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Anellated Heterophospholes

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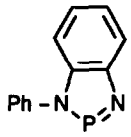
Contents

1. Introduction

In 1963 Pilgram and Korte[1] reported the condensation of *N*-phenyl-1,2-diaminobenzene and triphenylphosphite at 150 to 180°C to give in good yield a product which does not dissolve and does not melt up to 350°C. They attributed to it the formula of a 1,3,2-benzodiazaphosphole.



This was daring as in those days no other heterocycle with phosphorus participating in the cyclic delocalization and no stable compound of two-coordinate phosphorus at all was known. Dimroth and Hoffmann's phosphacyanines[2] and Märkl's first phosphinine[3] came, respectively, only one and three years later. The above formula was of course wrong as it was not in accord with the properties of the product (see Section 2.1) - but it was visionary, as it showed the first heterophosphole and in particular the first anellated heterophosphole. It thus anticipated a class of compounds which developed only two decades later and of which we now know quite an impressive number of stable representatives (see Section 7). They were all synthesized during the last 10 - 12 years.

Anellated heterophospholes constitute a special class of heterocyclic compounds in which a heterophosphole ring is fused with another ring. Heterophospholes are aromatic 6π-electron systems and may be thought as derived from typical five-membered heterocycles like pyrrole, furan or thiophene by substituting one CH moiety by an sp^2-hybridized phosphorus[4,5]. In the same sense anellated heterophospholes derive from classical fused systems[6] such as indole, indolizine, cumarone, thionaphthene, benzimidazole, benzthiazole or azapentalenes. Also in the scope of this report are compounds which derive from azulene or indenyl anion by a CH/P-exchange in the five-membered ring and which thus contain no heteromember other than phosphorus in the ring system. It will be of interest to compare structures and reactivities of the anellated (hetero)phospholes, as they become known, to those of their non-phosphorus containing analogues, and some notes on this aspect have already appeared[7].

This report gives an up-to-date (August 1993) account of all systems in which a five-membered ring containing a two-coordinate phosphorus is anellated to a fully unsaturated five-, six- or seven-membered ring. The phosphorus-containing ring may be a heterophosphole or a phosphole, in which case it will bear a negative charge. Complementary the report will include the synthesis of some systems with a saturated second ring; the list of compounds (Section 7) will not cover such systems, however.

Strategies for the synthesis of anellated heterophospholes can again be conceived by substituting P for CH or CR. For example, the method[7] of preparing 2-phosphaindolizines involving condensation of a 1,2-dialkylpyridininum salt with PCl_3 (Section 2.1) is analogous to Kröhnke's synthesis[8] of indolizines from the reaction of a pyridinium salt with a car-

boxylic acid anhydride while the alternative approach using phosphaalkynes[9] (Section 4.1) parallels the known cycloaddition of pyridinium ylides with acetylenecarboxylic esters to afford indolizines[10,11]. Such analogies open a vista of still to be used synthetic possibilities.

In almost all the syntheses employed for anellated (hetero)phospholes the phosphorus-containing ring is added to an existing ring. This is achieved by condensation reactions using electrophilic phosphorus reagents like PCl_3, $P(NR_2)_3$, $P(OPh)_3$, in a special case P_4, and $ClCH_2PCl_2$, or using nucleophilic phosphorus reagents like phosphines, alkaliphosphides and silylphosphines, or by cycloaddition reactions of phosphaalkynes and their precursor phosphaalkenes to 1,3-dipols. The syntheses are presented hereafter in this order.

2. Synthesis through Cyclocondensation Using Electrophilic Phosphorus

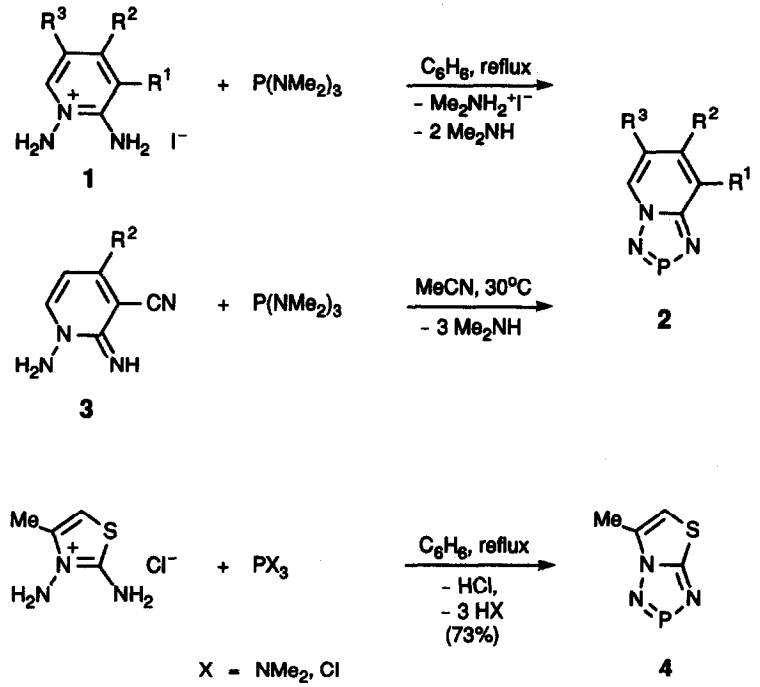
Cyclocondensations involving the use of electrophilic (electronegatively substituted) tervalent phosphorus resemble the syntheses of non phosphorus containing classical fivemembered heterocycles using carboxylic acid derivatives or α-halocarbonyl compounds for condensation.

2.1 *4+1-Cyclocondensation*

A four-membered chain with nucleophilic functions at both ends on condensing with an appropriate reagent - mostly PCl_3 or $P(NR_2)_3$ - incorporates phosphorus to complete the heterophosphole ring. To produce an anellated (hetero)phosphole, the four-membered chain must be part of a ring and may be composed of carbon atoms only or it may have one or more heteroatoms like nitrogen, oxygen, sulfur or even phosphorus again.

NNCN + P

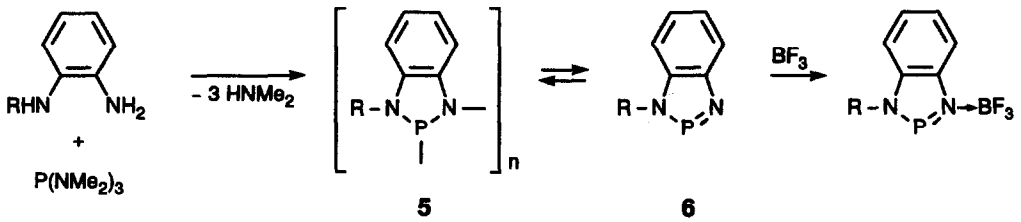
1,2-Diaminopyridinium iodides[12,13] **1** condense with $P(NMe_2)_3$ on refluxing in benzene to form 1,2,4,3-triazaphospholo[1,5-*a*]pyridines **2**[14]. In the same way, the 1,2,4,3-triazaphospholo[5,1-*b*]thiazole **4** has been prepared[15]. 1-Amino-2-imino-1,2-dihydropyridines **3** in place of **1** give the same condensation already at 30°C[15].



The method is analogous to the preparation of triazolo[1,5-*a*]pyridines from condensation of 1,2-diaminopyridinium salts with carboxylic acid anhydrides[12,13] and hence can be expected to be applicable to other diaminocycloimmonium salts also[16].

NCCN + P

N-Mono-alkyl *o*-phenylenediamines on refluxing with $P(NMe_2)_3$ form oligomers **5** (mostly tetramers) of 1,3,2-benzo-diazaphospholes which are found to be in equilibrium with the monomers **6** at elevated temperature. Complexation with BF_3 stabilizes the monomer[17–19].

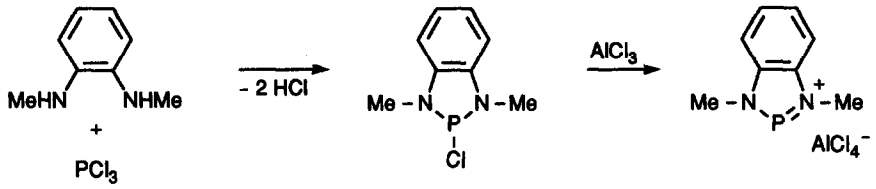


The formation of the oligomer **5** rather than of the monomer **6** was recently shown also for the *N*-phenyl derivative[20], thus correcting an earlier report[1]. The monomer **6**, R = Ph, is stabilized by complexation with $AlCl_3$[20]. Condensation of the iminophosphorane generated

from 2-dimethylamino-1,3,2-dithiaphospholane and phenylazide, also yields **5**; it involves a reductive disulfide elimination[21].

