Two equivalents of *tert*-butyllithium added to benzoisonitrile in the presence of TMEDA generate in an addition−orthometalation sequence a 1,4-dilithium reagent that undergoes consecutive disubstitution with $RPCl_2$ (R = Me, *t*Bu, Ph) at the two different nucleophilic sites forming 3*H*-1,3-benzazaphospholes.[96,97] The *tert*-butyl derivative on flash vacuum pyrolysis (fvp) eliminates the P-substituent, and the remaining fragment gives 2-*tert*-butyl-1*H*-1,3-benzazaphosphole **3a** (Scheme 18).[96]

Scheme 18



Scheme 19

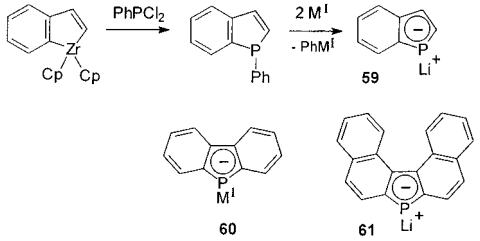


CCCC + P. Phospholide anions, extensively used in coordination chemistry,[5,19−22] are isoelectronic to heterophospholes and similar to classic organic heterol(id)es.[98] They have been prepared from reductive cleavage of the exocyclic P−C bond of phospholes. The latter have been synthesized, e.g., from the cycloaddition of a diene with dibromophosphine followed by dehydrobromination with a strong base like DBU or from substitution of 1,4-dilithium-1,3-dienes or zirconacyclopentadienes with RPX_2.[5,99,100]

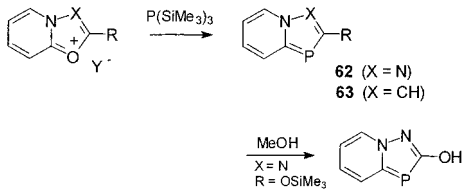
Cationic or neutral fused phospholides are less well investigated but find increasing interest in coordination chemistry and in the preparation of alkylene-bridged anellated diphospholes for use in transition metal diphosphine catalysts. *o*-Xylylenebis(triphenylphosphonium) bromide condenses with PCl_3 in the presence of Et_3N to give 1,3-bis(triphenylphosphonio)-benzo[*c*]phospholide, which was isolated as the bromide **55** (R = Ph, X = Br). The intermediate **54** could be detected by ^{31}P NMR. As analogues have also been synthesized.[101] More representatives **55** (R = Ph, 2-pyridyl, X = Cl, Br, F_3CSO_3) having other substituents at the phosphonio group and counteranions have been prepared in a similar manner.[102] The neutral monophosphonio species **56**, **57**, and alkali benzophospholide **58** have been obtained from the reduction of **55**.[103−105] Alkali naphthalenide,[103] magnesium,[103] and $NaBH_4$[104] have been used as the reducing agents (Scheme 19).

Potassium tetrahydrophosphindolide and dihydronaphtho[2,1-*b*]phospholide, respectively, with an isolated phospholide π-system were synthesized from the respective *P*-phenyl compounds and potassium in THF.[106] Lithium phosphindolide **59** is formed analogously from reductive cleavage of 1-phenylphosphindole with lithium in THF.[107,108] The generally long classic syntheses of the phosphindole ring system[100] have been replaced recently by the zirconacyclopentadiene method using $RPCl_2$ as electrophile.[108] The reductive cleavage of the phenyl groups from dianellated phenylphospholes, usually obtained from corresponding dilithiumbiaryls and $PhPCl_2$,[109−111] with alkali metals in THF, leads to salts of dibenzo[*b*,*d*]phospholide (9-phosphafluorenide) **60** (M = Li, Na, K, Cs)[109,110] and dinaphtho[2,1-*b*;1′,2′-*d*]phospholide **61** (M = Li)[111] (Scheme 20). The reaction can also

Scheme 20



Scheme 21



be carried out in liquid ammonia.[109b] A samarium bis(dibenzo[*b*,*d*]phospholide bis(THF) solvate was obtained from reductive P−P bond cleavage of the respective heterocyclic diphosphine with Sm activated by $HgCl_2$.[108] The required heterocyclic precursors are available from cyclocondensation of tetraphenylphosphonium bromide in the presence of excess amide or reaction of dilithiodiaryls with $PhPCl_2$.

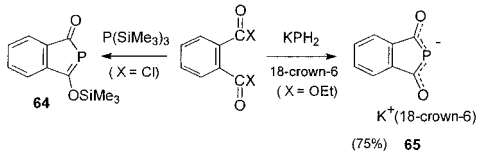
1.2. [4+1]Cyclocondensation Using Nucleophilic Phosphorus Reagents. Phosphines or their metal or silyl derivatives participate in a [4+1]-cyclocondensation to afford a heterophosphole ring. A four-membered chain may condense with a phosphorus reagent, or alternatively phosphorus may be a member of the four-membered chain which incorporates a carbon to complete the ring. The method is analogous to the synthesis of the benzo derivatives of pyrroles using amines.[27]

(a) [4+1]Cyclocondensation with P being Incorporated. The reagent of choice is $P(SiMe_3)_3$. In one case, potassium dihydrogenphosphide has been used.

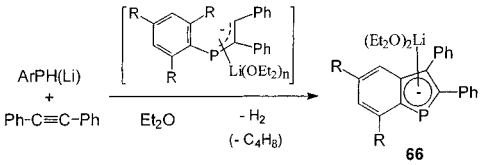
CNNC + P and CCNC + P. 1,3,4-Oxadiazolo[3,2-*a*]pyridinium salts condense with $P(SiMe_3)_3$ to give 1,2,4-diazaphospholo[1,5-*a*]pyridines, i.e., 3-aza-1-phosphaindolizines **62**.[112] Using the zwitterionic 1,3,4-oxadiazol-2-olato[4,5-*a*]pyridine (R = O^-, no Y^-) as the starting material, the 2-trimethylsilyloxy derivative **62** (R = $OSiMe_3$) is obtained which on reacting with methanol furnishes the corresponding hydroxy derivative. This can subsequently be O-acylated.[113] The methodology is applicable to 1,3-oxazolo[3,2-*a*]-pyridinium salts also which give 1,3-azaphospholo-[1,2-*a*]pyridines, i.e., 1-phosphaindolizines **63** under these conditions (Scheme 21).[112]

CCCC + P. The reaction of phthaloyl dichloride with $P(SiMe_3)_3$ leads to 3-trimethylsilyloxy-1*H*-isophosphindol-1-one **64** which is stable at low temperature but dimerizes at room temperature.[114,115] Other isophosphindoles having a partially or fully saturated six-membered ring have been prepared in similar manner.[115] Diethyl phthalate condenses with a stronger nucleophilic reagent, potassium dihydrogenphosphide, in the presence of 18-crown-6 to give the potassium 1*H*-isophosphindolin-1,3-dionide **65** (Scheme 22).[116]

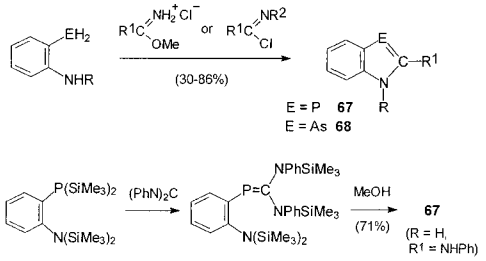
Scheme 22



Scheme 23



Scheme 24

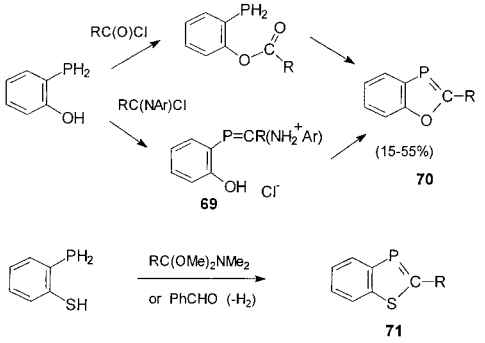


An uncommon [4+1]cyclization, involving addition and intramolecular 1,5-cyclocondensation, was observed in the reaction of aryllithium phosphides with tolane in ether. Whereas in DME a stable salt with isolated phosphaallyl anion and $Li(DME)_3^+$ cation was obtained,[117] in diethyl ether lithium 2,3-diphenylphosphindolides **66** (R = H, *t*Bu) were formed probably via an insufficiently stable η^3-coordinated $Li^+(OEt_2)_2$ species by elimination of hydrogen and concomitant loss of isobutene in the case of 2,4,6-tri-*tert*-butyl substituents (R = *t*Bu) (Scheme 23).[118]

(b) [4+1]Cyclocondensation with P in the Four-Membered Chain. This strategy was applied in condensations of phenylphosphines having an *ortho*-substituent like NHR, OH or SH with a suitable carboxylic acid[119−121] or carboxylic acid derivative[122−131] or aldehyde[132,133] to form benzoheterophospholes. 1,2-Diphosphinobenzene gives benzodiphospholes in related reactions.

NCCP + C. *N*-Primary *o*-aminophenylphosphines combine with various carboxylic acid derivatives to give 1,3-benzazaphospholes. For example, condensation with O-methylimidate hydrochloride leads to **67** (R = H, Me; R^1 = H, Me, Ph) (Scheme 24).[28,124,127,128] Imidoyl chlorides are also suitable C1 building blocks for the ring closure affording **67** (R^1 = *t*Bu).[128] Cyclization is favored by elimination of stable ammonium or anilinium salts, respectively. As shown for the related arsenic heterocycles **68**, the imidate hydrochlorides react primarily at the amino group whereas imidoyl chlorides add first to the E−H function.[134,135] Secondary *o*-ethylphosphino- and *o*-alkylarsinoanilines differ in their reaction with iminoester hydrochlorides giving **67**[127] by loss of the P ethyl group and nonaromatic 3*H*-3-alkyl-1,3-benzazarsoles,[134] respectively, which reveals much higher stability of two-coordinate phosphorus heterocycles as compared to the arsenic analogues.[124] Also, benzaldehyde[124] and veratraldehyde[133] have been used in

Scheme 25

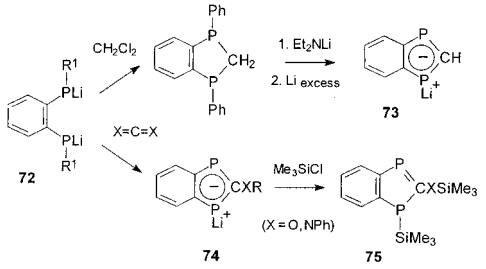


this condensation to give benzazaphospholes after elimination of hydrogen. In another approach, *o*-aminophenylphosphine was first persilylated. The resulting product on reaction with diphenylcarbodiimide followed by the action of MeOH gave 2-anilino-1,3-benzazaphosphole **67** (R = H, R^1 = NHPh) in high yield (Scheme 24).[121]

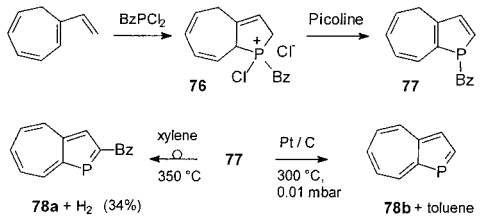
O/SCCP + C. 1,3-Benzoxaphospholes **70** have been prepared from the reaction of *o*-hydroxyphenylphosphines with either acyl chlorides followed by dehydration[125] or with arylimidoyl chlorides.[125,126] In one of the latter cases, the intermediate **69** could be isolated. Whereas the primary phosphaalkene formed from *o*-phosphinophenol and dimethylformamidoacetal, possessing *E*-configuration ($^2J_{P=CH}$ = 13.5 Hz), by steric reasons failed to give **70** (R = H) in favor of 1,3-diphosphetane,[125] the related but softer *o*-mercaptophenylphosphine condenses with amidoacetals or with benzaldehyde to give 1,3-benzothiaphospholes **71** (R = H, Me, Ph) (Scheme 25).[132]

PCCP + C. The above methodology has been used successfully also for the synthesis of 1,3-benzodiphospholes and their anions starting from *o*-diphosphinobenzene or its more reactive silyl or alkali metal derivatives **72**. The anions **73** and **74** are expected to be aromatic, and in P-silyl derivatives **75** a considerable stabilization by hyperconjugation and lowering of the barrier for planarization of phosphorus may be anticipated. The parent 1,3-diphosphindolide anion **73** was synthesized from **72** (R^1 = Ph) and dichloromethane followed by metalation with Et_2NLi and cleavage of the phenyl groups with lithium.[136] Reaction of *o*-bis(lithiophosphino)benzene **72** (R^1 = H) with diphenylcarbodiimide and subsequent silylation of the intermediate dilithio 2-anilino derivative **74** (XR = NPhLi) affords the disilylated derivative **75** (X = NPh).[120] Products of this type are formed also from persilylated *o*-diphosphinobenzene and phosgene imides ($RN{=}CCl_2$).[129] *o*-Bis(lithio-trimethylsilylphosphino)benzene **72** (R^1 = $SiMe_3$), obtainable from the reaction of P-persilylated *o*-diphosphinobenzene with *t*BuLi, reacts with electrophilic carbon reagents such as CO_2,[119] carbodiimide,[122] or an acyl chloride[122,123] to form 1,3-benzodiphospholides **74**, such as in the case of CO_2, **74** (XR = $OSiMe_3$), which can be silylated or alkylated to give **75** (X = O) or P-alkyl derivatives (Scheme 26). The latter can also be obtained from the corresponding monosodium phosphide with alkoxy-dimethylaminocarbenium tetrafluoroborate.[129,131] The cyclocondensation of *o*-diphosphinobenzene derivatives is often accompanied

Scheme 26



Scheme 27



by side products resulting from oxidative P−P bond formation.[130]

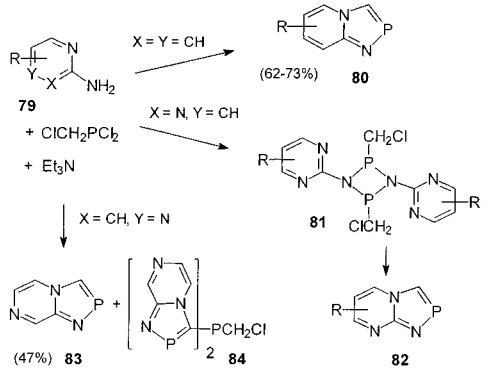
2. [4+1]Cycloaddition

[4+1]Cycloaddition reactions leading directly to anellated heterophospholes are unknown, but an example was reported to use this method for the access of suitable precursors. 1-Vinyl- and 2-vinyl-1,3,5-cycloheptatrienes on condensation with benzyldichlorophosphine in the presence of copper stearate give two isomeric dichlorotetrahydro-λ^5-phosphazulenes **76** which undergo dehydrochlorination with α-picoline to form the 1-benzyl-dihydro-1-phosphazulenes **77** (Scheme 27, one isomer shown). The latter on thermolysis in xylene yield 2-benzyl-1-phosphazulene **78a** through a 1,5-sigmatropic shift of the benzyl group and elimination of hydrogen,[137] while their gas phase pyrolysis in the presence of Pt/C gives exclusively the unsubstituted 1-phosphazulene **78b** (Scheme 27).[138]

3. [3+2]Cyclocondensation

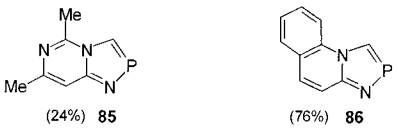
Chloromethyldichlorophosphine furnishes a C−P fragment in the construction of a heterophosphole ring by condensing with a three-membered chain. Its action parallels, although partially, that of α-haloketone in the construction of anellated azole rings. In contrast to the synthesis of anellated pyrroles from the condensation of 2-alkylazoles[93−95,139] and -azines[32,140] with α-haloketones, chloromethyldichlorophosphine, lacking a -M effect, appears to be unreactive toward these substrates. For example, it does not react with α-picoline in the presence of Et_3N even after several days.[141] But on the other hand, its condensation with 2-aminoazoles and -azines is found to be as facile as that of α-halocarbonyl compounds[33,93,94] furnishing a variety of anellated 1,4,2-diazaphospholes. Furthermore, reaction of chloromethyldichlorophosphine, like that of α-halocarbonyl compounds, proceeds often regioselectively. Regioselectivity of the reaction has been explained on the basis of the relative nucleophilicities of ring nitrogen and amino group.[142] This route has an additional

Scheme 28



advantage over the [4+1]cyclocondensation strategy—it gives access to the representatives having an unsubstituted carbon ring member adjacent to phosphorus.