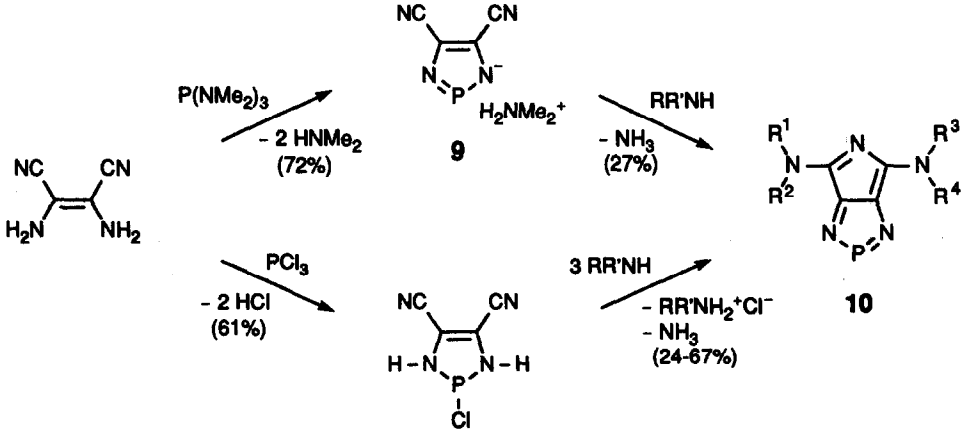
4,5-Diaminopyrimidine is reported to react with triphenylphosphite to give 1,3,2-diazaphospholo[1,5-*d*]pyrimidine. Formation of 1,3,2-diazaphospholopyridines from diaminopyridines under similar conditions is also claimed[22]. In both cases, however, the physical properties of the isolated materials are in accord with oligomers analogous to **5** rather than with monomeric azaphospholes.

The 1,3-dimethyl-1,3,2-benzodiazaphospholium cation could be prepared as tetrachloroaluminate **8** from 2-chloro-1,3-dimethyl-2,3-dihydro-1*H*-1,3,2-diazaphosphole **7**[23]; the latter was obtained from the condensation of PCl_3 with *N*,*N'*-dimethyl *o*-phenylene diamine[24].



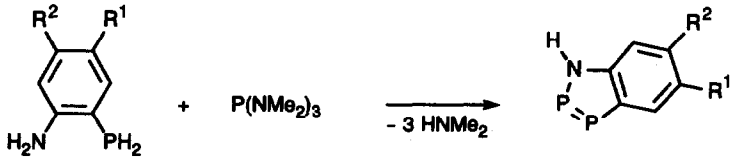
7 **8**

Condensation of diaminomaleodinitrile (DAMN) with $P(NMe_2)_3$ first gives the dimethylammonium diazaphospholate **9** which on heating with dimethylamine changes into 4,6-bis(dimethylamino)-1,3,5-triaza-2-phosphapentalene **10**, R^1-R^4 = Me[25,26]. With other dialkylamines unsymmetrically substituted diamino pentalenes **10**, R^1,R^2 = Me, R^3,R^4 = other alkyl groups, are obtained. More symmetrically substituted derivatives are prepared by refluxing 2-chloro-4,5-dicyano-2,3-dihydro-1*H*-1,3,2-diazaphosphole **11**, formed from the cyclocondensation of DAMN with phosphorus trichloride, with dialkylamines.



NCCP + P

o-Aminophenylphosphines condense with $P(NMe_2)_3$ in toluene at 90°C to form 1,2,3-benzazadiphospholes **12**[27,28].

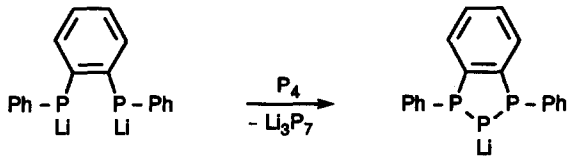


12

Reaction with $As(NMe_2)_3$ gives the corresponding 2-arsa derivative, while with $Sb(NMe_2)_3$ the dimer of the 2-stiba derivative is obtained[28].

PCCP + P

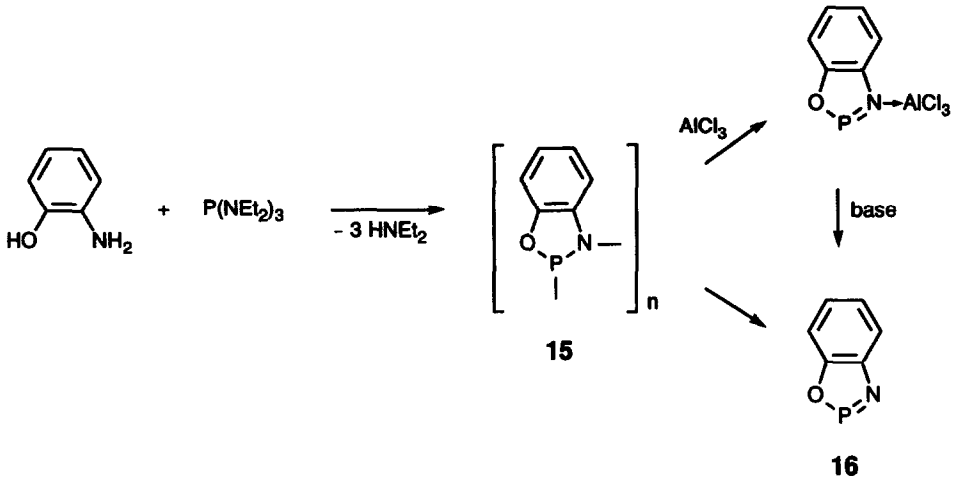
o-Phenylene bis(lithiumphosphide) **13** reacts with white phosphorus to give 2-lithio-2,3-dihydro-1,3-diphenyl-1*H*-benzotriphosphole **14**[29].



13 **14**

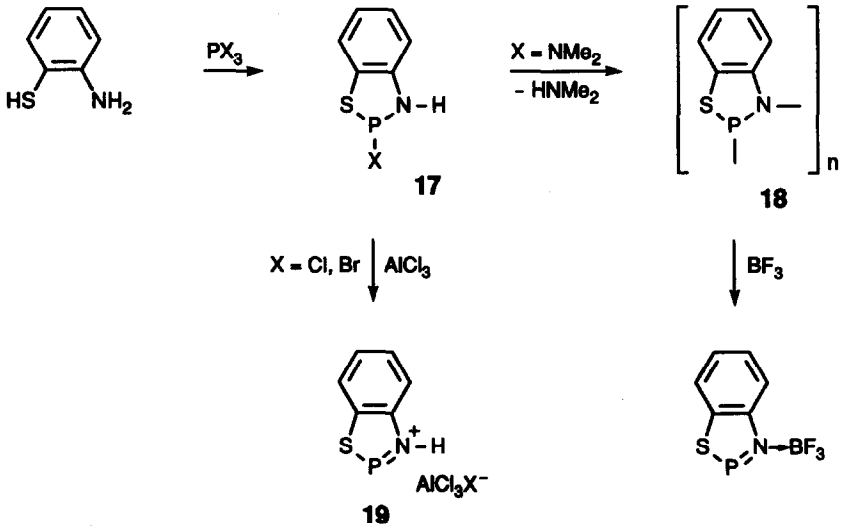
OCCN + P

o-Aminophenol and $P(NEt_2)_3$ form oligomers **15** of 1,3,2-benzoxazaphosphole which on treating with $AlCl_3$ (or some other Lewis acid) can be changed into the complexed monomer. The latter on reacting with a base may generate free benzoxazaphosphole **16** which again oligomerizes after some time[18].



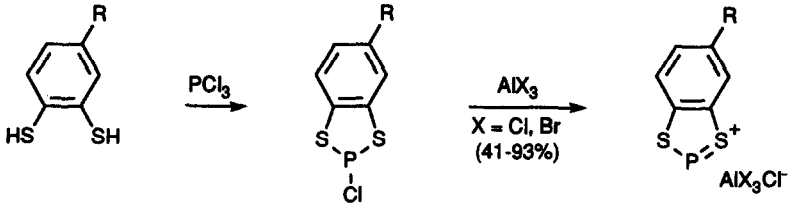
SCCN + P

o-Aminothiophenol and $P(NMe_2)_3$ condense at ambient temperature to give the 2-dimethylamino-2,3-dihydro-1*H*-1,3,2-benzothiazaphosphole **17**, X = NMe_2. On heating in vacuo (120°C/20 mbar) it loses $HNMe_2$ and yields 1,3,2-benzothiazaphosphole oligomers **18**. As in the case of **6** and **16** the monomer can be stabilized by complexation with BF_3[18,30]. The 1,3,2-benzthiazaphospholium cation in **19** has been generated by halide ion abstraction from the dihydro derivatives **17**, X = Cl,Br, which are obtained from the condensation of *o*-aminothiophenol with PCl_3 or PBr_3, respectively[31].



SCCS + P

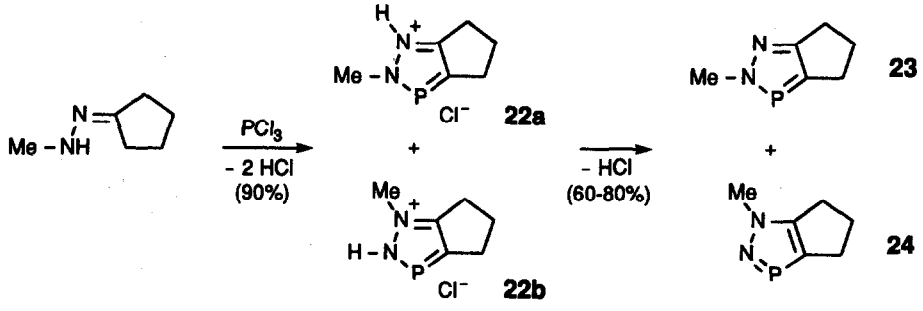
The method used for the generation of 1,3,2-benzodiaza- and -thiazaphospholium cations has been extended to the generation of the benzodithiaphospholium cation in **21**[32–34]. Starting compounds are the 2-chloro-1,3,2-benzodithiaphospholes **20**, which are obtained from the cyclocondensation of *o*-phenylenedithiols with PCl_3[35].



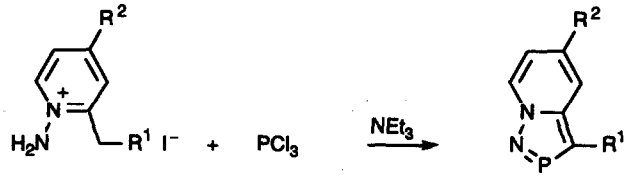
20 **21**

NNCC + P

Cyclopentanone methylhydrazone condenses with PCl_3 to give the two isomeric diazaphospholes **23** and **24**[36,37]. The reaction has been found to proceed through the intermediate formation of the salts **22a,b**, which could be isolated and characterized[38].



2-Alkyl-1-aminopyridinium iodides condense with PCl_3 in presence of NEt_3 to give 1,2,3-diazaphospholo[1,5-*a*]pyridines **25**[39].



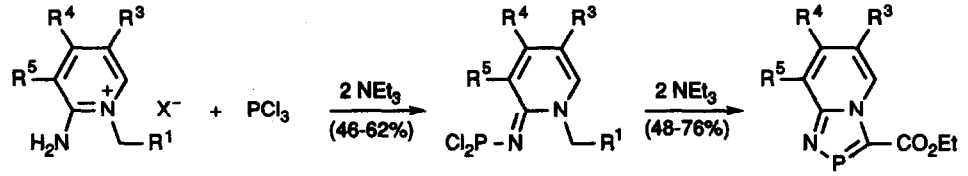
25

2-Methyl-1-aminopyridinium iodide on reacting with 2 equivalents PCl_3 under these conditions forms 1-dichlorophosphino-1,2,3-diazaphospholo[1,5-*a*]pyridine (**25**, $R^1 = PCl_2$, $R^2 = H$)[39].

The condensation of 2-alkyl-1-aminopyridinium iodides with PCl_3 is analogous to the synthesis of pyrazolo[1,5-*a*]pyridine derivatives from the same salts and acyl halides in presence of a base[40,41] and it should be possible to extend this method to other *N*-aminocycloimmonium salts also[16].

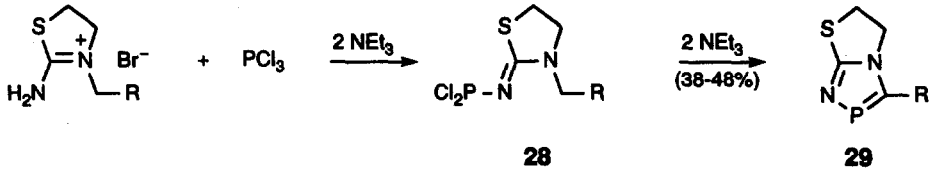
NCNC + P

Condensation of 1-alkyl-2-aminopyridinium halides (X = Cl, Br; $R^1 = CO_2Et$) with PCl_3 in the presence of NEt_3 affords 1,4,2-diazaphospholo[4,5-*a*]pyridines **27**. The reaction is initiated at the 2-amino group of the pyridinium salt as revealed by isolation of the intermediate 2-(1-alkyl)pyridinylidenamino-dichlorophosphines **26** under mild conditions. The latter could be subsequently cyclized by the action of an additional amount of triethylamine. However, when R^1 does not sufficiently activate the adjacent methylene group (R^1 = Ph, 4-MeC_6H_4), the reaction stops at the stage of **26** and cyclization does not occur even on prolonged heating[42].

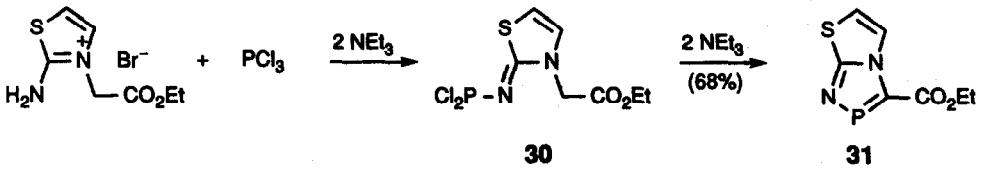


26 **27**

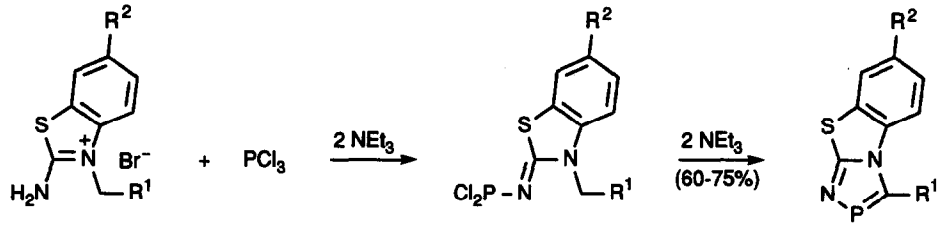
3-Alkyl-2-aminothiazolium and -benzothiazolium bromides undergo cyclocondensation with PCl_3 under similar conditions to give the 3-substituted thiazolo[3,2-*d*][1,4,2]diazaphosphole **31** and the corresponding benzoanellated derivatives **33**, respectively[43]. Starting from 3-alkyl-2-aminodihydrothiazolium bromides the 5,6-dihydrothiazolo[3,2-*d*][1,4,2]diazaphospholes **29** have been obtained likewise[43]. In these cases also, an aminodichlorophosphine (**30**, **32** and **28**, respectively) has been isolated as an intermediate[44,45]. Sufficient activation of the *N*-methylene group is again a prerequisite for cyclization.



28 **29**



30 **31**

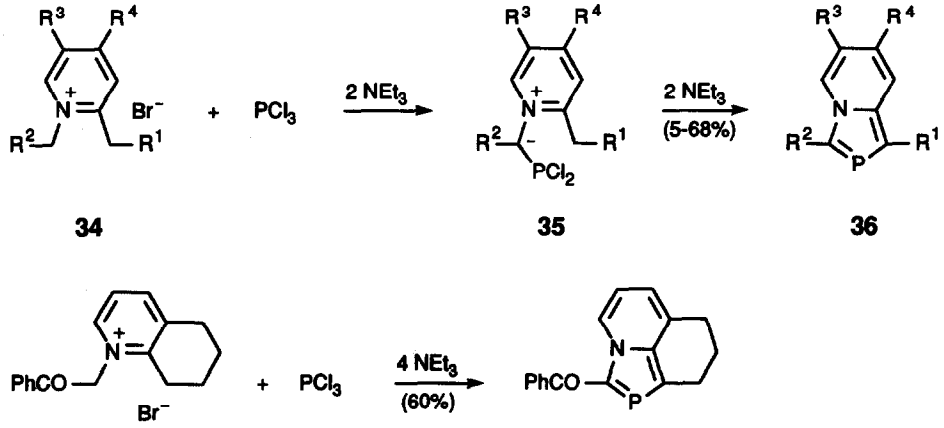


32 **33**

The above synthetic procedure finds an analogy with the synthesis of imidazo[1,2-*a*]-pyridines and other related systems from the condensation of 2-amino-1-benzylcycloimmonium salts with carboxylic acid anhydride[46,47].