2-Aminopyridines **79** (X = Y = CH) condense with chloromethyldichlorophosphine in the presence of Et_3N to give 1,4,2-diazaphospholo[4,5-*a*]pyridines, i.e., 1-aza-2-phosphaindolizines **80**, regiospecifically (Scheme 28).[40,142,143] Likewise, 1,4,2-diazaphospholo-[4,5-*a*]pyrimidines **82**,[40,142] 1,4,2-diazaphospholo[4,5-*a*]pyrazine **83**,[142] 5,7-dimethyl-1,4,2-diazaphospholo-[4,5-*c*]pyrimidine **85**,[142] and 1,4,2-diazaphospholo[4,5-*a*]quinoline **86**[142] are obtained regiospecifically from the condensation of $ClCH_2PCl_2$ with the respective amino derivatives. In the reaction of 4,6-dimethyl-2-aminopyrimidine **79** (X = N, Y = CHMe, R = 6-Me), it is possible to isolate the intermediate diazadiphosphetidine **81** (R = 4,6-Me_2).[40,142] The formation of **83** is accompanied by minor amounts of the bis(diazaphospholyl)-substituted phosphine **84** (Scheme 28).[142]



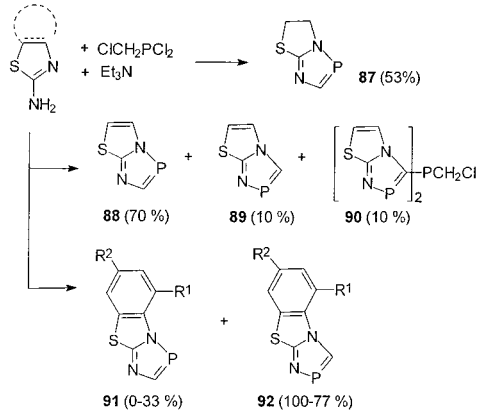
2-Aminothiazole and its 4,5-dihydro- and -benzo derivatives also react with chloromethyldichlorophosphine to give anellated heterophospholes, but the regioselectivity is different. The first two systems are attacked by the dichlorophosphino group preferably at the ring nitrogen atom and CH_2Cl at the amino substituent. While the reaction of 4,5-dihydro-2-aminothiazole proceeds regiospecifically affording 5,6-dihydro-1,3-thiazolo[3,2-*d*][1,4,2]diazaphosphole **87** only, two regioisomers, **88**, **89** and **91**, **92**, respectively, are formed each in the case of aminothiazole and aminobenzothiazole (Scheme 29). In the reaction of 2-aminothiazole, bis(diazaphospholyl)-phosphine **90** is detected as a minor side product. The regioselectivity of the condensation of 2-aminobenzothiazoles is influenced by the substituents in the benzene ring and is found to be opposite to that of the 2-aminothiazole.[40,142]

The above synthetic method appears to be quite general and it should be possible to extend it to other cyclic amidines.[144,145]

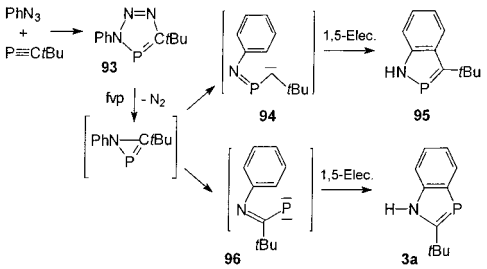
4. [3+2]Cycloaddition

[3+2]Cycloadditions of azomethine ylides and -imines with appropiate 1,3-dipolarophiles lead to anellated pyrroles and pyrazoles, respectively.[30,32,34,41,93,140] This synthetic strategy has been recently employed to introduce a two-coordinate phosphorus as a ring member by the use of phosphaalkynes as 1,3-dipolarophiles.[9] Azomethine ylides, α-diazoketones, and heptafulvene have been used as 1,3-dipoles, but no report has so far appeared about the application of azomethine imines. 1,3-Dipoles have been generated in situ from photolysis of selenadiazole and from diphenylmetallocenes also.

Scheme 29



Scheme 30

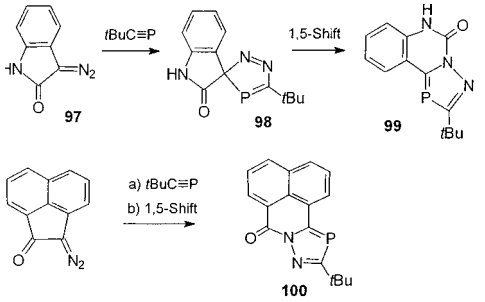


NNN + CP. Phenyl azide undergoes [3+2]cycloaddition with phosphaalkynes to give 3-phenyl-1,2,3,4-triazaphospholes **93** which on flash vacuum pyrolysis change to 1,2-benzo[*d*]azaphosphole **95** and 1,3-benzazaphosphole **3a** through the loss of nitrogen followed by 1,5-electrocyclization of the intermediate carbene **94** and phosphinidene **96**, respectively (Scheme 30). 3-Naphthyl-1,2,3,4-triazaphosphole formed from the reaction of naphthyl azide with phosphaalkynes shows similar behavior.[146,147]

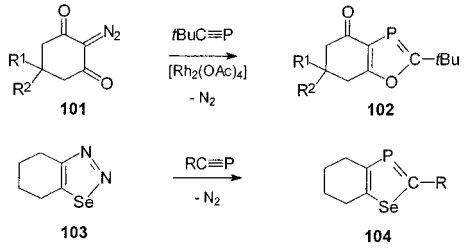
NNC + CP. The cyclic α-diazolactam **97** adds *tert*-butylphosphaethyne to form the spirocyclic product **98** which rearranges through a 1,5-sigmatropic shift to the anellated 1,2,4-diazaphosphole **99** favored by cyclodelocalization. Likewise, **100** and some other saturated or partially saturated anellated heterophospholes have been obtained (Scheme 31).[148−150]

OCC + CP and SeCC + CP. The presence of two electron withdrawing carbonyl groups lowers the reactivity of α-diazo-β-dicarbonyl compounds **101** toward *tert*-butylphosphaethyne considerably, and catalysis by $Rh_2(Oac)_4$ induces a change of the selectivity. Instead of anellated diazaphospholes (cf. Scheme 31) the anellated 1,3-oxaphospholes **102** (Scheme 32) are obtained.[151] Formation of a rhodium carbene complex followed by successive cycloaddition and 1,5-electrocyclization has been suggested as the

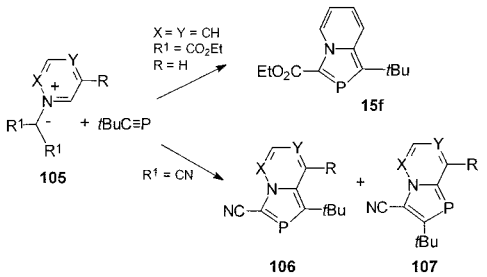
Scheme 31



Scheme 32



Scheme 33

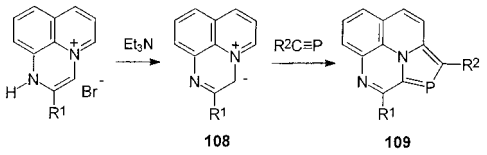


likely mechanism.[151] As shown with a selenium compound, similar products are accessible by elimination of nitrogen from anellated 1,2,3-heterodiazoles in the presence of a phosphaalkyne. Bicyclic 1,2,3-selenadiazole **103** on photolysis or thermolysis generates an electron deficient selenocarbene species which is trapped by a phosphaalkyne to form anellated 1,3-selenaphospholes **104** regiospecifically (Scheme 32).[152]

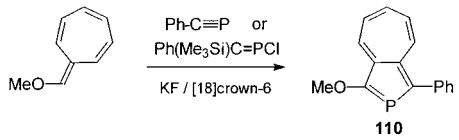
CNC + CP. Pyridinium bis(ethoxycarbonyl)methylide **105** (X = Y = CH, R = H, $R^1 = CO_2Et$) reacts with *tert*-butylphosphaethyne to give 2-phosphaindolizine **15f** regiospecifically.[153] The reactions of the pyridinium **105** (X = Y = CH, R^1 = CN), pyridazinium **105** (X = N, Y = CH, R^1 = CN), and pyrazinium **105** (X = CH, Y = N, R^1 = CN) dicyanomethylides with *tert*-butylphosphaethyne are however not regiospecific, a mixture of two regioisomers **106** and **107** being formed in each case. But regioselectivity is observed again on introducing a *tert*-butyl- or isopropoxy group in the α-position of the iminium fragment of **105** (X = Y = CH, R = *t*Bu or *i*PrO) (Scheme 33).[153]

[3+2]Cycloadditions of isoquinolinium and phthalazinium ylides with phosphaalkynes lead to isoquinoline- and phthalazine-anellated 1,3-azaphospholes, respectively.[153] Similarly, ylides **108**[154] generated from the deprotonation of 3*H*-pyrido[1,2,3-*de*]-quinoxalinium bromides undergo [3+2]cycloaddition with phosphaalkynes to give azaphosphaullazines, i.e., 4,9*b*-diaza-2-phosphacyclopenta[*c,d*]phenalene **109** regiospecifically (Scheme 34).[155]

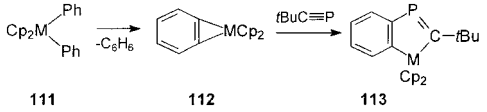
Scheme 34



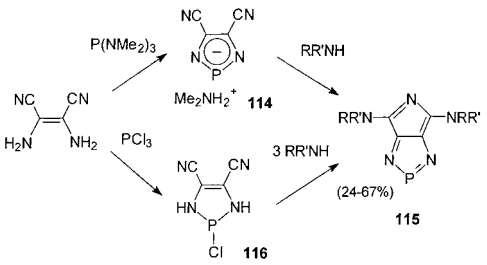
Scheme 35



Scheme 36



Scheme 37



CCC + CP. 8-Methoxyheptafulvene reacts with phenylphosphaethyne or its precursor 1-chloro-2-phenyl-2-trimethylsilylphosphaethene to give 2-phosphazulene **110** regiospecifically (Scheme 35). The reaction is carried out in the presence of KF and [18]-crown-6.[156]

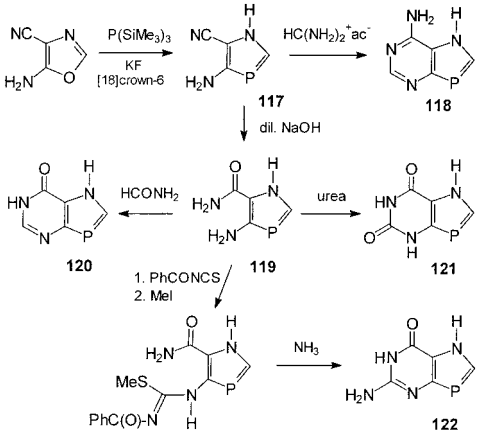
MCC + CP (M = Ti, Zr). Bis(cyclopentadienyl)-diphenyltitanium and -zirconium **111**, M = Ti, Zr react with *tert*-butylphosphaethyne to give benzometallaphospholes **113**. The reaction proceeds through dehydrobenzometal complex **112** which undergoes [3+2]cycloaddition with phosphaalkyne to form the final product (Scheme 36).[157]

D. Synthesis by Anellation of a Heterophosphole Ring

The high reactivity of P═C or P═N bonds in many heterocycles with low-coordinated phosphorus may be the reason that attempts to build up fused rings at functionally substituted phospholes or heterophospholes have found little attention. However, the resistance of some π-excessive heterophospholes toward addition reactions of NH- or OH-functional compounds enables such reactions. An early example is the ring closure reaction of dimethylammonium 4,5-dicyano-1,3,2-diazaphospholide **114**, prepared from the condensation of diaminomaleodinitrile with $P(NMe_2)_3$, with secondary amines which affords 4,6-bis(dialkylamino)-1,3,5-triaza-2-phosphapentalenes **115** (Scheme 37). A similar reaction takes place with 2-chloro-dihydro-diazaphosphole **116**.[24,25]

Broader use of this strategy was made recently in a patent claiming syntheses of phospha-analogous

Scheme 38



nucleobases, mainly pyrimidine-anellated 1,3-azaphospholes, but also some pyrimidine-anellated 1,3,2-diazaphospholes and phospholes as well as triazine-anellated 1,3-azaphospholes.[26,158] 1-Amino-1*H*-1,3-azaphospholo[4,5-*d*]pyrimidine **118** (Scheme 38) and some of its derivatives have therapeutic potential as cytokine inhibitors and exhibit, e.g., superior activity against TNF-α and IL-1*β* production in some cell cultures but is not toxic to mice in a five-day study. Some compounds, documented by a detailed description of synthesis and characteristic analytic and spectroscopic data, are depicted in the following. The key compounds for syntheses of various 1,3-azaphospholo[4,5-*d*]pyrimidine derivatives are 4-amino-1*H*-1,3-azaphosphole-5-carbonitrile **117**, obtained by O,P-exchange from the respective nitrile-activated oxazole and $P(SiMe_3)_3$ in the presence of naked fluoride (KF/[18]crown-6), and its hydrolysis product **119**. Condensation of **117** with formamidinium acetate affords the NH-tautomer **118** of phospha-adenine, whereas fusion of **119** with formamide or urea gives the hypoxanthine or xanthine analogues **120** and **121,** respectively. The guanine analogue **122** is formed from the reaction of **119** with benzoylisothiocyanate followed by *S*-methylation and ring closure with NH_3 in DMF (Scheme 38).[26,158] Derivatives of 1,3-azaphospholo[5,4-*d*]pyrimidine have also been claimed, but neither full procedures nor substance data are given in this case.