CNCC + P

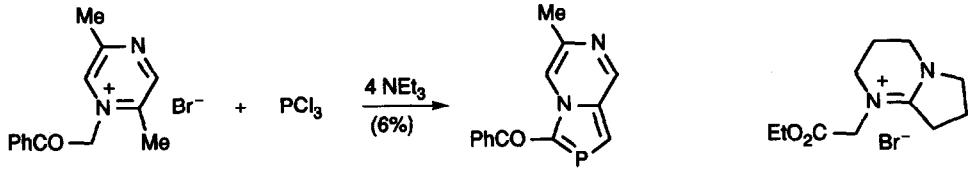
1,2-Dialkylpyridinium bromides condense with PCl_3 in the presence of NEt_3 to give 2-phosphaindolizines **36**. By this method a number of differently substituted 2-phosphaindolizines could be prepared[7,48]. The reaction appears quite general, but sufficient activation of the *N*-methylene group is essential. In the case of 2-ethyl-1-(2-ethoxy-2-oxoethyl)pyridinium bromide **34**, R^1 = Me, R^2 = CO_2Et, R^3 = R^4 = H, bearing a mildly activated *N*-methylene group, an intermediate ylide **35** could be isolated which cyclized to the 2-phosphaindolizine on heating with additional amount of NEt_3[7]. Obviously, the pyridinium salt bearing an activated *N*-methylene group first changes into the *N*-pyridinium ylide which subsequently reacts with PCl_3 to generate a new *N*-(dichlorophosphinomethylene)pyridinium ylide. When R^2 = COPh, CN or 4-$NO_2C_6H_4$, it immediately loses more HCl to form the final product. The 5,6,7,8-tetrahydro-1-phenacylquinolinium bromide **37** also condenses with PCl_3 and gives **38**[7].



34 **35** **36**

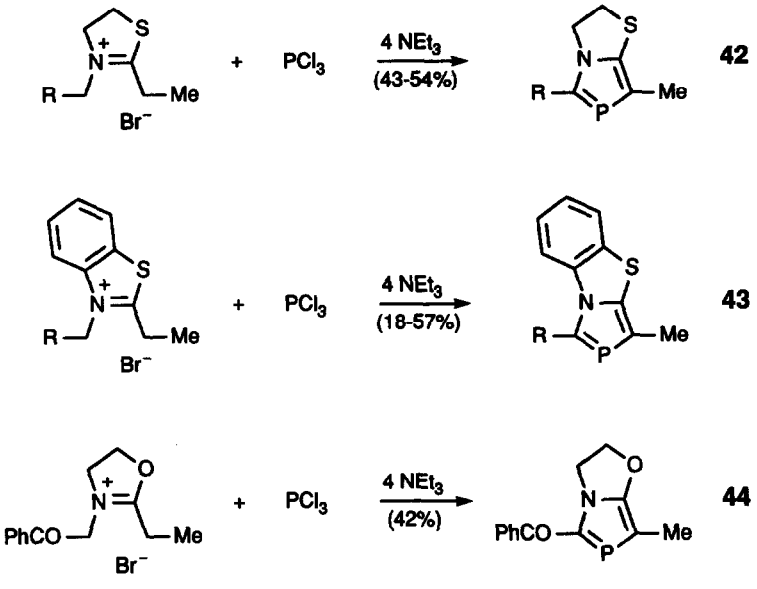
37 **38**

2,5-Dimethyl-1-phenacylpyrazinium bromide **39** has been found to react with PCl_3 to form the corresponding 1,3-azaphospholo[1,5-*a*]pyrazine **40**[7]. Although the behaviour of the related pyridazinium and pyrimidinium salts has not been investigated so far, **41** does not undergo cyclocondensation with PCl_3 and NEt_3[49].

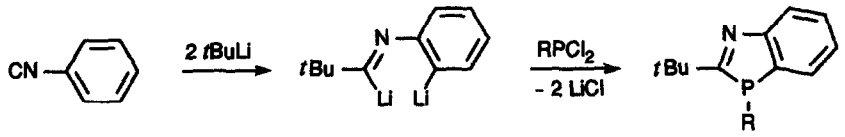


39 **40** **41**

1,3-Azaphospholo[5,1-*b*]thiazolines **42**[50], -benzothiazoles **43**[50] and -oxazoline **44**[51] have also been obtained from the condensation of the corresponding 2,3-dialkylcycloimmonium salts with PCl_3 under similar conditions.



The dilithio-derivative obtained from phenylisonitrile and *tert*-butyllithium reacts with alkyldichlorophosphines $RPCl_2$ (R = Me, *t*Bu) to furnish the 3*H*-1,3,2-benzazaphospholes **45**. Flash vacuum pyrolysis (550°C/0.01 mbar) of the *tert*-butyl derivative yields 2-*tert*-butyl-1*H*-1,3,2-benzazaphosphole **46**[52].



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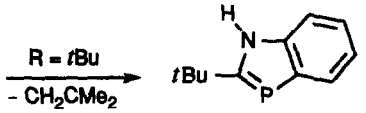
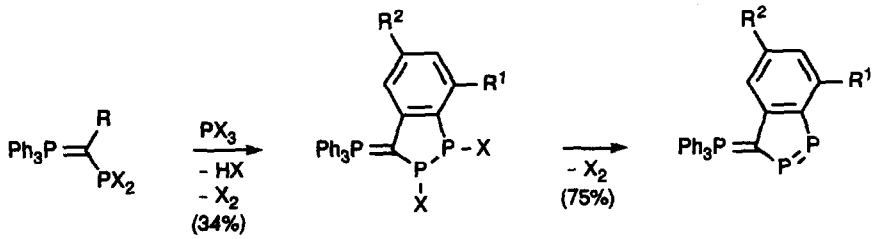


46

PCCC + P

The dihalogenophosphino-substituted triphenylphosphonium ylids **47**, R = Ph, X = Cl,Br, resulting from benzyl triphenylphosphonium bromide and PX_3 in the presence of NEt_3, undergo with more PX_3 a ring closure to give the 1,2-dihalogeno-3-triphenylphosphinediyl-1,2-diphosphaindanes **48**, R^1,R^2 = H, X = Cl,Br. This reaction involves an electrophilic *ortho*-substitution of the ylidic phenyl ring and a reductive diphosphine formation. Dehalogenation of **48** with magnesium or triphenylphosphine yields orange yellow crystalline 3-triphenylphosphonio-1,2-diphosphaindenide **49**, R^1,R^2 = H[53].

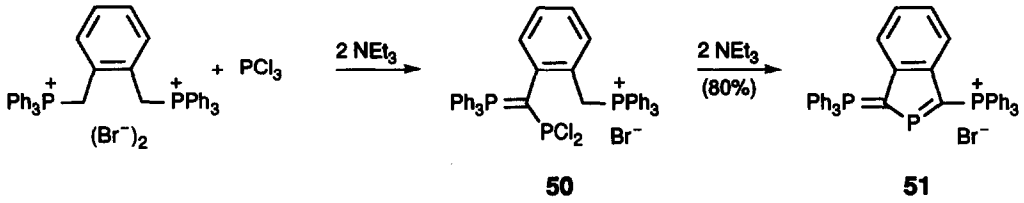


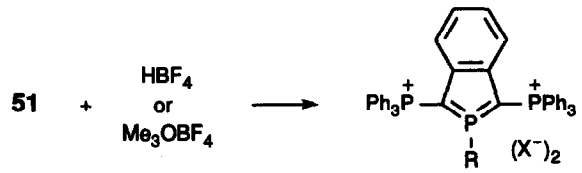
47 48 49

Starting from **47**, R = 3-MeC_6H_4, X = Cl,Br, likewise results in a mixture of the 5- and 7-methylsubstituted diphosphaindenides **49** (R^1/R^2 = H/Me, Me/H)[53].