III. Structural and Spectral Characteristics

A. NMR Spectra

The ^{31}P NMR chemical shifts of a large number of anellated heterophospholes covering the literature up to mid-1993 are compiled in a review.[2] Two earlier overviews on low-coordinated phosphorus compounds[18,159] also include some of these systems. The ^{31}P NMR chemical shifts of two-coordinate phosphorus in fully unsaturated anellated heterophospholes lie in the range $\delta = +495$ to -5, but the majority of the values fall between $\delta = +300$ and $+50$. The actual value of the chemical shift is influenced by several factors, such as ring members adjacent to P, additional heteroatoms, size of the ring anellated, position of anellation, and nature of the α-substituent. To illustrate the effects of these structural features, $\delta^{31}P$ values of some selected anellated heterophospholes are reproduced in Figure 1.

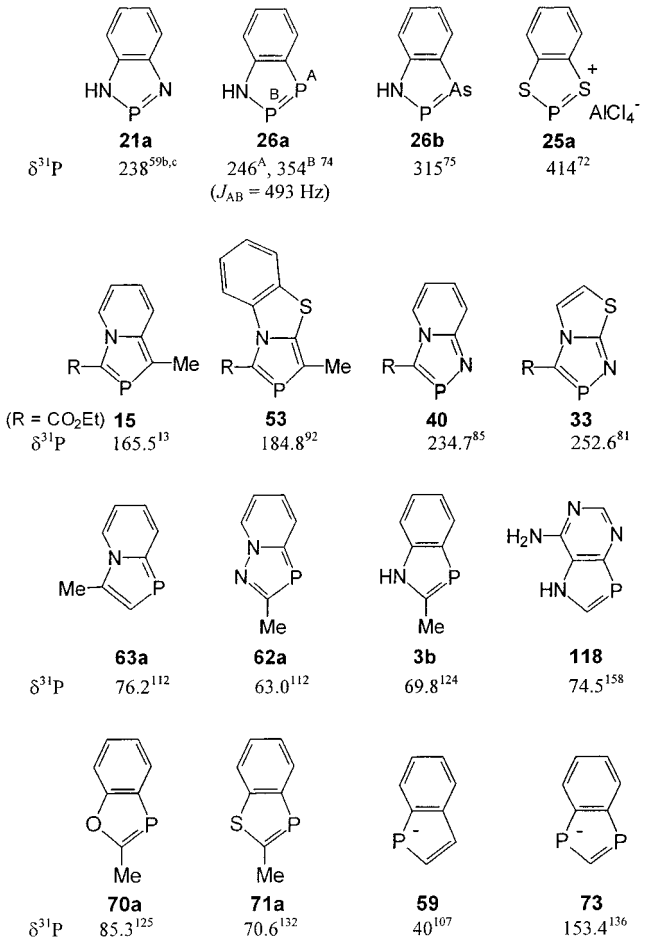


Figure 1. ^{31}P NMR Chemical Shifts of Some Anellated Heterophospholes

The ^{31}P values depending on the nature of the ring members adjacent to two-coordinate phosphorus tend to shift downfield in the order C < N < P, As < S(Se) (cf. **21a**, **26a, 26b**, **25a**, etc.). With identical adjacent atoms, anellation of heterophospholes to a five-membered ring causes a downfield shift by about 20 ppm as compared to anellation to a six-membered ring (cf. **15**, **53; 40**, **33**; R = COOEt). However, more examples are necessary to generalize this aspect. The ^{31}P value is remarkably influenced by the type of anellation of the heterophosphole ring, which is illustrated by pyrido- or benzo-derivatives of 1,3-azaphospholes, respectively, for which all the three types of anellation have been accomplished (cf. **15** (R = COOEt), **63a**, **3b**). It is found that two-coordinate phosphorus in **63a** (1,2-anellation) and in **3b** (4,5-anellation) is highly shielded as compared to that in **15** (1,5-anellation). As shown by MNDO calculations, the *π*- and total electron density is higher in 1- than in 2-position of indolizine and particularly its 1- or 2-phospha-analogues.[13] Besides the electronic effect, the adjacent bridgehead carbon atom in **63a** and **3b** may effect the shielding. Furthermore, the substituents have a strong influence on the phosphorus resonance. The effect of an α-substituent on $\delta^{31}P$ in anellated heterophospholes is similar to that in monocyclic heterophospholes[18,160] and in acyclic two-coordinate phosphorus com-

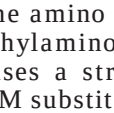
pounds.[160,161] This is well documented for 1-unsubstituted or 1-methyl-1*H*-1,3-benzazaphospholes with various substituents in 2-position. A group with a +M effect like the amino group in 2-anilino- ($\delta = 7.6$[121]) or 2-(dimethylamino)-1,3-benzazaphosphole ($\delta = -4.6$[124]) causes a strong shielding effect, whereas conjugated -M substituents induce efficient deshielding (cf. 2-carboxy-1-methyl-1,3-benzazaphosphole, $\delta = 127.4$,[128] $\Delta\delta \approx 57$). The electronic influence of the substituents in 2-phosphaindolizines is demonstrated by a nearly linear correlation between ^{31}P NMR chemical shifts and the total charge density on phosphorus with different substituents in 3-position, established by PM3 calculations.[89] The ^{31}P NMR signal of the two-coordinate phosphorus shifts further downfield on introducing one more phosphorus in the heterophosphole ring.[74,75,120,123] In 1,3-benzodiphospholes, the three-coordinate phosphorus does not participate in the π-delocalization, as revealed by its chemical shift and also by the absence of any effect on the strong downfield shift of two-coordinate phosphorus when three-coordinate P is oxidized.[123] But in 1,3-diphospholide anions both phosphorus atoms are equivalent and give a signal at much higher field,[123] which may be attributed to π-coordination of alkali metal counterions. The one bond P−P coupling constants in 1*H*-1,2,3-benzazadiphospholes ($J_{PP} = 493-496$ Hz[74,75]) and in 3-triphenylphosphonio-1,2-benzodiphospholides ($J_{PP} = 476-480$ Hz[45]) compare well with those in diphosphenes.[160,161] The two bond P−P coupling constants in 1*H*-1,3-benzodiphospholes vary from 9 to 39 Hz.[119,120,123,131] But in 1-phosphino substituted 2-phosphaindolizines $^2J_{PP}$ is influenced by the substituents on the exocyclic phosphorus.[162]

^{31}P solid-state NMR studies of benzodithiaphospholium and benzo-1,3,2-thiazaphospholium salts indicate phosphorus chemical shift anisotropy in excess of 500 ppm. Orientations of the principal components of the ^{31}P chemical shift tensor agree well with the ab initio chemical shielding calculations. The results also confirm integration of the two-coordinate phosphorus in the 10π system.[163]

^{13}C and ^{1}H NMR data for a number of anellated heterophospholes are available. The characteristic feature of the ^{13}C NMR spectrum is the coupling of the heterophosphole ring carbons with phosphorus. The typical magnitudes are for one bond P−C coupling $^1J_{PC} = 38-64$ Hz (formal single bond $^1J_{PC} = 38-47$ Hz, formal double bond $^1J_{PC} = 45-64$ Hz) and for two bond P−C coupling $^2J_{PC} = 2-18$ Hz. Phosphorus coupling to carbon atoms of the anellated ring over three (1−20 Hz), four (1−5 Hz), five (1−4 Hz), and even six bonds (1 Hz) has been observed.[13,31,89,92] In the anellated heterophospholes with a -P=CH- structural unit, $^2J_{PH}$ ranges from 29 to 56 Hz which is of the same order as in 2-phosphaalkenes.[160]

The structural similarity between the anellated heterophospholes and the related non-phosphorus systems is exemplified by ^{13}C and ^{1}H chemical shifts of a few representatives of each type (Table 1). The presence of phosphorus causes significant deshielding of the adjacent carbon and α-hydrogen nuclei which results from the field effect associated with its unshared electrons. The ring current is not much affected by the CH/P exchange as indicated, e.g., by the similar typical low-field signals of NMe protons of 1-methylindole ($\delta = 3.65$[164]) and 1-methyl-1,3-benzazaphospholes ($\delta = 3.47-3.79$[128]), which are not directly subjected to the anisotropic influence of the P=C fragment. ^{15}N chemical shifts of 1,4,2-diazaphospholo[4,5-*a*]pyridines[85,143] and 1-phenyl-1,3,2-benzodiazaphospholium tetrachloroaluminate[60] have been reported.

Table 1. ^{13}C and ^{1}H Chemical Shifts of Selected Anellated Heterophospholes and the Related Non-Phosphorus Analogues

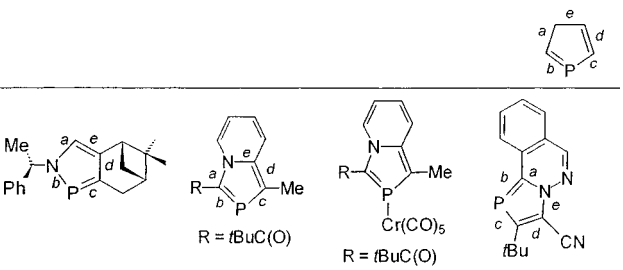
				
^{13}C	($CDCl_3$)[142]	(neat)[165]	(CD_3OD)[127]	($CDCl_3$)[167]
^{1}H	($CDCl_3$)[142]	($CDCl_3$)[166]	(CD_3OD)[127]	(acetone)[168]
C-1				
C-2		134.05	159.5	123.7
C-3	151.2	113.41		101.8
C-4			142.1	119.9
C-5	127.8	126.96	129.4	121.1
C-6	112.7	112.19	120.8	119.0
C-7	126.5	124.59	125.3	110.4
C-8	119.3	117.62	115.3	127.0
C-9	152.1	145.6	144.0	134.8
H-1			>10	10.12
H-2		7.77	8.53	7.27
H-3	8.87	7.60		6.45
H-5	8.14	8.05	7.86	7.55
H-6	6.73	6.55	7.07	7.00
H-7	7.17	6.97	7.07	7.08
H-8	7.52	7.97	7.45	7.40

B. X-ray Crystal Structures

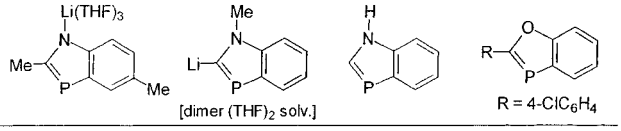
X-ray crystal structures of a variety of anellated heterophospholes are now available which reveal some general patterns of these molecules. The bond distances in the heterophosphole ring and the bond angle at the two-coordinate phosphorus of a few representative anellated 1,2- and 1,3-heterophospholes are given in Table 2.

The CH/P exchange in the five-membered ring does not disturb its planarity. The angle at the phosphorus atom, which ranges from 88 to 100°, is much smaller than the respective angle in the non-phosphorus analogues and decreases further on going to arsenic analogues, 83.3° in the strictly planar 1*H*-1,3-benzazarsole.[169] This may be attributed to the longer bonds at phosphorus (or arsenic) and the inert s-pair effect.[170] The other angles within the five-membered rings are in the range 110° and 116°, halfway between the average pentagon angle of 108° and 120° of ideal sp^2 hybridization. The P−C distances range from 170 to 180 pm as compared to 167 and 185 pm for the localized double and single PC bonds in phosphaalkenes.[8c] The two bonds at phosphorus are usually not equal; the difference in lengths is influenced by the π-delocalization and symmetry within the ring. Thus, the 3-*t*BuCO group in 2-phosphaindolizine **15** (R^1 = Me, R = *t*BuCO, $R^3 = R^4$ = H) alters the lengths of the two bonds at phosphorus by affecting the π-delocalization within the ring through exocyclic conjugation.[89] The $Cr(CO)_5$ complex of this compound exhibits a much smaller difference in the two P−C bond lengths since the coplanar arrange-

Table 2. Bond Lengths (in pm) and Angles (°) at Phosphorus in Selected Anellated Heterophospholes



a:	136.7(1)	140.0(4)	138.2(3)	136.5(4)
b:	170.6(1)	174.7(3)	172.4(2)	173.4(4)
c:	171.2(1)	170.8(4)	171.7(2)	175.4(3)
d:	140.8(1)	139.5(5)	138.7(3)	137.1(5)
e:	137.7(1)	139.5(4)	140.4(3)	137.2(2)
bc:	90.2(1)	91.9(2)	93.51(11)	89.9(2)
ref.	86	89	171	153



a:	135.3(5)	138.3(3)	135.1(11)	136.9(3)
b:	174.1(5)	173.1(9)	169.5(9)	171.2(7)
c:	177.8(5)	178.9(3)	180.7(7)	178.8(4)
d:	142.8(6)	140.2(3)	142.2(9)	139.3(3)
e:	138.7(5)	138.8(3)	137.1(9)	137.4(9)
bc:	88.0(2)	92.26(11)	88.2(4)	88.1(1)
ref.	176	175	172	174

ment of the *t*BuCO group is sterically prevented.[171] The quite different P−C bond lengths in 1*H*-1,3-benzazaphosphole[172] are in part due to the low symmetry. The ratio of these two bonds, adjacent and nonadjacent to the benzene ring, is found in the same (1*H*-1,3-benzazarsole[169]) or only slightly reduced magnitude also in indole[173] and even in the somewhat less aromatic 2-*p*-chlorophenyl-1,3-benzoxaphosphole.[174] Repulsion of π-charge density from C2 toward the benzene ring in 2-lithium-1-methyl-1,3-benzazaphospholide, a dimer with C-bridged $Li^+(THF)_2$ cations, reduces these differences.[175] Also in the monomer lithium 2,5-dimethyl-1,3-benzazaphospholide, with lithium coordinated at nitrogen and three THF molecules, the differences are smaller.[176] The angle at phosphorus depends on the size of the other heteroatom(s) in the ring. In the case of O,N, it ranges from 88 to 92°, but increases to 94−100° when S or additional P is present. Coordination on phosphorus increases the endocyclic angle on it slightly.[171] The experimental and PM3 calculated structures of 1,5-, 1,2-, and 4,5-anellated 1,3-azaphospholes have been compared.[89]

Complexes with phospholide ligands are structurally well investigated, and a variety of coordination modes is known,[5,19−22,98] but the knowledge of structures of fused phospholides and heterophospholides is quite limited and growing only since the mid-90s. Lithium phosphindolide forms two independent π-complexes with η^5- and η^3-coordination,[118] and similarly a samarium(II) indolide complex prefers η^5-coordination.[108] In samarium(II) dibenzophospholide, the metal is bound to phosphorus.[108] The preference of the η^1(P) coordination mode was attributed to the lower aromaticity due to dianellation. The feasibility of π-complexes of phosphonioisoindolides was shown very recently by preparation and X-ray structural characterization of a η^5 coordinated $LCr(CO)_3$ complex.[104] The majority of the recently reported and structurally investigated (di)phosphonioisoindolide complexes are however η^1(P) [$Cr(CO)_5$,[104] Ag(THF)(OSO_2CF_3), and $Ag(OSO_2CF_3)_2$[102e]] or dinuclear μ_2(P) bridging Cu[177] and Ag[104] complexes. A η^1(P)-benzodiphospholide-$W(CO)_5$ as well as a η^5-benzodiphospholide-$Mo(CO)_3$ complex have been characterized by X-ray crystal structure analysis.[122,123] π-Complexes of anellated heterophospholes containing other heteroatoms than phosphorus have not been reported so far.