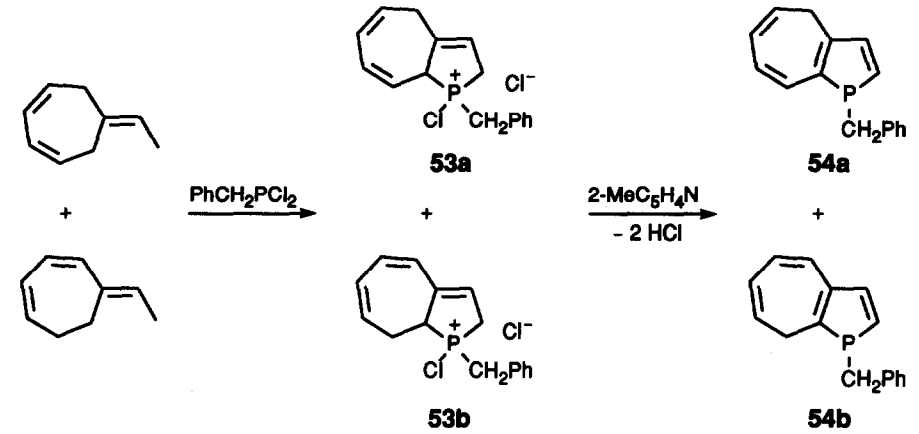
CCCC + P

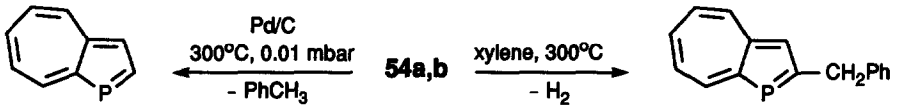
With no heteroatom in the chain the terminal methylene groups can be activated by phosphonium groups. Thus *o*-xylenebis(triphenylphosphonium)bromide condenses with PCl_3 in the presence of NEt_3 to give the 1,3-bis(triphenylphosphonio)isophosphindole cation, which is isolated as the bromide **51**; the intermediate **50** could be detected ^{31}P-NMR spectroscopically[54]. More representatives having other substituents at the phosphonio groups have been prepared by the same method[55]. **51** could be converted to the BPh_4, $SbCl_6$ and HgI_3 salts. Protonation and methylation of **51** yield the dication salts **52** R = H, Me, X = Br, BF_4, which represent the first phospholes with a planar three-coordinate phosphorus capable of participating in the cyclic conjugation[54].





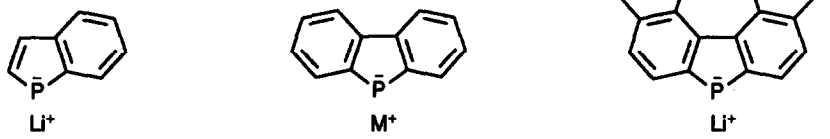
1-Vinyl- and 2-vinyl-1,3,5-cycloheptatrienes condense with benzyldichlorophosphine in the presence of copper stearate to give the dichlorotetrahydro-1λ^5-phosphaazulenes **53**, which on dehydrochlorination with α-picoline are converted to the 1-benzyl dihydro-1-phosphaazulenes **54a,b**. Thermolysis of **54a,b** in xylene (sealed tube, 300°C) yields 2-benzyl 1-phosphaazulene **56**, involving a 1,5-sigmatropic shift of the benzyl group and the elimination of hydrogen[56]. However, gas phase pyrolysis (300°C/0.01 mbar) in the presence of Pt/C gives exclusively the fully unsubstituted 1-phosphaazulene **55**[57].





55 56

Phospholyl anions are obtained by reductive cleavage of the exocyclic P-C bond of phospholes. In a typical procedure, the cycloadduct of a diene with an organophosphorus dibromide is subjected to dehydrobromination with DBU to yield the phosphole which loses the substituent R on reacting with potassium in tetrahydrofuran. Some phospholyl anions anellated to saturated rings[58,59] have been made this way.



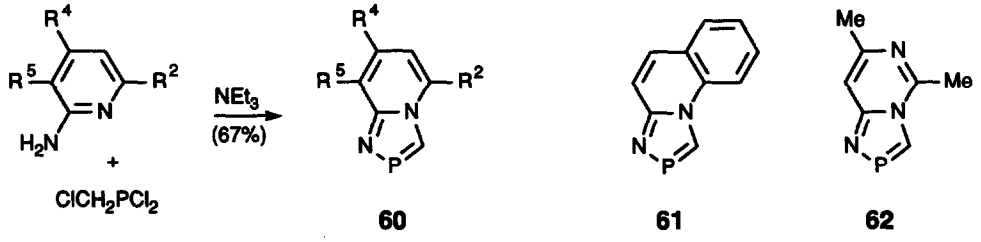
57 58 59

1-Phenylphosphindole, obtainable by two methods[60,61], on reacting with lithium in tetrahydrofuran furnishes phosphindolyllithium **57**[62]. Similarly, **58**, M = Li, Na, K, Cs, has been generated from the reaction of phenylbiphenylenephosphine with alkali metals[63]. The dinaphthophospholyl anion **59** has been prepared from the reaction of lithium on dinaphtho-1-phenylphosphole which was obtained by 4+1-condensation of bis-dialine or 2,2'-dilithiobinaphthyl with phenyldichlorophosphine[64].

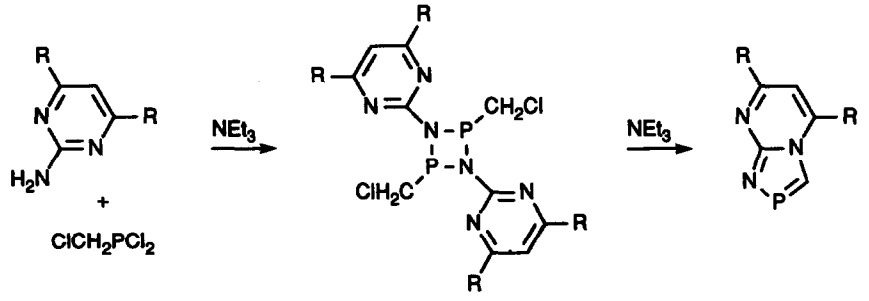
2.2 *3+2 Cyclocondensation*

Chloromethyldichlorophosphine, acting as two atom component condenses with a variety of 2-aminosubstituted azoles and azines (containing an amidine structure) to give anellated 1,4,2-diazaphospholes[65]. In fact, as such heterocyclic amidines have widely been used to synthesize bi- and polycyclic non phosphorus containing heterocycles[66,67], it seems possible to extend the reaction with chloromethyldichlorophosphine to more of them. This reagent is used here in place of an α-halocarbonyl compound.

In analogy to the synthesis of pyrazolo[1,2-*a*]pyridines[68,69] condensation of 2-aminopyridines with chloromethyldichlorophosphine leads to 1,4,2-diazaphospholo[4,5-*a*]pyridines **60** regiospecifically[65,70].



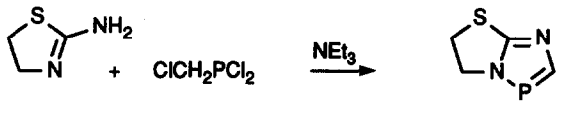
60 **61** **62**



63 **64**

2-Aminoquinoline, 2,6-dimethyl-4-amino-pyrimidine and 2-aminopyrimidines behave analogously under these conditions and give 1,4,2-diazaphospholo[4,5-*a*]quinoline **61**[30], 5,7-dimethyl-1,4,2-diazaphospholo[4,5-c]pyrimidine **62**[30] and 1,4,2-diazaphospholo[5,4-*b*]pyrimidines **64**[30,65], respectively. In the case of 2-aminopyrimidines it has been possible to isolate the diazadiphosphetidine **63**, R = Me[65], as an intermediate. On treatment with NEt_3 it changes into the final product, presumably through intramolecular nucleophilic displacement of the chlorine atom by the pyridinic nitrogen atom accompanied by the rupture of the diazadiphosphetidine ring and loss of hydrogen chloride.

In analogy to the synthesis of imidazo[2,1-*b*]thiazoles[71] 2-aminothiazoline condenses with chloromethyldichlorophosphine. The reaction is again regiospecific, but the orientation is reversed and the 5,6-dihydro-thiazolo[3,2-*e*][1,2,4]diazaphosphole **65** is obtained[65]. In this case the reaction probably initiates at the ring nitrogen atom[65].



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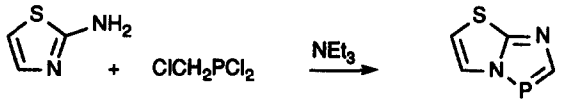
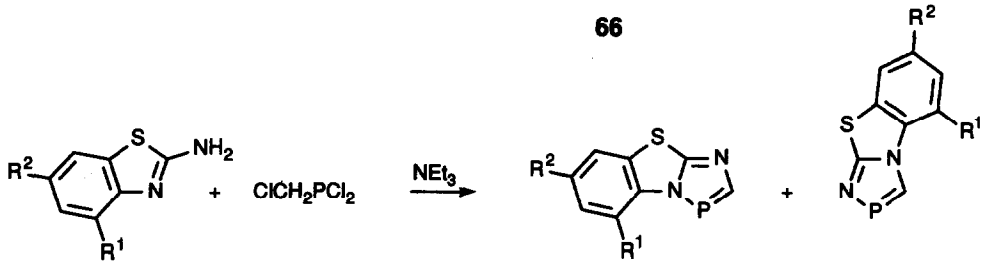


66



67 **68**

R^1, R^2 =			
H, H	33%	67%
H, OMe	50%	50%
Me, H	-	100%

2-Aminothiazole reacts analogously and yields the thiazolo[3,2-*e*][1,2,4]diazaphosphole **66**[30]. Regiospecificity is not maintained in the reaction of chloromethyldichlorophosphine with 2-aminobenzothiazoles and a mixture of the two benzothiazolo-diazaphospholes **67** and **68** results. Their ratio depends strongly on the substituents in the benzo ring[72].

3. Synthesis through Cyclocondensation Using Nucleophilic Phosphorus

Phosphines and their metal and silyl derivatives undergo condensation reactions with carbonyl compounds and carboxylic acid derivatives. For the synthesis of anellated phospholes and heterophospholes this reaction can be employed in two ways of a 4+1-cyclocondensation: The four-membered chain may incorporate the phosphorus, or it may contain the phosphorus already and incorporate a carbon member to complete the ring. Examples of both approaches

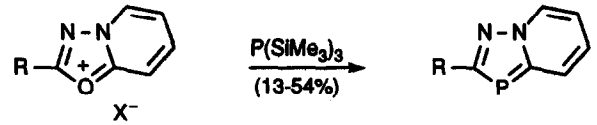
have become accessible. They resemble the synthesis of anellated azoles using ammonia or anilines.

3.1 *4+1 Cyclocondensation with P as the Member Being Introduced*

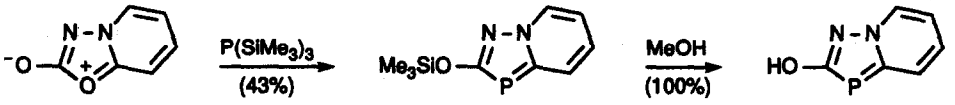
Tris(trimethylsilyl)phosphine has been commonly used for this purpose. In one case, potassium dihydrogenphosphide finds use as the nucleophilic phosphorus reagent.

CNNC + P

1,3,4-Oxadiazolo[3,2-*a*]pyridinium salts react with $P(SiMe_3)_3$ to give 1,2,4-diazaphospholo[1,5-*a*]pyridines **69**[73]. The use of $As(SiMe_3)_3$ yields the corresponding arsole.



69

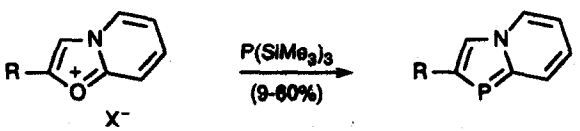


70

The 2-hydroxy derivative **70** has been obtained using 1,3,4-oxadiazol-2-olato[4,5-*a*]pyridine; it could be converted to *O*-acyl derivatives[74].

CCNC + P

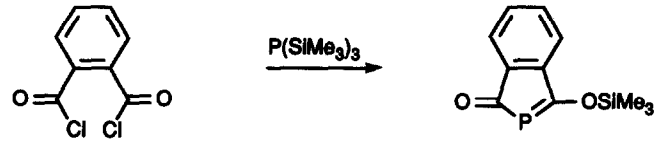
1,3-Oxazolo[3,2-*a*]pyridinium salts react with $P(SiMe_3)_3$ to afford 1-phosphaindolizines **71**[73].



71

CCCC + P

Phthaloyldichloride condenses with $P(SiMe_3)_3$ to form 3-trimethylsiloxy-1*H*-2-benzophosphol-1-one **72** which subsequently dimerizes[75,76] (see 6.2).



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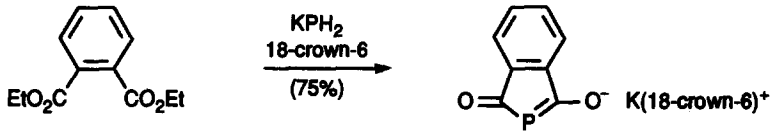


73

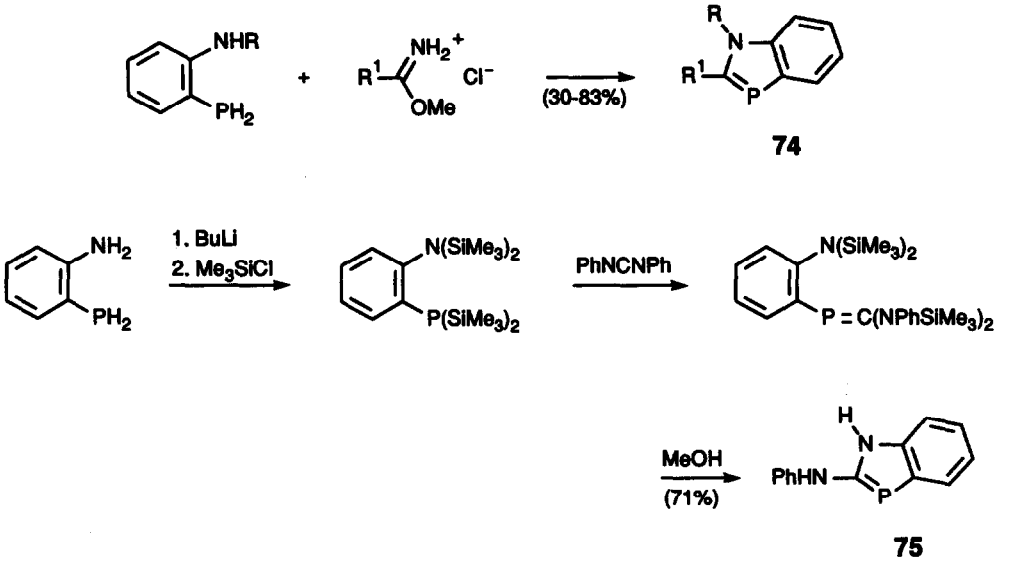
The synthesis of other phospholes having a partially or fully saturated anellated six-membered ring has been accomplished in a similar manner[76]. Diethylphthalate requires a stronger nucleophilic reagent, potassium dihydrogenphosphide, which condenses in the presence of 18-crown-6 to produce the potassium salt of the 2*H*-isophosphindoline-1,3-dione anion **73**[77].

3.2 *4+1-Cyclocondensation with P in the Four-Membered Chain*

Phenylphosphines having a substituent like amino, hydroxy or mercapto group in the *ortho*-position provide a four-membered chain which condenses with an appropriate carbonic acid derivative to form benzoheterophospholes. 1,2-Diphosphinobenzene condenses to yield benzodiphospholes. A variety of carbonic[78–80] and carboxylic acid derivatives[81–90] and aldehydes[91] have been used for this purpose.

NCCP + C

1,3-Benzazaphospholes have been obtained from the condensation of *o*-aminophenylphosphines with different carboxylic acid derivatives. As an example, condensation with *O*-methylimidate hydrochlorides gives **74**, R = H, Me; R^1 = H, Me, Ph[83,86,87]. **74**, R = Me, R^1 = *t*Bu, was obtained through condensation with *N*-tolyl-*tert*-butyl imidoyl chloride, however[87].

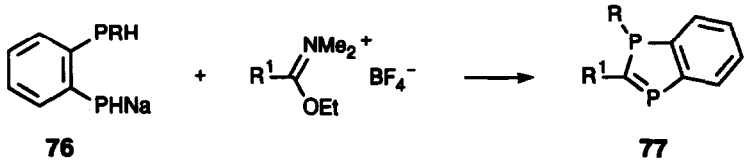


In another version, *o*-aminophenylphosphine was first persilylated. The product on reacting with diphenylcarbodiimide followed by the action of methanol afforded 2-anilino-1,3-benzazaphosphole **75**[80].

PCCP + C

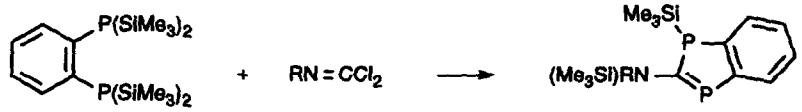
1,2-Diphosphinobenzene condenses directly with amideacetals to give 1,3-benzodiphospholes[88]. Alternatively it is first converted to an alkalimetal or silyl derivative which subsequently condenses with a suitable electrophilic moiety to form the 1,3-benzodiphosphole.

The monosodiumphosphide **76** reacts with an alkoxy-dimethylamino-carbenium tetrafluoroborate to give 2-substituted 1,3-benzodiphospholes **77**[88,90]. In the case of the corresponding disodium phosphide, however, cyclization does not occur and 1,2-bis(dimethylaminoalkylidenephosphino)benzene is formed[90].