C. Quantum Chemical Calculations and PE Spectra

Heteroaromaticity has been a subject of controversial discussion since it has not been satisfactorily defined, but investigations by Schleyer et al.[178] have shown that it reflects well-correlated structural, thermodynamic, and magnetic properties of the unsaturated five-membered heterocycles including phospholes. Theoretical calculations have been carried out also of a limited number of anellated heterophospholes. Close similarity of P=C with C=C rather than with N=C analogues has been established by ab initio calculated ionization energies of several heterocycles including 1,3-benzazaphospholes and 1,3-benzoxaphospholes[6] as well as cyclohexa[d]- and cyclohepta[d]-1,3-selenaphosphole[179] and their corresponding non-phosphorus analogues. The similar conjugative interaction between the P=C or the C=C unit and the rest of the ring and the similar delocalization energy of P=C and C=C moieties have been confirmed also by investigations of isodesmic reactions, i.e., ab initio calculated energies of isodesmic reactions, bond-separation reactions, and ring fragmentation reactions.[6,179,180] He(I) PE spectra of 1,3-benzazaphospholes and -arsoles,[181] 1,3-benzoxaphospholes and -arsoles,[181] as well as of 1,2,3-benzazadiphospholes[75] and cyclohexa[*d*]- and cyclohepta[*d*]-1,3-selenaphospholes[179] correlate well with the calculated orbital energies using either MNDO, CNDO/S, or ab initio methods and indicate strong interactions between the E=C bond (E = P, As) and the π-system of the molecule. In isomeric σ^3-1,3-benzazaphospholes and -arsoles, interaction of the P or As lone pair with the π-system is weak.[181] Recent quantum chemical studies (B3LYP-6-311+G** level) reveal however low or even zero inversion barriers for the bridgehead tricoordinated phosphorus of phosphaindolizines, diaza- and diphosphaindolizines (3.5, 2.8, 0 kcal/mol), and appreciable aromaticity of the planar or nearly planar rings. It is likely that the chemistry of such, up-to-now experimentally unknown compounds, differs considerably from that of the phosphines or nonplanar phospholes.[182]

Semiempirical calculations confirm the close similarity of indole[183,184] and indolizine[32,184,185] with their P analogues, 1,3-benzazaphosphole[186] and 2-phosphaindolizine,[13] respectively, and the maintenance of the electron-rich character of the five-membered ring, but the distribution of π- and total charge densities in the five-membered ring being somewhat changed (Table 3). The introduction of the phosphorus atom

Table 3. Comparison of Selected Calculated Total and π-Charge Densities and HOMO−LUMO Energies of Some Benzo- (A)[a] and Pyrido-anellated (B)[b] Heterophospholes and Their Non-Phosphorus Analogues

A

B

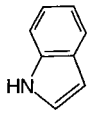
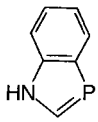
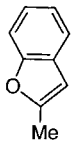
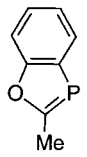
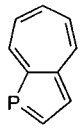
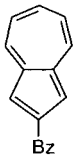
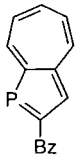
total (π-electron) charge at	**A** (N)	**A** (CH)	**A** (P)
(1) X	−0.218	−0.114	0.111
	(−0.223)	(−0.092)	(−0.258)
(2) C	0.107	0.126	−0.074
	(0.050)	(−0.035)	(0.031)
(3) N	−0.268	−0.235	−0.226
	(0.322)	(0.365)	(0.357)
HOMO (eV)	−8.86	−8.71	−8.60
LUMO (eV)	−0.02	0.14	−0.37

total (π-electron) charge at	**B** (CH/CH)	**B** (P/CH)	**B** (CH/P)
(1) X	−0.122	0.092	−0.237
	(−0.102)	(−0.277)	(−0.075)
(2) Y	−0.097	−0.203	0.146
	(−0.058)	(−0.024)	(−0.198)
(3) C	−0.046	−0.049	−0.147
	(−0.123)	(−0.118)	(−0.060)

[a] MNDO (MOPAC 6.0, Stewart, J. J. P. QCPE, Nr 455, 1989), minimum control by FORCE.[186] [b] MNDO (Thiel, W. QCPE, Nr 353, 1978) calculated values.[13]

lowers the π-charge density at the adjacent carbon atom somewhat in favor of phosphorus while the opposite is found for the total charge density in this case.[13] The local differences between the C/P analogues as well as lower HOMO energies and HOMO−LUMO gaps of the heterophospholes are reflected in the different reactivity of the latter (see Section IV) and their non-phosphorus analogues. Similarly, reactivity patterns of 1,3-benzazaphospholes and 1,3-benzodiphospholes and their anions have been explained by MNDO calculations of the model systems.[187] MNDO calculations of a 1,3,5-triaza-2-phosphapentalene derivative confirm its zwitterionic character and locate HOMO and LUMO at the anionic 1,3,2-diazaphosphole part and the cationic 1,3-diamino-2-azaallyl part of the molecule.[25] Theoretical calculations of the carbene-like 1,3,2-benzodiaza-, 1,3,2-benzothiaza-, and 1,3,2-benzodithiaphospholium cations show that the HOMO−LUMO gap decreases in this order and that the LUMO is localized mainly on phosphorus which makes it the preferred site for nucleophilic attack. Energy levels and atomic coefficients in the π-orbitals of 1,3,2-benzodithiaphospholium cations and its carbon analogue are very similar.[69] A close relationship with these systems was shown for the isophosphindolide anion and the diphosphonioisophosphindolide cation by ab inito calculations, except that the closely spaced π_4- and π_5-orbitals are exchanged for the latter. Homodesmic reaction energies reveal that π-electron delocalization is more important in isophosphindolide anions but adds also significantly to the stability of diphosphonioisophosphindolide cations.[102d] MINDO/3 and extended Hückel calculations of the isophosphindolide-1,3-dione anion have been carried out to explain its maroon color.[116]

Table 4. λ_{max} Values of Some Anellated Heterophospholes and Their Non-Phosphorus Analogues

				
λ_{max} [nm] (log ε)	216 (4.54)[188] (EtOH)	226 (2.79)[127] (MeOH)	246 (4.09)[188] (EtOH)	272 (3.59)[125] (MeOH)
				
λ_{max} [nm] (log ε)	695 (2.25)[189] (Hexane)	730 (2.23)[138] (Heptane)	677 (2.11)[189] (Hexane)	700 (2.43)[137] (Hexane)

D. UV Spectra

UV spectra of only a few anellated heterophospholes have been reported.[25,62,114,121,123,125−128,137,156] The available data, however, confirm the related electronic nature of the analogous CH/P and even As heterocycles by similar band shapes and regular shift trends. The CH/P exchange induces a bathochromic shift in the long-wave λ_{max} values (Table 4) which is enhanced in the As analogues and corresponds with a decreasing HOMO−LUMO gap (for indole/benzazaphosphole cf. Table 3).

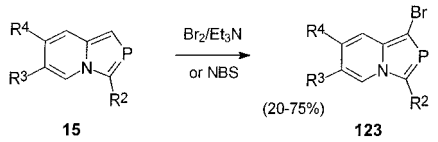
E. IR Spectra

IR spectra have not been used much in the structure elucidation of anellated heterophospholes, although data are available for a few of these compounds.[62,69,71−73,107,113−115,123,124,128,146,149] They are valuable to characterize functional groups, e.g., esters, but the coupled P=C valence vibrations cannot be assigned easily as is the case of species with isolated P=C bonds.

F. Mass Spectra

It has been found that the fragmentation of 3-aza-2-phosphaindolizine occurs similar to that of its non-phosphorus analogue, pyrazolo[1,5-*a*]pyridine.[190] In analogy to the loss of HCN from the molecular ion of the latter, the molecular ion of 3-aza-2-phosphaindolizine splits off P≡N, as supported by the appearance of a metastable ion.[80] Mass spectral fragmentation patterns of 2-phosphaindolizines,[89] 3-aza-2-phosphaindolizines,[80] 1,3-diaza-2-phosphaindolizines,[56b] 1,3-azaphospholo[5,1-*a*]isoquinoline,[50] 5,6-dihydro-1,3-azaphospholo[5,1-*b*]oxazole,[91] and 1,3-benzoxaphospholes[125] have also been described. Mass spectral data are available for many further heterophospholes (1,3-benzazaphospholes,[127,128] 1-phosphaindolizines,[112] 3-aza-1-phosphaindolizines,[112] 1-aza-2-phosphaindolizines,[142] 1,3-benzodiphospholes,[123,131] 1,2,3-benzazadiphosphole,[74] 1,2,3-benzazarsaphosphole,[75] 1,3,2-benzazathiaphospholium tetrachloroaluminate,[69] 1,3,2-benzodithiaphospholium tetrachlo-

Scheme 39



roaluminate,[72] 2-benzyl-1-phosphaazulene,[137] and 1,3-benzometallaphospholes [M = Ti, Zr][157]).

IV. Reactivity

Chemical reactivity of the anellated heterophospholes in comparison to their non-phosphorus analogues has been investigated to much lesser extent. The results obtained so far, however, confirm analogy on one hand but at the same time reveal some distinct dissimilarities on the other hand. The CH/P exchange in the five-membered ring does not alter its electron-rich character, which makes it, like in indole[191,192] and indolizine,[30,32,193] the center of reactivity. But some reactions commonly observed for heterocyclic compounds are not given by anellated heterophospholes or they occur less readily and therefore, or due to some other reasons, they proceed more selectively.[162] Thus, in contrast to indolizines which form complex mixtures on bromination,[193] 2-phosphaindolizines undergo bromination in 1-position regioselectively,[162] probably due to slightly lower π-charge excess in this position as compared to indolizine.[13] Furthermore, presence of a polar P=C (as compared to C=C) and easier polarizable moiety and the lone electron pair at phosphorus introduce additional functionalities in the system which let these compounds undergo some reactions that are not shown by the related non-phosphorus systems. Examples are η^6-, η^5-, or N-coordination in indole or indolide transition metal complexes,[98,194] while in case of its phosphorus analogous 1,3-benzazaphosphol(id)e complexes only P-coordination is observed.

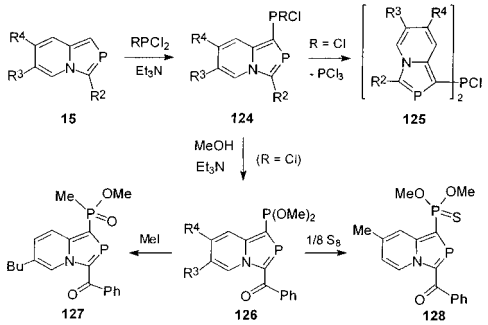
A. Substitution Reactions

1. Substitution at Carbon

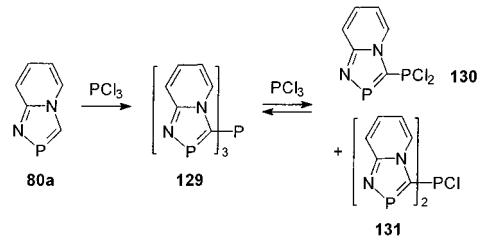
2-Phosphaindolizines are much less reactive than indolizine toward electrophilic substitution. In contrast to the latter,[32] 1-unsubstituted 2-phosphaindolizines fail to react with MeCOCl, PhCOCl, or Me_3SiCl even on prolonged heating in the presence of Et_3N.[195] The reduced reactivity of 2-phosphaindolizines has been correlated with the decrease of π-charge at the 1-position.[13] 2-Phosphaindolizines however react with stronger electrophiles such as Br_2 and PCl_3. In contrast to indolizine, which reacts with bromine to form a complex mixture of several products,[193] the reaction of 2-phosphaindolizines **15** occurs regioselectively to give 1-bromo derivatives **123**, although in poor yields. The yields are improved by the reaction with bromine in the presence of Et_3N or with *N*-bromosuccinimide (Scheme 39).[162,196]

Like indolizines,[197] 1-unsubstituted 2-phosphaindolizines can be phosphinylated by PCl_3 or $PhPCl_2$ (but not by Ph_2PCl) in the presence of Et_3N to give **124**.[162] A similar reaction is given by a 1,3-azaphospholo[1,5-*a*]pyrazine derivative.[162] 1-Dichlorophosphino-2-phosphaindolizines **124** (R = Cl) tend to

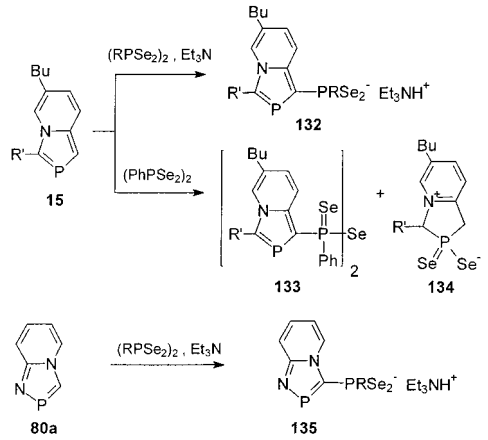
Scheme 40



Scheme 41



Scheme 42



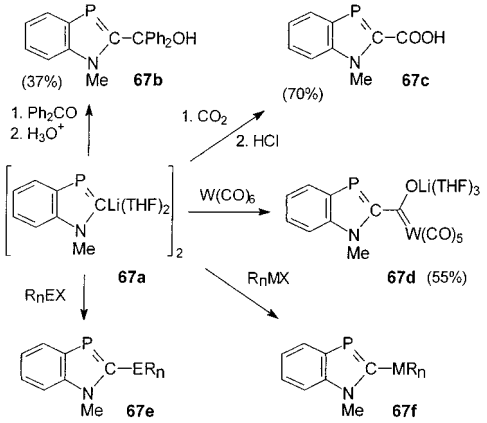
disproportionate in solution to form bis(2-phosphaindolizinyl)chlorophosphines **125**.[162] Furthermore, methanolysis of **124** yields 1-dimethoxyphosphino derivatives **126** which undergo MeI-catalyzed Arbuzov rearrangement to form **127** or can be oxidized by sulfur at the exocyclic phosphorus to yield **128** (Scheme 40).[162] Two-coordinate phosphorus remains unaffected under these conditions.