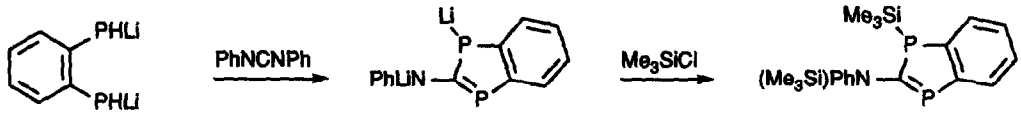
76 **77**

Persilylated 1,2-diphosphinobenzene reacts with phosgene imides to form 2-amino-1,3-benzodiphosphole derivatives **78**[88].

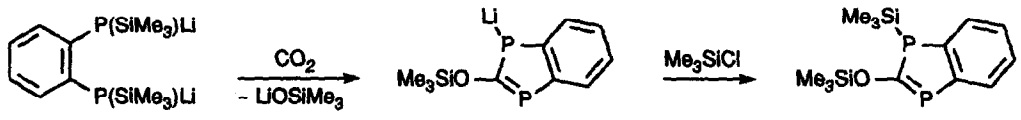


78

The more reactive 1,2-di(lithiophosphino)benzene condenses with diphenylcarbodiimide to give the dilithiated 2-anilino derivative **79** which undergoes silylation to yield **78**, R = Ph[79].



79 **(78)**



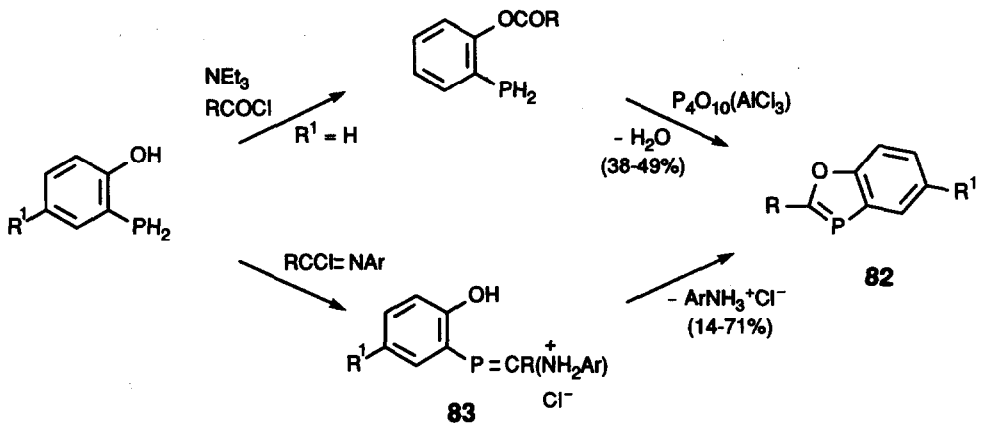
80 **81**

The reaction of 1,2-bis(lithio-trimethylsilylphosphino)benzene with electrophilic carbon moieties like carbon dioxide[78], carbodiimide[81] or an acyl chloride[81,82] leads to a 1,3-benzodiphospholyl anion such as **80** in the case of CO_2. The products can be alkylated or silylated to furnish the neutral 1,3-benzodiphosphole, e.g. **81**.

It has been found that the cyclocondensation of 1,2-diphosphinobenzene is accompanied by the formation of side products resulting from oxidative P-P bond formation[89].

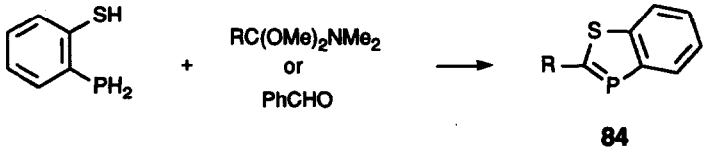
OCCP + C

1,3-benzoxaphospholes **82** could be obtained from the reaction of *o*-hydroxyphenylphosphine with acyl chlorides followed by dehydration[84] or with arylimidoyl chlorides[84,85]. In one of the latter cases the intermediate **83** could be isolated.



SCCP + C

o-Mercaptophenylphosphines undergo condensation with amideacetals as well as benzaldehyde to give 1,3-benzothiaphospholes **84**[91].



4. Synthesis through Cycloaddition

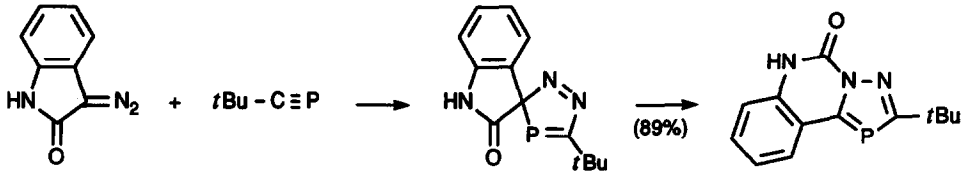
4.1 *3+2-Cycloaddition of Phosphaalkenes and -alkynes*

Phosphaalkynes and phosphaalkenes have been found to act as dienophiles and 1,3-dipolarophiles and undergo 4+2-and 3+2-cycloadditions leading to the formation of a variety of organophosphorus compounds[92–94]. Anellated phospholes and heterophospholes have been synthesized from 3+2-cycloadditions of these synthons with appropriate, ring derived 1,3-dipoles. Although only a limited number of anellated heterophospholes and phospholes have

been obtained this way so far, some well-formulated synthetic processes have been developed which can be exploited for phosphorus analogues of other anellated heterocycles.

NNC + CP

Diazo compounds undergo 3+2-cycloaddition with phosphaalkynes to form anellated 1,2,4-diazaphospholes. The reaction of cyclic α-diazoketones such as **85** with *tert*-butyl phosphaacetylene first gives the spirocyclic product **86** which undergoes a 1,5-sigmatropic shift to yield the 2,3-anellated 1,2,4-diazaphosphole **87**[95–97].

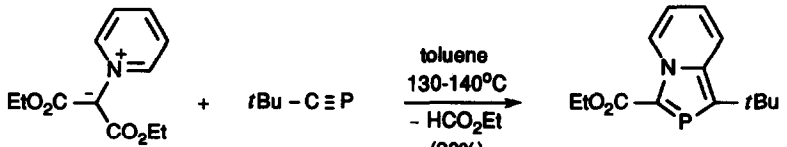


85 **86** **87**

CNC + CP

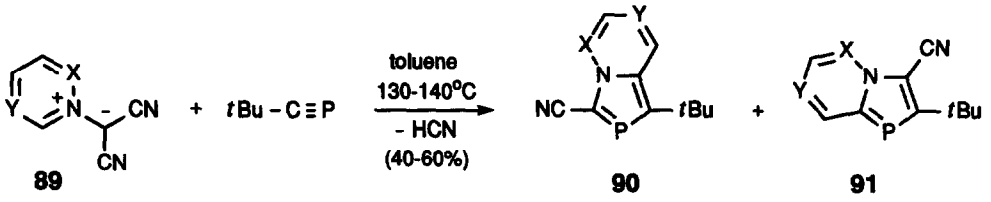
Azomethine ylides and azomethine imines of pyridine, quinoline, isoquinoline and related nitrogen heterocycles are potential 1,3-dipoles which undergo 3+2 cycloaddition with a variety of dipolarophiles leading to the formation of fused heterocycles[98]. This method has been extended to the use of a phosphaalkyne as dipolarophile and different anellated 1,3-azaphospholes have been obtained[9].

The pyridinium ylide **88** undergoes regiospecific 3+2-cycloaddition with *tert*-butylphosphaacetylene to give the 2-phosphaindolizine **36** (R^1 = *t*Bu, R^2 = CO_2Et, R^3,R^4 = H)[9].

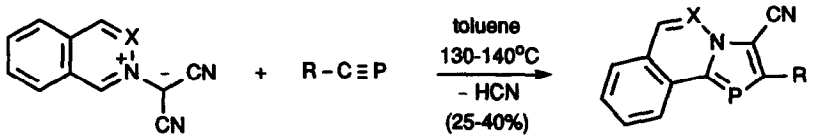


88 **(36)**

3+2-Cycloadditions of pyridinium (**89**, X = CH, Y = CH), pyridazinium (**89**, X = N, Y = CH) and pyrazinium (**89**, X = CH, Y = N) dicyanomethylides with *tert*-butylphosphaacetylene have also been carried out, but the reaction is not regioselective and a mixture of the two isomers **90** and **91** is obtained in each case. However, regioselectivity is observed when *tert*-butyl and isopropoxy groups are introduced in 4-position of **89**, X = CH, Y = CH[9].