3-Unsubstituted 1-aza-2-phosphaindolizine **80a** reacts with PCl_3 to form **129** which exists in equilibrium with **130** and **131** in the presence of PCl_3 at room temperature (Scheme 41).[40] Exocyclic phosphorus in **129** can be oxidized with oxygen, sulfur, or selenium.[40]

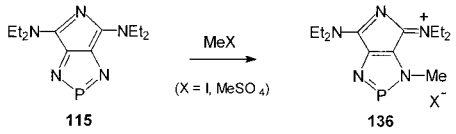
2-Phosphaindolizine **15** and 1-aza-2-phosphaindolizine **80a** react with selenium homologues of Lawesson's reagent $(RPSe_2)_2$ (R = Ph, 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$) in the presence of Et_3N to form selenophosphinates **132** and **135**, respectively (Scheme 42). ^{31}P NMR studies show that in the absence of Et_3N, 2-phosphaindolizine **15** forms a mixture of two diastereoisomers of the selenoanhydride **133** and the zwitterionic diselenophosphinate **134** as well.[198,199]

2-Lithioindoles are useful intermediates for the preparation of a variety of 2-substituted indoles.[200,201]

Scheme 43



Scheme 44



A related approach is possible for 1,3-benzazaphospholes and -arsoles as well. *t*BuLi attacks 2-unsubstituted N-alkyl derivatives to form regioselectively and nearly quantitatively the 2-lithio derivatives which are isolable and belong to the most stable C-lithiated E=C compounds (E = P, As). As shown by X-ray crystal structure analysis of the bridging dimer **67a**, lithium is bonded to carbon indicating a lower stability of an alternative lithium phosphidoaminocarbene structure. Substitution reactions of **67a** with various electrophiles occur regioselectively at carbon to give 2-functionalized derivatives **67b**−**d** as well as organoelement and organometallic substituted representatives **67e** (ER_n = $SiMe_3$, PPh_2, P(O)Ph_2, SMe) and **67f** (MR_n = $SnMe_3$, $Fe(CO)_2Cp$) (Scheme 43).[128,135,175] The carbinol **67b** as well as the acid **67c** are surprisingly stable; their OH groups do not add to the P=C bond. **67c** does not form a zwitterion but exists in the COOH form indicating integration of the N lone electron pair into the aromatic π-system. A crystal structure analysis gives evidence that the carbene and benzazaphosphole π-planes in **67d** are perpendicular, and thus the metals have no contact to phosphorus. Attempts to replace the $SiMe_3$ group of **67e** (ER_n = $SiMe_3$) by acetylation were not successful; bromination of this species led to a mixture of products.[128,175]

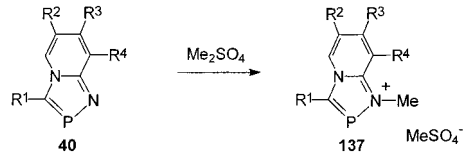
2. Alkylation and Substitution at Nitrogen or Phosphorus

The +M effect of the exocyclic diethylamino groups in 1,3,5-triaza-2-phosphapentalene **115** (R = R′ = Et) induces the nitrogen atom of the diazaphosphole ring to undergo methylation to give **136** (Scheme 44). In this case, even reaction with MeI occurs.[25]

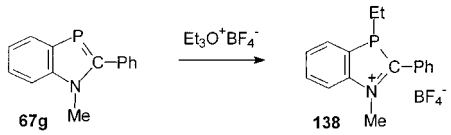
1,4,2-Diazaphospholo[4,5-*a*]pyridines **40** do not react with MeI, but reaction with Me_2SO_4 leads to σ^2*N*-methylated salts **137** (Scheme 45).[40,85] 1,2,3-Diazaphospholo[1,5-*a*]pyridines,[80] thiazolo[3,2-*d*][1,4,2]diazaphospholes,[81] and 5,6-dihydrothiazolo[3,2-*e*][1,2,4]-diazaphospholes[40] show similar behavior.

2-Phosphaindolizines do not show any reactivity toward methyl iodide,[13] but 1-phosphaindolizine as

Scheme 45



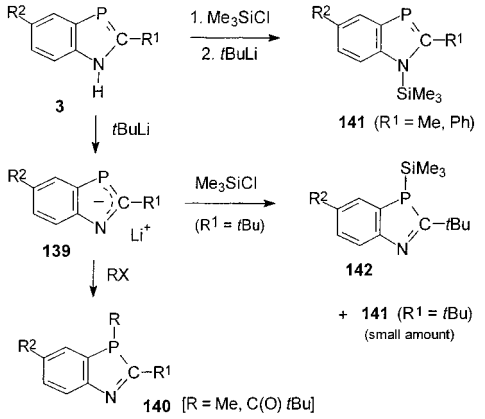
Scheme 46



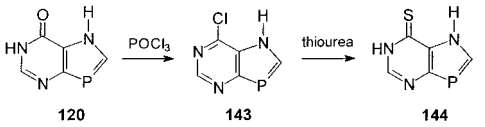
well as 3-aza-1-phosphaindolizine react with methyl iodide to give salts which, however, have not been isolated in pure form.[112] 1-Methyl-2-phenyl-1,3-benzazaphosphole **67g** does not react with MeI, but the reaction with $Et_3O^+BF_4^-$ gives the P-ethylated 1,3-benzazaphospholium salt **138** in rather low yield (25%) (Scheme 46).[135] Substitution at nitrogen of 1,3-benzazaphosphole **3** (R^1 = R^2 = H) was reported to take place in its direct reaction with PCl_3 affording a *N*-dichlorophosphino derivative. On heating **3** (R^1 = Ph, R^2 = H) with sulfur, a product is formed which is described to have the nitrogen atom of two benzazaphosphole molecules bonded to a S_8 bridge.[124]

Lithiation of 1-unsubstituted 2-alkyl(aryl)-1,3-benzazaphospholes **3** can be achieved with strong bases such as Et_2NLi.[124] Problems with equilibrium amounts of diethylamide or residual Et_2NH in reactions with acyl or organoelement halides are overcome by the use of *t*BuLi while *n*BuLi gives mixtures.[176] The analogous 1,3-benzazarsole behaves differently and forms a dilithiated metalation-addition product with *t*BuLi.[135] The benzazaphospholide anions **139** are ambident and can react at N or P depending upon the nature of the electrophile and the reaction conditions. Reaction with MeI gives P-methylated products.[124,176] Acetylation of **139** (R^1 = Ph, R^2 = H) was claimed to occur on nitrogen[124] but **139** (R^1 = Ph, R^2 = Me) was recently found to afford a P-substituted product **140** having a characteristic one-bond P−C coupling constant (49.7 Hz) for the carbonyl ^{13}C signal.[176] The pivaloylation that works in case of 1,3-benzazarsolide on nitrogen[135] takes place on phosphorus with **139** (R^1 = Ph, R^2 = Me).[176] The difference may be attributed to the higher nucleophilicity and smaller size of the P as compared to the As atom. The course of the reaction in trimethylsilylations depends on the sequence of addition of the reagents and steric or electronic effects of the substituents in 2-position. Clean N-silylation of **3** (R^1 = Me, R^2 = H, Me) to **141** occurs if *t*BuLi is added to the benzazaphosphole in the presence of Me_3SiCl. Lithiation of the bulkier substituted **3** (R^1 = *t*Bu, R^2 = H) with *t*BuLi followed by addition of Me_3SiCl, however, leads to a mixture of **3**, the P-silylated product **142**, and only traces of the N-silylated product **141** (Scheme 47). The results have been explained by proposing formation of intermediate lithium clusters containing NLi/*t*BuLi units which are more reactive and undergo clean N-silylation in contrast to the rather ionic lithium compounds **139**. In the crystal **139** (R^1 = R^2 = Me) was found to be a monomer with Li^+ coordinated to nitrogen and three

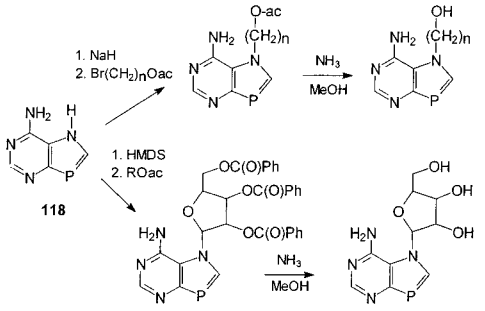
Scheme 47



Scheme 48



Scheme 49



THF molecules.[176]

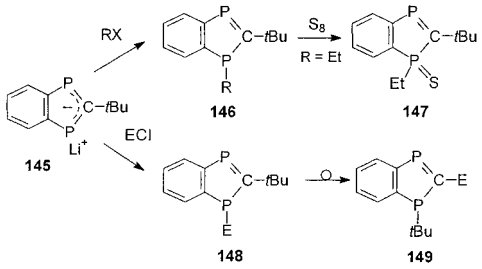
The 1,3-azaphospholo[4,5-*d*]pyrimidine-7-one **120** is claimed to react with $POCl_3$ to give **143** which is converted by thiourea into the thiopurine analogue **144** (Scheme 48).

Treatment of **120** with $Me_2NCH(OMe)_2$ in DMF leads to permethylation at all three nitrogen atoms. The phospha-adenine tautomer **118** is claimed to be selectively N-alkylated by simple or suitably protected functional alkyl halides after metalation with NaH in DMF or by glycosyl derivatives after pretreatment with excess $(Me_3Si)_2NH$ in pyridine (Scheme 49).[158]

If nitrogen in 1,3-position to phosphorus is replaced by oxygen, the reactivity toward electrophilic substitution is lowered. 2-*tert*-Butyl-1,3-benzoxaphosphole does not react with MeI, CCl_4, MeCOCl, Me_3SiCl, or PCl_3 at room temperature or even on mild heating. Only the more reactive arsenic analogue forms 1:1 addition products with MeI and with CCl_4.[202]

Anionic anellated mono- and diphospholides have been found to undergo substitution reactions at phosphorus easily. Dibenzo[*b*,*d*]phospholide **60** (M = Li, Na)[110] and dinaphtho[2,1-*b*;1′,2′-*d*]phospholide **61** (M = Li)[111] react with asymmetric linear or cyclic ditosylates affording diphosphine ligands for use in transition metal catalyzed asymmetric hydroformylation. Lithium 2-*tert*-butyl-1,3-benzodiphospholide **145** reacts with ethyl bromide or pivaloyl chloride to give 1-substituted products **146** (R = Et, *t*BuCO)

Scheme 50



which can be oxidized by sulfur to **147**. Hydrogen chloride (but not EtOH) reacts with **145** to form 1,3-benzodiphosphole **148** (E = H) which, as confirmed by NMR, undergoes an unusual rearrangement to **149** (E = H). Analogous results (E = Me_3Si, Ph_2P) are obtained in reactions with Me_3SiCl and Ph_2PCl (Scheme 50).[122,123]

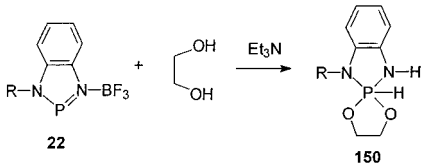
Bis(lithium)-2-anilide-1,3-benzodiphospholide **74** (XR = NPhLi) reacts with Me_3SiCl to give 2-(phenyltrimethylsilylamino)-3-trimethylsilyl-1,3-benzodiphosphole **75** (X = NPh) (cf. Scheme 26).[120]

B. Addition Reactions

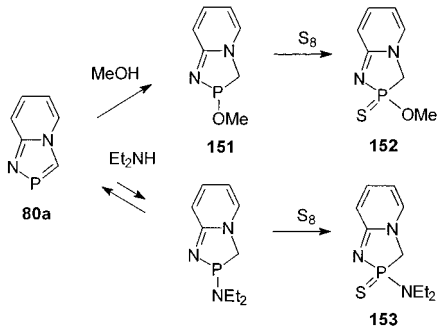
1. 1,2-Additions on C═P– or N═P–Bond and Oxidative Additions at Phosphorus

The chemistry of anellated non-phosphorus aromatic heteroles such as indoles[200] and benzimidazoles[63] is characterized by a variety of substitution reactions. Except rare examples of 2,3-hydrogenation in indoles, 1,2-addition reactions seem to be strongly disfavored while the reversal, aromatization of the dihydro derivatives by oxidative elimination, is a favored reaction. With some limitations, this is found even for the less aromatic benzofurans[203] and benzoxazoles.[204] Indolizines[30] are protonated by strong acids yielding a saturated carbon atom adjacent to the ring junction N atom. A polar >C═P- or -N═P- moiety in anellated heterophospholes makes these compounds generally more susceptible to the attack of protic reagents leading to 1,2-addition, the proton being bonded to carbon or nitrogen. Heterocycles with P−N bonds and even 2-phosphaindolizines are attacked by water and get hydrolyzed. Bis(phosphonio)-isophosphindolides, which display a related but symmetric π-excessive aromatic system with charge compensation by substituents, lack this high sensitivity to water or alcohol.[101] However, electron withdrawal from phosphorus by coordination to transition metal cations or by oxidation enhances the reactivity and promotes rapid reaction with H_2O, alcohols, or H_2S.[102c,105,205−207] In 1,3-benzazaphospholes and 1-phosphaindolizines, the +M effect of the nitrogen electron-pair reduces the polarity of the C═P bond and makes these compounds more resistant to hydrolysis. Analogously, 1,3-benzoxaphospholes are stabilized by the +M effect of the O-atom. Thus, 1-phosphaindolizines could be purified by repeated chromatography on silica gel[112] and 1,3-benzazaphospholes as well as 1,3-benzoxaphospholes are in most cases at ambient temperature stable to water and even to dilute sulfuric acid or alkaline hydroxide solutions.[28,127,128] In the presence of oxidizing agents, however, addition reactions are also strongly facilitated.

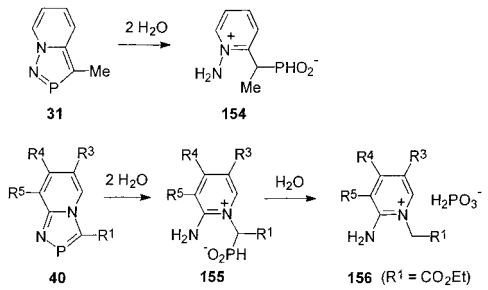
Scheme 51



Scheme 52



Scheme 53



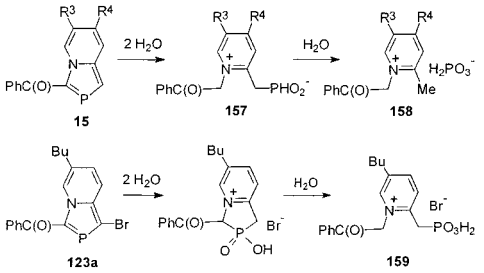
1,3,2-Benzodiazaphosphole-BF_3 complexes **22** form 1,2-addition products with alcohols in the presence of Et_3N. In the reaction with butanol, the intermediate 1,1-addition product could be observed. A 1,2-addition product was obtained with diethylamine. The reaction with ethylene glycol leads to a spirocyclic σ^5P product **150** through 1,2-addition followed by the 1,1-addition of the other hydroxy group (Scheme 51).[59c] A cyclohexane-anellated 1,2,3-diazaphosphole is reported to undergo 1,2-addition with MeOH, but as the product is unstable it loses phosphorus to form a hydrazone.[208]

1-Aza-2-phosphaindolizine **80a** undergoes 1,2-addition with methanol to form **151** which could be oxidized to **152**.[40,143] Similar behavior is shown by 4,6-bis(diethylamino)-1,3,5-triaza-2-phosphapentalene.[15,209] The reaction of **80a** with Et_2NH is reversible and can be completed only with concomitant oxidation of phosphorus to yield **153** (Scheme 52).[40,143]

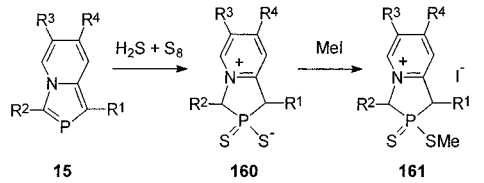
3-Aza-2-phosphaindolizine **31**[80] and 1-aza-2-phosphaindolizines **40**[85] or **80**[40,143] are hydrolyzed involving ring opening at the P=C bond to form phosphinates **154** and **155**, respectively. The structure of **155**, R^1, R^3-R^5 = H, has been confirmed by X-ray crystal studies.[143] In the case of **155**, R^1 = CO_2Et, further hydrolysis occurs to form the *N*-pyridinium salt **156** (Scheme 53).

The hydrolysis of 2-phosphaindolizines **15** (R^2 = PhCO) proceeds in similar manner to initially form zwitterionic **157** which is finally converted to the *N*-pyridinium salts **158**.[13] Interestingly, the hydrolysis of the 1-bromo-substituted 2-phosphaindolizine

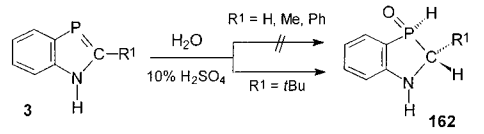
Scheme 54



Scheme 55



Scheme 56



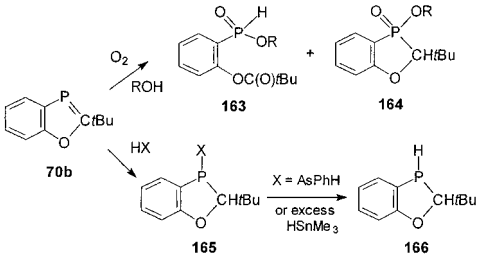
123a involves debromination of C-1 accompanied by oxidation of phosphorus to give a phosphonic acid derivative **159**[162] (Scheme 54). A similar observation has been made in the hydrolysis of 4-bromo-1,2,3-diazaphospholes.[196]

2-Phosphaindolizines **15** react with H_2S in the presence of elemental sulfur to give zwitterionic pyridinium dithiophosphinates **160** through 1,2-addition of H_2S with concomitant oxidation of phosphorus followed by a 1,3-proton shift. A mixture of two diastereoisomers is formed with **15**, R^1 = Me, R^2 = CO_2Me, 4-$NO_2C_6H_4$, R^3 = R^4 = H. In some cases the S-methylated products **161** were obtained on reaction of **160** with MeI (Scheme 55). A selenium analogue of **160** has also been obtained.[198,199]

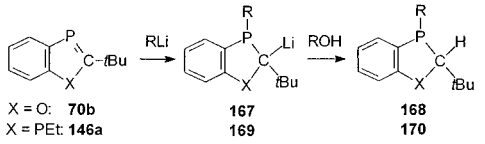
2-Unsubstituted as well as 2-methyl- and 2-phenyl-1,3-benzazaphospholes are resistant to cold dilute sulfuric acid but somewhat more P-basic 2-*tert*-butyl derivatives add water under these conditions, e.g., **3a** forms **162** diastereoselectively (Scheme 56).[28]

2-*tert*-Butyl-1,3-benzoxaphosphole **70b**, although itself resistant to water or alcohols, adds these reagents in the presence of oxygen and undergoes ring-opening to form the phosphinate derivative **163**. The reaction is assumed to proceed via 1,2-addition of oxygen followed by [2+2]cycloreversion to a short-lived σ^2-P=O intermediate which is trapped by ROH. A small quantity of **164** (mixture of diastereoisomers) is formed as side product via an intermediate σ^3-benzoxaphosphol-3-oxide (Scheme 57). **164** can be obtained in pure form from oxidation of **70b** with H_2O_2 (30%) in ethanol and subsequent alkylation with Meerwein salt. Oxidation in absence of alcohol yielded oligomeric phosphine oxides.[210] An investigation of addition reactions of **70b** with further polar hydrogen compounds revealed that HX with soft higher-row substituents X (X = Cl, I, PhS, PhAsH, $SnMe_3$) are added to the P=C bond to give 2,3-dihydro-1,3-benzoxaphospholes **165** while Ph_2PH re-

Scheme 57



Scheme 58

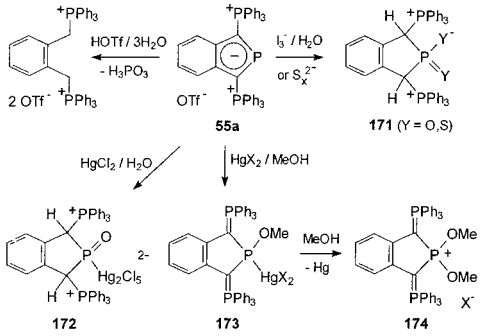


acts only with the more reactive As=C analogues. Addition of HCl is reversible; heating of **165** (X = Cl) with DBU regenerates the benzoxaphosphole. **165** (X = Cl) on reaction with MeOH gives the methoxy derivative which is otherwise not accessible by direct addition of MeOH. The product **165** (X = AsPhH) formed primarily with phenylarsine undergoes dismutation under the reaction conditions to give the cyclic secondary phosphine **166** and $(AsPh)_6$. Addition of Me_3SnH to **70b** is catalyzed by azobis(isobutyronitrile) and proceeds stereospecifically to the *trans*-2,3-dihydro-1,3-benzoxaphosphole **165** (X = $SnMe_3$) which is reduced to **166** by heating with excess Me_3SnH (Scheme 57). The silicon hydride Et_2PhSiH does not add to **70b** or its As-analogue, even on prolonged heating.[202]

Reaction of 2-*tert*-butyl-1,3-benzoxaphosphole **70b** with *t*BuLi leads to the 1,2-addition product **167** (X = O, R = *t*Bu), which is solvolyzed by water or MeOH affording **168**. Because of steric reasons the addition proceeds with high diastereoselectivity to give mainly the *trans*-product (*E*/*Z* ca. 93:7%).[202] The formally related but nonaromatic 1-ethyl-2-*tert*-butyl-1,3-benzodiphosphole **146** (R = Et) displays similar 1,2-addition reactions but is generally more reactive. With *n*BuLi, it gives **169** (X = PEt) and on hydrolysis **170** (X = PEt, R = *n*Bu) (Scheme 58). HCl and even methanol are easily added to form 1,2-addition products.[122,123]

The reaction of lithium-1,3-bis(diphenylphosphino)-isophosphindolide **58** (M = Li) with MeI leads to disubstitution at both of the exocyclic phosphorus atoms.[103,105] 1,3-Bis(triphenylphosphonio)isophospholide **55a** (X = OTf) is resistant to electrophilic alkylation by $[Me_3O^+][BF_4^-]$ in absence of water. In the presence of water, the oxonium salt decomposes forming an acid which attacks **55a**. Equimolar amounts of TfOH lead to an equilibrium with two species, in which one or both carbon atoms adjacent to phosphorus are protonated. Addition of small amounts of water to the acidic THF solution causes rapid hydrolysis yielding the acyclic bis(phosphonium) salt via a cyclic phosphinoxide and a phosphonous acid intermediate detected by NMR.[206] The hydrolytic sensitivity of **55a** (X = I_3) is markedly increased by the mildly oxidizing counterion giving rise to a cyclic phosphinic acid derivative if the solution is exposed to moist air. The dithioanalogous

Scheme 59

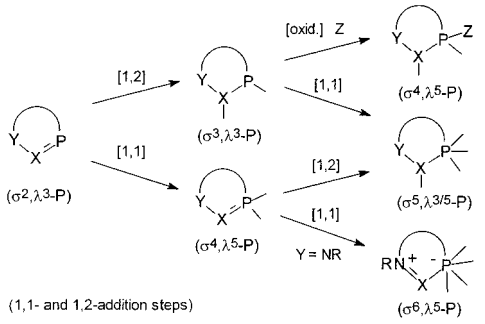


derivative **171** (Y = S) is obtained on treatment of **55a** with a polysulfide formed in situ from sulfur, Et_3N, and H_2S when the latter is bubbled in the methylene chloride solution.[206] Complexes of **55a** are also much more sensitive to hydrolysis or alcoholysis than **55a** itself as shown by the easy formation of **172**. Addition of MeOH in the presence of HgX_2 (X = Oac, Cl, Br, OTf) proceeds via an assumed complex [**55a**−HgX_2] and the structurally characterized (X = Oac) MeOH/HgX_2-adduct **173** to the dimethoxyphosphonium salt **174** (Scheme 59). On using triethylene glycol, an analogous macrocyclic phospha crown ether is formed.[205] The metal-assisted oxidative addition of alcohols to **55** can also be achieved in the presence of oxygen and catalytic amounts of Cu(I).[205b] Oxidative halogenation of **55** (R = Ph) by Cl_2 and Br_2 is accompanied by substitution of the benzene ring, whereas $PhICl_2$ affects selective P-dichlorination.[105,207]

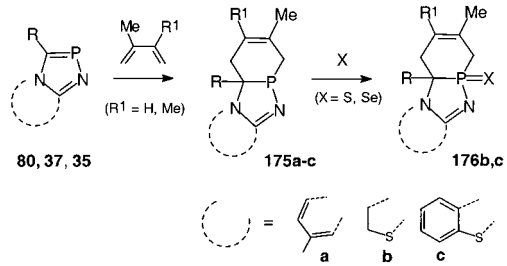
2. Cycloadditions

In cycloaddition reactions, the anellated heterophospholes exhibit distinct dissimilarities from the related non-phosphorus systems. In contrast to many [2+4]cycloadditions given by properly activated indole derivatives with 1,3-dienes,[200] no such reaction has been reported so far for 1,3-benzazaphospholes. Although benzo[*b*]furans do not take part in Diels−Alder reactions,[203] 2-*tert*-butyl-1,3-benzoxaphosphole reacts with 2,3-dimethylbutadiene under forced conditions to give a [2+4]cycloadduct.[211] Indolizine does not undergo [2+4]cycloadditions; instead, it forms a [8+2]cycloadduct with dimethyl acetylenedicarboxylate (DMAD).[212,213] However, 1,3-bis(alkoxycarbonyl)-2-phosphaindolizine as also its isoquinoline analogues react with 1,3-dienes to form [2+4]cycloadducts.[50,214] As phosphaalkenes are known to take part in [2+4] cycloadditions under milder conditions than their carbon analogues,[215] the ability of the more reactive heterophospholes for [2+4]cycloadditions may be attributed to similarities with phosphaalkenes in the frontier orbitals (cf. HOMO of 1,3-benzoxaphospholes[181a]). But this similarity is limited as phosphaalkenes have energetically closely spaced π- and σ-orbitals, HOMO and HOMO-1,[216] while benzoxaphospholes are cyclodelocalized 10π-systems with the three highest occupied orbitals being π-orbitals.[181a] A striking difference of heterophospholes and its non-phosphorus analogues is that σ^2-phosphorus in some of the heterophospholes such as 1,3-benzazaphosphole,[217] 2-phosphaindolizines,[196,217] and 1,3,5-triaza-2-phosphapentalenes[196,209] may act as the center of cheletropic (see later) [1+4]cycload-

Scheme 60



Scheme 61

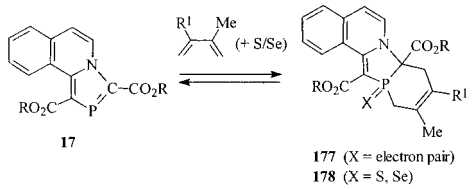


ditions[218,219] leading to spirocyclic ylides or zwitterionic σ^6P species. A strongly electron demanding heterodiene prefers the [1+4]route involving the σ-orbital on phosphorus. In benzoxaphospholes (high P=C character of HOMO), however, even with chloranil [2+4]cycloaddition takes place, as given by phosphaalkenes.[215] The mechanistic aspects of these reactions are not yet clear. Different modes of additions across the X = P (X = CR, N, P; Y = CR$^-$, NR, PR, O, S, Se) moiety in the heterophosphole ring leading to the final cycloadduct are outlined in Scheme 60.

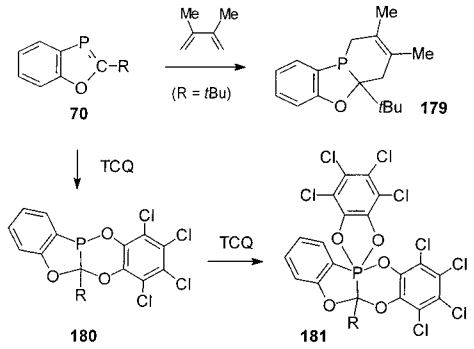
2.1. Cycloaddition on C=P/P=P Bond. Anellated diazaphospholes are comparatively more reactive toward [2+4]cycloaddition than anellated azaphospholes. 1-Aza-2-phosphaindolizine **80** (R = 7-Me) forms a [2+4]cycloadduct **175a** with 2,3-dimethyl-1,3-butadiene.[40,143] 1,4,2-Diazaphospholo[5,4-*b*]thiazoline **37** and its benzothiazole analogue **35** react analogously affording **175b**,**c**, respectively, which have been converted to the corresponding sulfides or selenides **176b**,**c** (Scheme 61). Cycloaddition with isoprene occurs regioselectively.[2]

1,3-Bis(alkoxycarbonyl)-1,3-azaphospholo[5,1-*a*]isoquinolines[50] **17** react with 2,3-dimethyl-1,3-butadiene in the presence of sulfur at room temperature to give the [2+4]cycloadduct **178**. Selenium or methyl iodide can also be used instead of sulfur. In the absence of the oxidizing agent, reaction with 2,3-dimethylbutadiene could be completed by refluxing in $CHCl_3$ for 4 days. The role of the oxidizing agent appears to be to push a reversible reaction between **17** and the diene in the forward direction by oxidizing σ^3P of the initially formed [2+4]cycloadduct **177**. Isoprene reacts regiospecifically; the structure of **178**, R = Et, R^1 = H, X = S, has been confirmed by X-ray crystal studies (Scheme 62). 1,3-Bis(alkoxycarbonyl)-2-phosphaindolizines show similar behavior.[50,214] However, 3-ethoxycarbonyl-1-methyl-2-phosphaindolizine does not react with 2,3-dimethyl-1,3-butadiene in the presence of sulfur, even on refluxing in toluene for

Scheme 62



Scheme 63

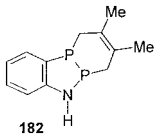


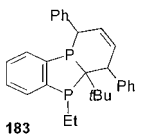
several days.[195] On the basis of PM3 calculations, it has been shown that the relative reactivities of mono- and bis-alkoxycarbonyl substituted 2-phosphaindolizines as well as of 1,3-azaphospholo[5,1-*a*]isoquinolines depend on the energy gap between the HOMO of the diene and the LUMO of the phosphaindolizine.[50] Ab initio investigations of a model [2+4]-cycloaddition of phosphaethene with 1,3-dienes, which confirm the aromatic character of the transition states in these reactions by ^{1}H NMR chemical shifts and nucleus independent chemical shifts (NICS) values, also support these conclusions.[220]

The [2+4]cycloaddition of 1,3-azaphospholo[5,1-*b*]-benzothiazole with 2,3-dimethylbutadiene or isoprene could be accomplished only in the presence of O_2, S_8, or Se_n. The reaction with isoprene occurs regioselectively.[2] 1,3-Benzazaphospholes did not react with 2,3-dimethylbutadiene, even in the presence of sulfur. Only the more reactive As-analogues undergo a [2+4]-cycloaddition to 2,3-dimethylbutadiene on prolonged heating in a closed tube.[221]

1,3-Benzoxaphospholes **70** form [2+4]cycloadducts **179** and **180** with 2,3-dimethyl-1,3-butadiene on prolonged heating and with tetrachloro-*o*-benzoquinone (TCQ) at room temperature, respectively.[211] The structure of **180** (R = Me) has been confirmed by X-ray crystal studies which reveal *cis*-anellation.[222] On reacting the cycloadduct **180** with more TCQ oxidative [1+4]cycloaddition occurs on phosphorus to give the 1:2 adduct **181** (Scheme 63).[211]

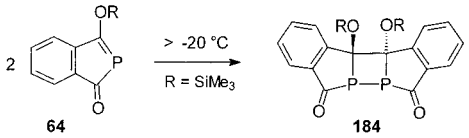
[2+4]Cycloaddition takes place between 1*H*-1,2,3-benzazadiphosphole **26** (E = P) and 2,3-dimethyl-1,3-butadiene to afford **182**.[74,75] Likewise, 1,3-benzodiphosphole **146** (R = Et) reacts with 1,4-diphenyl-1,3-butadiene to give the [2+4]cycloadduct **183**.[122,123]



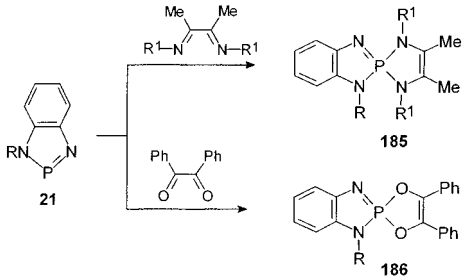


The isophosphindole derivative **64** which is stable up to −20 °C dimerizes in head to head mode to form

Scheme 64



Scheme 65



184 (Scheme 64).[115] The structure of the latter has been confirmed by X-ray studies which corrected an earlier report suggesting head to tail dimerization[114] and revealed *trans*-orientation of the two $OSiMe_3$ groups.[115]

1,3-Dipolar cycloadditions of diazoalkanes on a cyclohexane-anellated 1,2,3-diazaphosphole have been reported. The products are, however, unstable and lose nitrogen to form a mixture of acyclic bis(hydrazones) and σ^3P compounds.[208]

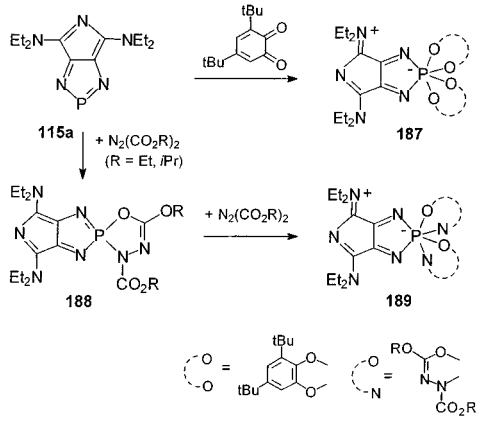
2.2. Cheletropic Cycloaddition on the P Atom. Anellated heterophospholes having high π-charge density on phosphorus undergo oxidative cheletropic [1+4]cycloadditions with heterodienes such as *o*-quinones, α-diketones, α-diimines, and azodicarboxylic esters to give spirocyclic products. The less electron-rich phosphorus in 1,3,2-benzodiazaphospholes **21** combines with only one equivalent of α-diimines[223] or benzil[224] to form spirocyclic adducts **185** and **186**, respectively (Scheme 65). The substrates **21** were generated from their tetramers by heating (see Scheme 7). Similar reactions are given by $AlCl_3$-complexed 1-phenyl-1,3,2-benzodiazaphosphole[60] and 1,3,2-benzoxazaphosphole[223] with α-diimines.

The reactions of a cyclohexane-anellated 1,2,3-diazaphosphole with cyclohexanone and phenyl azide leading to 1,1-additions on phosphorus have been reported.[208]

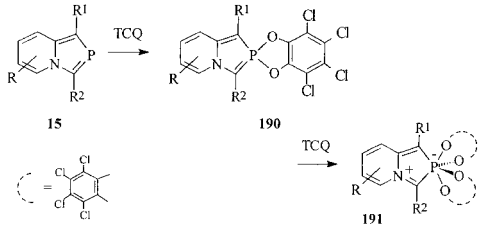
4,6-Bis(diethylamino)-1,3,5-triaza-2-phosphapentalene **115a** forms the zwitterionic 1:2 adducts **187**[209] and **189**[196] with 3,5-di-*tert*-butyl-*o*-benzoquinone (TBQ) and azodicarboxylic esters, respectively, the latter via a monoadduct **188** (Scheme 66). NMR studies reveal each product to be a mixture of three stereoisomers.[196,209]

2-Phosphaindolizines **15** (R^1 = Me or Ph) undergo double [1+4]cycloadditions at phosphorus with two equivalents of tetrachloro-*o*-benzoquinone (TCQ) to give the zwitterionic products **191** that have a hexacoordinate phosphorus atom ($\delta^{31}P = -134$ to -141). The reaction cannot be stopped at the stage of the 1:1 addition product even if one equivalent of TCQ is used. But 1,3-bis(alkoxycarbonyl)-2-phosphaindolizines **15** ($R^1 = R^2$ = COOEt/Me) form only the 1:1 adducts **190** ($\delta^{31}P$ = 45 to 46) even if excess TCQ is used. The -M effect of the 1-alkoxycarbonyl group

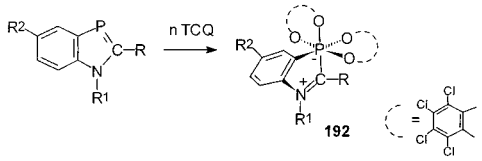
Scheme 66



Scheme 67



Scheme 68



in the latter which suppresses the electron-donating effect of the pyridinic nitrogen is responsible for this difference in reactivity (Scheme 67).[196,217]

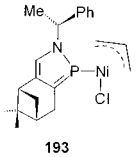
The reaction of 1,3-benzazaphospholes **3** with TCQ also leads to the formation of the zwitterionic 1:2 adducts **192**. The reaction cannot be stopped at a 1:1 product even if the reactants are used in a 1:1 or 1:0.5 molar ratio (Scheme 68). The two tetrachlorocatechol groups differ from each other by *trans*-orientation either toward C2 or the benzene ring, respectively, and thus exhibit two sets of ^{13}C resonances. Excess TCQ (1:4) leads to degradation. Crystals of an 1:3 intermediate allowing a structure determination displayed cleavage of the P−C2 bond by addition of a third equivalent of TCQ to C2.[217]

C. Coordination to Transition Metals

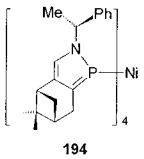
The coordination chemistry of anellated heterophospholes is very limited and has started to develop only recently. Even the knowledge on anellated phospholide complexes is relatively small as compared with the extended complex chemistry of nonanellated phospholides.[5,19−22,98] Complexes of fused heterophospholes or phospholides with Cr(0),[13,104,124,171,226,227] Mo(0),[123,171,226,227] W(0),[123,171,176,226,227] W(II),[176] Mn(I),[107] Ni(0),[86] Ni(II),[86,227] Cu(I),[177] Ag(I),[102e] Au(I),[102c] and Hg(II)[205] have been reported. On the basis of structural investigations of the complexes, it is possible to make some generalizations. Non-anellated and anellated heterophospholes seem to have a very low tendency to form (semi)sandwich

complexes, whereas their carbon-analogues, pyrroles, indoles, or thiophenes and anellated rings thereof,[98,194,225] as well as non- or benzo-anellated phospholides[5,19−22,98,225] are able to enter η^5- and η^1-, in benzo derivatives sometimes also η^6-coordination modes. Only 1,3-bis(phosphonio)isophosphindolides are restricted to weak η^1-coordination of coinage metals by steric factors.[22] The coordinating ability of heterophospholes is usually controlled by the σ^2P atom and is comparable to that of the electron-poor phosphanes. Both are weak σ-donor and more efficient π-acceptor ligands. These features are manifested by the ^{31}P coordination chemical shifts $\Delta\delta$. In general, the magnitude and sign of the δ^{31}P values of phosphine complexes depend on the nature of the substituents at the α-position as well as on the coordinated metal. In $Cr(CO)_5$ complexes of the anellated heterophospholes, the downfield shift on coordination is comparatively small. Increasing size of the group 6 metal causes increasing shielding of the phosphorus and results in reduced downfield or even small upfield shifts in the case of $Mo(CO)_5$ complexes and generally in upfield shifts of the $W(CO)_5$ species. The ^1J(P−W) coupling constants range between 254 and 268 Hz.[171,226,227] Coordination does not disturb the planarity of the heterophosphole ring appreciably. In contrast to three-coordinate triorganophosphanes, the three-coordinate phosphorus in these complexes remains planar supporting back-bonding from the metal to a suitable π*-orbital of the ligand. Thus, the properties of neutral heterophospholes resemble those of σ^3P compounds with high acceptor strength like phosphites but small Tolman angle. Attempts to use the 2-phosphaindolizine **15** (R^1 = H, R^2 = COOEt) in the Rh-catalyzed hydroformylation of styrene failed but a more bulky *o*,*o*′-disubstituted phosphabenzene derivative with larger Tolman angle furnishes a highly active catalyst.[228] For bulky α,α′-disubstituted heterophospholes similar properties may be expected. The recent development of a cyclobutene-diphosphene-Pd chelate catalyst for the polymerization of ethene raises expectations that low-coordinated phosphorus compounds will find more use in catalysis.[229]

The anellated 1,2-azaphosphole **43** reacts with (η^3-allylNiCl)$_2$ yielding the 1:1 adduct **193** through P-coordination. The reaction with (1,5,9-cyclododecatriene)Ni(0) affords the L_4Ni(0) complex **194**. The structures of the complexes have been confirmed by X-ray crystal structure investigations.[86]



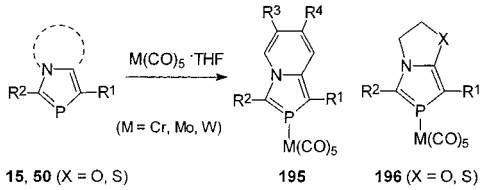
193



194

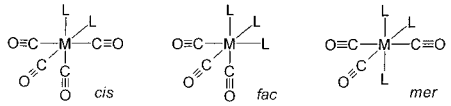
The η^1(P)(2-phosphaindolizine)$M(CO)_5$ complexes **195** have been obtained from the reaction of 2-phosphaindolizines **15** with $M(CO)_5$(THF) (Scheme 69).[171] The η^1(P)-(1,3-azaphospholooxazoline and -thiazoline)$M(CO)_5$ complexes **196** (X = O, S) have been synthesized in a similar manner from **50** (X = O, S) with $M(CO)_5$(THF).[226] In one case, (2-cyclooctene)Cr(CO)$_5$ was used as the transfer reagent.[13] The structure of **195** (R^1 = Me, R^2 = CO-*t*Bu, R^3 = R^4 = H, M = Cr) has been investigated by X-ray crystallography.[171] The heterophosphole ring retains its planarity with a trigonal planar geometry at phosphorus. However, the pivaloyl group, in contrast to that in the ligand,[89] is rotated to a staggered conformation. The difference between the two P−C bond lengths as compared to that in the ligand decreases showing more effective delocalization in the heterophosphole ring on complexation. Whether this is only due to the changed orientation and loss of the -M effect of the α-acyl substituent or also due to the lack of repulsion by the phosphorus lone electron pair is still not clear and needs further structural studies on complexes of the nonfunctional substituted heterophospholes.

Scheme 69



15, **50** (X = O, S) **195** **196** (X = O, S)

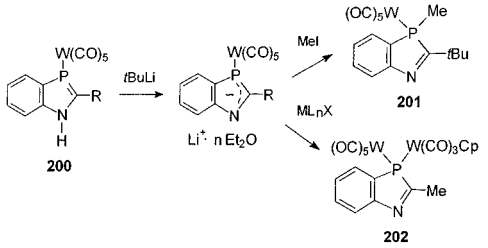
The reaction of **15** (R^1 = Me, R^2 = CO_2Me, R^3 = R^4 = H) with (norbornadiene)$Cr(CO)_4$ affords the *cis*-$L_2M(CO)_4$ complex **197**. An analogous complex was formed in the reaction of **15** (R^1 = Me, R^2 = CO_2Et, R^3 = R^4 = H) with $Cr(CO)_5$(THF) as a minor product. An attempt to obtain π-complexes from the reaction of **15** with (cycloheptatriene)$Mo(CO)_3$ or (mesitylene)$W(CO)_3$ failed; instead a variety of complexes of the types $L_2M(CO)_4$ or $L_3M(CO)_3$ (**197**−**199**) were formed.[171]



197 (M = Cr) **198** (M = Mo, W) **199** (M = Mo)

1,3-Benzazaphospholes exhibit analogous behavior and form the η^1(P)-coordinated $M(CO)_5$ complexes on reacting with $M(CO)_5$(THF) (M = Cr, Mo, W).[124,171,172] As studied with the tungsten complexes **200** (R = Me, *t*Bu), lithiation with *t*BuLi provides ambident anions that undergo substitution reactions with MeI or soft complex metal halides ML_nX like $CpW(CO)_3Cl$ at phosphorus to give **201** and the mixed W(0),W(II) complex **202** (Scheme 70).[176]

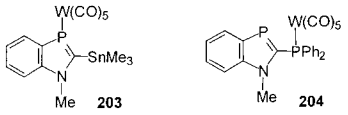
Scheme 70



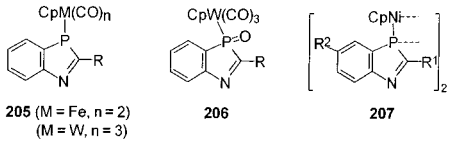
200 **201** **202**

Attempts to lithiate (*N*-methyl-1,3-benzazaphosphole)$W(CO)_5$ at C2, like the noncomplexed ligand (cf. Scheme 43), or to trap the lithiated product with

Me_3SiCl failed however. Even the $W(CO)_5$ complex of the 2-stannyl derivative **203**, accessible from the ligand **133** ($ER_n = SnMe_3$) and $W(CO)_5$(THF), decomposes slowly on repeated crystallization.[175] **133** ($ER_n = PPh_2$) reacts with $W(CO)_5$(THF) preferably at the more basic phosphino-P atom to give **204**.[175]

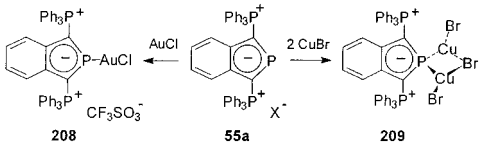


The noncomplexed lithium benzazaphospholides **139** react similarly affording monomer phosphido complexes **205** (M = Fe, $n = 2$; M = W, $n = 3$). The tungsten complex is oxidized in THF by air or peroxide to give the respective monomer tungstaphosphine oxide complex **206** characterized by a crystal structure analysis.[176] Benzazaphospholes **3** on heating with nickelocene provide directly the benzazaphospholide complexes **207**. NMR and MS data are consistent with a dimer structure and μ-P coordination of the NiCp fragment, which is confirmed by a crystal structure analysis of **207** (R^1 = *t*Bu, R^2 = Me). The two benzazaphospholide rings are arranged nearly perpendicular to the Ni_2P_2 ring and adopt a *trans* configuration.[227]

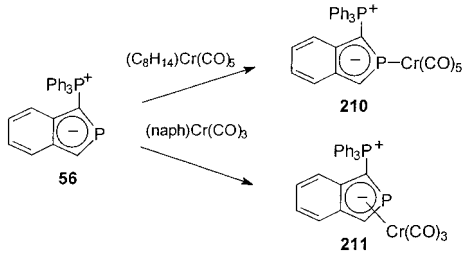


Coordination compounds of some anellated monophospholide anions have been reported. 1,3-Bis(triphenylphosphonio)isophosphindolium bromide **55a** (X = Br) fails to react with neutral metal carbonyls or $W(CO)_3(MeCN)_3$ and forms salts **55a** (X = CpM$(CO)_3$) with the carbonylmetalates $NaCpM(CO)_3$ (M = Mo, W). However, with AuCl the triflate **55a** (X = CF_3SO_3) affords the η^1(P)-LAuCl complex **208**, which on reaction with a second equivalent of AuCl gives a mixture of ionic complexes [(**55a**)AuX]$^+$[AuYZ]$^-$ (X, Y, Z = Cl, Br) and compared to the ligand displays enhanced reactivity toward MeOH and water to form 1,2-addition products.[102c] The reaction of **55a** (X = Br) with CuBr gives a binuclear complex **209** with a μ_2,η^1(P) bridge. The structure of the latter, also determined by X-ray crystal analysis, shows a planar four-membered ring consisting of P and Br^- bridges and two trigonal planar Cu(I) atoms (Scheme 71).[177a] CuCl reacts similarly, whereas CuI, as shown by X-ray structural investigation, furnishes a solid salt (**55a**)$_2$[Cu_4I_6] and a complex [(**55a**)$_2Cu_4I_6$] with a terminal η^1(P)-coordinated ligand. In solution, however, in all cases binuclear complexes [(**55a**)Cu_2X_3] were detected by ^{31}P NMR studies.[177b] Reactions of the ligands **55a** with Ag(I) salts yielded both, mononuclear and dinuclear complexes; structures of two of them have been determined by X-ray crystal studies.[102e]

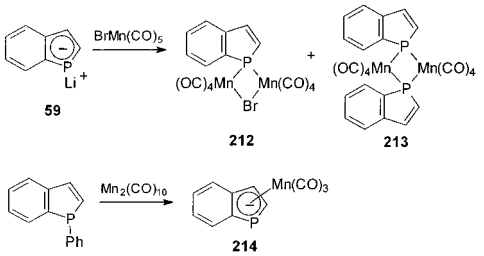
Scheme 71



Scheme 72



Scheme 73

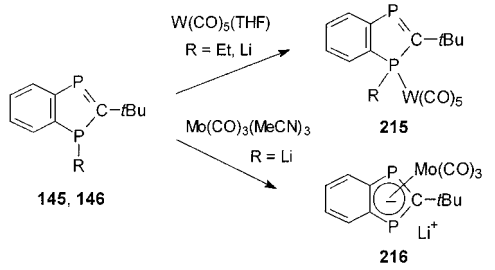


1-Triphenylphosphonio-isophosphindolide **56**, obtainable from the reduction of **55a**, gives the σ(P)−$LCr(CO)_5$ complex **210** on reaction with (cyclooctene)-$Cr(CO)_5$, whereas reaction with (naphthalene)$Cr(CO)_3$ yields the η^5-$LCr(CO)_3$ semi-sandwich complex **211** (Scheme 72). The structures have been confirmed by X-ray crystal investigations.[104] The reaction of lithium-1,3-bis(diphenylphosphino)isophosphindolide **58** with $Ni(CO)_4$ leads to coordination of the exocyclic phosphorus atoms.[103,105]

The reaction of the phosphindolide ion **59** with bromomanganese pentacarbonyl leads to a mixture of the binuclear complexes **212** and **213**. Attempts to synthesize a benzoanellated diphosphaferrocene from reaction of **59** with $FeCl_2$ failed, which underlines the lower tendency of anellated phospholes to undergo π-coordination. The η^5-phosphindolide−manganesetricarbonyl semi-sandwich complex **214** could however be obtained from a direct reaction of 1-phenylphosphindole with dimanganese decacarbonyl in refluxing xylene (Scheme 73).[107] An analogous cleavage of the P-phenyl substituent from a doubly hexene-fused phosphole derivative gave a η^5-dihexenophospholide−$Mn(CO)_3$ complex.[230] A bis(η^5-phosphindolide) samarium(II)$(THF)_2$ complex was synthesized from the reaction of a lithium phosphindolide with $SmI_2(THF)_2$. However, the Sm(II) complex with double-anellated dibenzophospholide ligands formed by P−P cleavage of bis(dibenzophosphole) with activated Sm prefers σ-coordination.[108]

1-Lithio-**145** as well as 1-ethyl-2-*tert*-butyl-1,3-benzodiphosphole **146** (R = Et) react with $W(CO)_5$-(THF) to form the η^1-$W(CO)_5$ complexes **215**. Treatment of the lithium compound with $Mo(CO)_3(MeCN)_3$, however, leads to replacement of all three acetonitrile ligands and gives the semi-sandwich complex **216** (Scheme 74).[122,123]

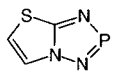
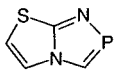
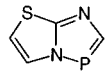
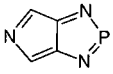
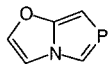
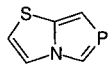
Scheme 74



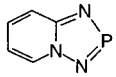
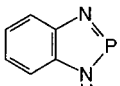
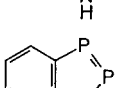
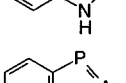
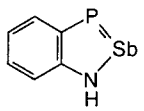
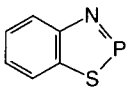
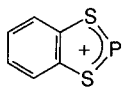
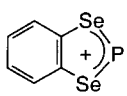
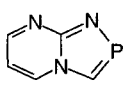
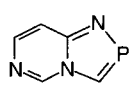
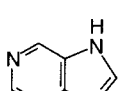
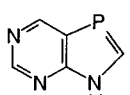
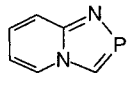
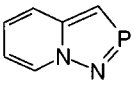
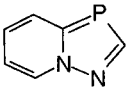
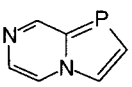
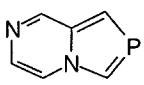
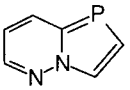
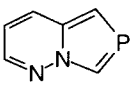
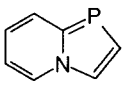
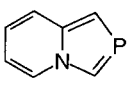
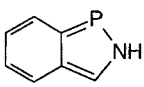
V. List of Known Ring Systems

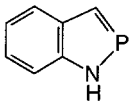
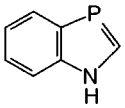
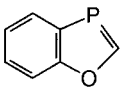
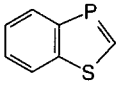
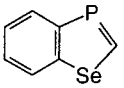
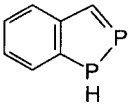
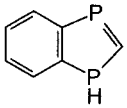
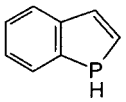
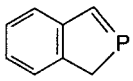
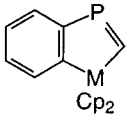
In the following list, basic skeletons of the anellated heterophospholes reported so far are given along with their IUPAC names and relevant references. For ordering and classification of the ring systems, ring indices given in the Comprehensive Heterocyclic Chemistry-I and -II[3] have been followed. The existence of anions is indicated. Some of the systems are known only as anions.

A. 5,5 Ring Systems

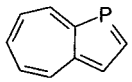
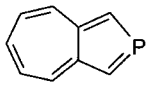
Structure	Name	References
	Thiazolo[2,3-*e*][1,2,4,3]triazaphosphole	57
	Thiazolo[3,2-*d*][1,4,2]diazaphosphole	40,81-83,142
	Thiazolo[2,3-*e*][1,4,2]diazaphosphole	40,142
	Pyrrolo[3,4-*d*][1,3,2]diazaphosphole (1,3,5-Triaza-2-phosphapentalene)	24,25,196,209
	1,3-Azaphospholo[5,1-*b*]oxazole - 5,6-Dihydro derivative	91,226
	1,3-Azaphospholo[5,1-*b*]thiazole - 5,6-Dihydro derivative	92,226

B. 5,6 Ring Systems

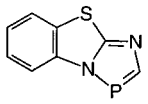
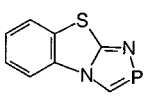
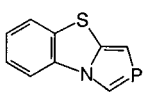
Structure	Name	References
	1,2,4,3-Triazaphospholo[1,5-*a*]-pyridine (1,3-Diaza-2-phosphaindolizine)	56,57
	1*H*-1,3,2-Benzodiazaphosphole	59,60
	1*H*-1,2,3-Benzazadiphosphole	74,75
	1*H*-1,2,3-Benzazaphosphaarsole	75
	1*H*-1,2,3-Benzazaphosphastibole	75
	1,3,2-Benzothiazaphosphole	59b,74
	1,3,2-Benzodithiaphospholium cation	69,71-73
	1,3,2-Benzodiselenaphospholium cation	69
	1,4,2-Diazaphospholo[4,5-*a*]-pyrimidine	40,142
	1,4,2-Diazaphospholo[4,5-*c*]-pyrimidine	142
	1,3-Azaphospholo[4,5-*d*]pyrimidine	158
	1,3-Azaphospholo[5,4-*d*]pyrimidine	158
	1,4,2-Diazaphospholo[4,5-*a*]-pyridine (1-Aza-2-phosphaindolizine)	40,85,142,143,198,199
	1,2,3-Diazaphospholo[1,5-*a*]-pyridine (3-Aza-2-phosphaindolizine)	80
	1,2,4-Diazaphospholo[1,5-*a*]-pyridine (3-Aza-1-phosphaindolizine)	112,113
	1,3-Azaphospholo[1,2-*a*]pyrazine	153
	1,3-Azaphospholo[1,5-*a*]pyrazine	153
	1,3-Azaphospholo[1,2-*b*]pyridazine	153
	1,3-Azaphospholo[1,5-*b*]pyridazine	153
	1,3-Azaphospholo[1,2-*a*]pyridine (1-Phosphaindolizine)	112
	1,3-Azaphospholo[1,5-*a*]pyridine (2-Phosphaindolizine)	13,50,88,89,153,162,171,195,196,198,199,214
	1*H*-1,2-Benzo[*c*]azaphosphole - 4,5,6,7-Tetrahydro derivative	86

	1*H*-1,2-Benzo[*d*]azaphosphole	146,147
	1*H*-1,3-Benzazaphosphole - 1,3-Benzazaphospholide	28,96,121,124,127, 128,146,147,172, 175,176,187,217, 227
	1,3-Benzoxaphosphole	125,126,151,174, 202,210
	1,3-Benzothiaphosphole	132
	1,3-Benzoselenaphosphole 4,5,6,7-Tetrahydro derivative	152
	1*H*-1,2-Benzo[*c*]diphosphole (1*H*-1,2-Diphosphaindene) - 1,2-Benzo[*c*]diphospholide	45
	1,3-Benzodiphosphole (1,3-Diphosphaindene) - 1,3-Benzodiphospholide	119,120,122,123, 129,131,136
	1*H*-Benzo[*b*]phosphole (Phosphindole) - Phosphindolide	106-108,118,230
	1*H*-Benzo[*c*]phosphole (1*H*-Isophosphindole) - Isophosphindolide	101-105, 114-116, 205-207
	1,3-Benzometallaphosphole (M = Ti, Zr)	157

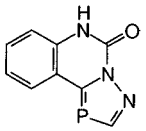
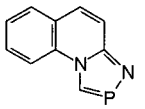
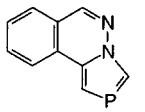
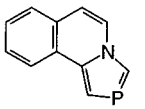
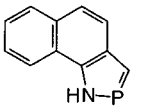
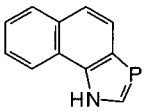
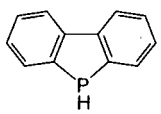
C. 5,7 Ring Systems

Structure	Name	References
	1-Phosphazulene	137,138
	2-Phosphazulene	156

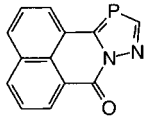
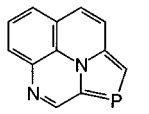
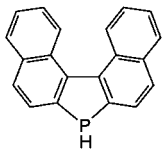
D. 5,5,6 Ring Systems

Structure	Name	References
	1,4,2-Diazaphospholo[5,1-*b*]benzothiazole	40,142
	1,4,2-Diazaphospholo[5,4-*b*]benzothiazole	40,81,82,142
	1,3-Azaphospholo[5,1-*b*]benzothiazole	92

E. 5,6,6 Ring Systems

Structure	Name	References
	1,2,4-Diazaphospholo[1,5-*c*]quinazolin-5(6*H*)-one	148-150
	1,4,2-Diazaphospholo[4,5-*a*]quinoline	142
	1,3-Azaphospholo[5,1-*a*]phthalazine	153
	1,3-Azaphospholo[5,1-*a*]isoquinoline	50
	1*H*-Naphtho[2,1-*d*][1,2]azaphosphole	146,147
	1*H*-Naphtho[2,1-*d*][1,3]azaphosphole	146,147
	Dibenzophosphole (9-Phosphafluorene) - Dibenzophospholide	108-110

F. 5,6,6,6 and 5,6,6,6,6 Ring Systems

Structure	Name	References
	7*H*-Benzo[*de*][1,2,4]diazaphospholo[5,1-*a*]isoquinolin-7-one	148-150
	4,9*b*-Diaza-2-phosphacyclopenta-[*c*,*d*]phenalene (Azaphosphaullazine)	155
	Dinaphtho[2,1-*b*,1',2'-*a*]phosphole - Dinaphtho[2,1-*b*,1',2'-*a*]-phospholide	111

VI. Conclusion

Anellated heterophospholes display a close analogy, particularly in the synthetic and structural aspects, with their non-phosphorus analogues. It is expected therefore that by applying various synthetic strategies available for the latter many new σ^2P heterocycles would become accessible in the coming years. The additional reactivity characteristics due to the presence of a σ^2-P in these heterocycles, based mainly on higher polarity and polarizability of P=C versus

C═C bonds and the availability of a lone pair at phosphorus, have so far been investigated to a limited extent. The synthesis of P−C or P−N analogues of natural anellated heterocycles, cycloadditions, and coordination chemistry are such areas that deserve more attention, particularly since a variety of these compounds can now be synthesized easily or will become readily accessible in the future. Catalytic applications of complexes with anellated heterophospholes have to our knowledge not yet been reported, but endeavors to find catalysts with these ligands should be increased considering the useful properties of recently developed catalysts with low-coordinated phosphorus or of metallocene polymerization catalysts bearing indolide ligands. We hope that this article will stimulate more activity in the hitherto unexplored areas and shed more light upon the analogies as well as the distinguished specific features of the anellated heterophospholes and their carbon analogues.

VII. Acknowledgments

We thank Prof. Dr. A. Schmidpeter (München) for helpful discussions and take this opportunity to thank the Indian National Science Academy, New Delhi, and the Deutsche Forschungsgemeinschaft, Bonn, for supporting the visit of R.K.B. in Greifswald.

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