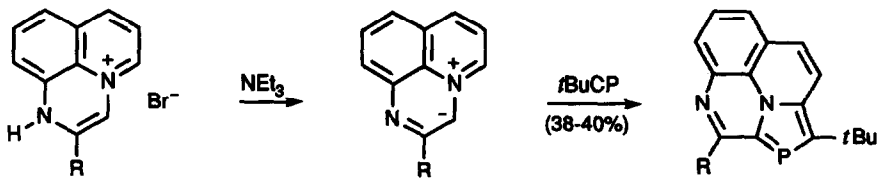
Isoquinolinium and phthalazinium ylides, **92** and **93** respectively, react with phosphaalkynes similarly to form **94** and **95**; the reaction is again regiospecific, though the dipole orientation is reversed as compared to the formation of **36** (R^1 = *t*Bu, R^2 = CO_2Et, R^3,R^4 = H)[9].



92 X = CH
93 X = N

94 X = CH
95 X = N

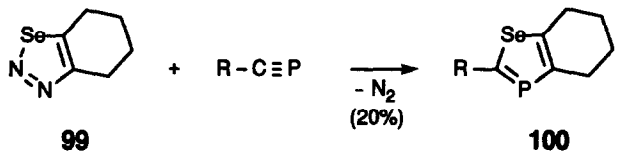
The 1,3-dipoles **97**, generated from the 3*H*-pyrido[1,2,3-*de*]quinoxalinium bromides **96** and triethylamine, react analogously with *tert*-butylphosphaacetylene and yield regiospecifically the phosphazaallacines **98**, R = Me, Ph[99].



96 **97** **98**

SeCC + CP

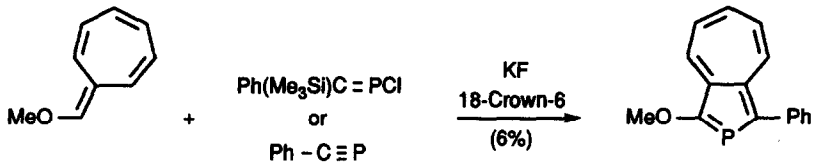
Bicyclic 1,2,3-selenadiazoles such as **99** on photolysis or thermolysis generate an electron deficient species which is trapped by a phosphaalkyne to give 1,3-selenaphospholes **100**[100].



99 **100**

CCC + CP

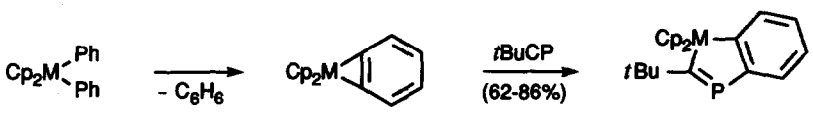
Electron-rich heptafulvenes undergo [8+2]-cycloaddition with reactive polyenophiles to form azulene derivatives[101]. Phenylphosphaethyne or its precursor, 1-chloro-2-phenyl-2-trime- thylsilylphosphaethene, reacts with 8-methoxyheptafulvene **101** likewise to form 2-phospha- azulene **102** regioselectively. The reaction is carried out in the presence of KF and [18]-crown-6[102].



101 **102**

MCC + CP (M = Ti, Zr)

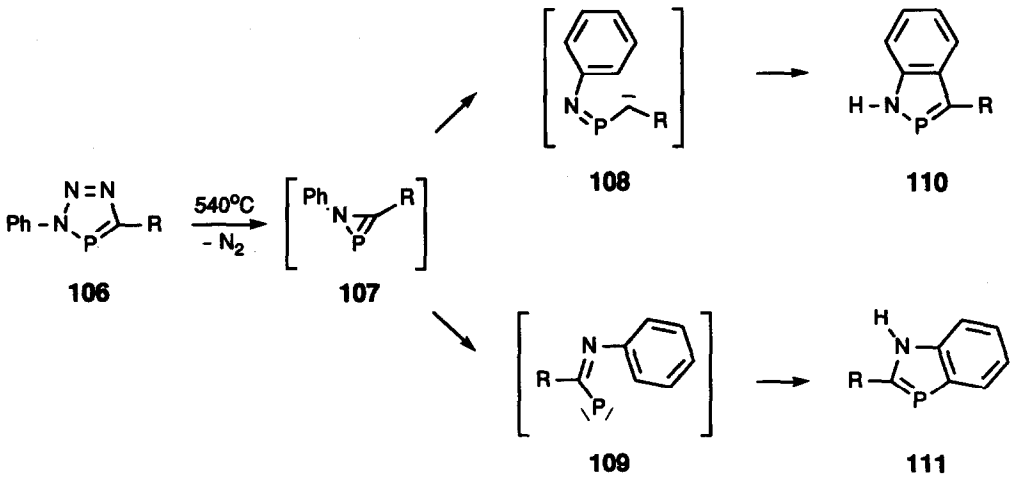
Benzometallaphospholes have been obtained by heating bis(cyclopentadienyl)diphenyl-titanium and zirconium **103**, M = Ti, Zr, with *tert*-butylphosphaacetylene[103]. The reaction involves initial formation of the dehydrobenzometal complex **104** which undergoes 3+2-cycloaddition with the phosphaalkyne to furnish **105**.



103 **104** **105**

4.2 *[1,5]-Electrocyclization*

3-Phenyl-1,2,3,4-triazaphospholes **106**, R = Me, *t*Bu, prepared from the 3+2-cycloaddition of phosphaalkynes with phenylazide, on flash vacuum pyrolysis split off nitrogen giving two types of species: the carbene **108** and the phosphinidene **109** formed through the azaphosphirene **107**. These species subsequently undergo [1,5]-electrocyclization followed by proton migrations to form anellated azaphospholes: **108** leads to the 1,2-benzazaphosphole **110** whereas the 1,3-benzazaphosphole **111** results from **109**. The analogous reactions are observed for the 3-naphthyl-1,2,3,4-triazaphosphole[104,105].



5. Physical, Spectral and Structural Characteristics

5.1 *UV/VIS Spectra*

While anellated heterophospholes generally are colourless to yellow, they exhibit in some cases intense colours. For example 4,6-diamino-1,3,5-triaza-2-phosphapentalenes **10** are deep red due to a CT transition[26]. 1,3-Benzodithiaphospholium tetrachloroaluminates are deep orange solids[32–34]. 1-Phosphaazulene[57] and its 2-benzyl derivative[56] are green and blue-green, respectively, while 1-methoxy-3-phenyl-2-phosphaazulene **102** forms red crystals[102].

The UV spectra of several anellated heterophospholes have been reported[22,26,56,75,80 82,84–87,102]. Exchange of N in an azole for P is accompanied by a bathochromic shift of λ_{max}. Thus λ_{max} shifts from 200-205 nm in benzimidazole to 226-256 nm in 1,3-benzazaphospho-

les[84–86]. 1-Phosphaazulene (λ_{max} = 730 nm) and 2-benzyl-1-phosphaazulene (λ_{max} = 700 nm) also show a bathochromic shift as compared to azulene (λ_{max} = 695 nm) and its 2-benzyl derivative (λ_{max} = 677 nm)[56,57]. In the case of 2-aryl-1,3-benzoxaphospholes the bathochromic shift of λ_{max} at longest wavelength has been correlated with the conjugative effect of the substituent in the phenyl ring, which decreases in the order 4-$MeOC_6H_4$ > 4-ClC_6H_4 > Ph. Solutions of 2-aryl-1,3-benzoxaphospholes (10^{-2} to 10^{-4} M) exhibit strong blue fluorescence (λ_{Em} 416 nm)[84].

5.2 *Photoelectron Spectra*

The He(I) photoelectron spectra of 1,3-benzazaphospholes and 1,3-benzoxaphospholes along with their nitrogen and arsenic analogues have been determined and correlated with the results of MNDO and CNDO/S quantum chemical calculations[106,107]. Although there is a strong interaction between the E=C (E = N, P, As) bond and the π-system of the benzene ring, the HOMO possesses predominantly E=C character.

In the photoelectron spectra of 1,2,3-benzazadiphosphole, the first six ionisation bands could be resolved[28]. The first two bands (8.1 and 8.6 eV) correspond to π-orbitals, the lower one indicating strong localization on the P=P bond, whereas the third (9.4 eV) and the fifth (10.4 eV) are related to the lone pairs at the two phosphorus atoms.

5.3 *IR Spectra*

The IR spectral data of several anellated heterophospholes have been reported[22,31–34,62,74–76,82,83,87,96,104]. The ν_{PS} stretching vibration in the 1,3-benzodithiaphospholium cation is observed at 716.1 cm^{-1} [32–34].

5.4 *Mass Spectra*

Mass spectral data of various anellated heterophospholes have been reported[18,22,27,31–34,56,62,73,74,82,86,90,103,105]. In a few cases the molecular ion forms the base peak[74,82,86].

5.5 *NMR Spectra*

The chemical shift range of the two-coordinate phosphorus in fully unsaturated anellated heterophospholes and phospholes extends from δ = +495 to −5 with most of the shifts between +300 and +50 (Figure 1; for compilations see ref.[108] and Section 7).

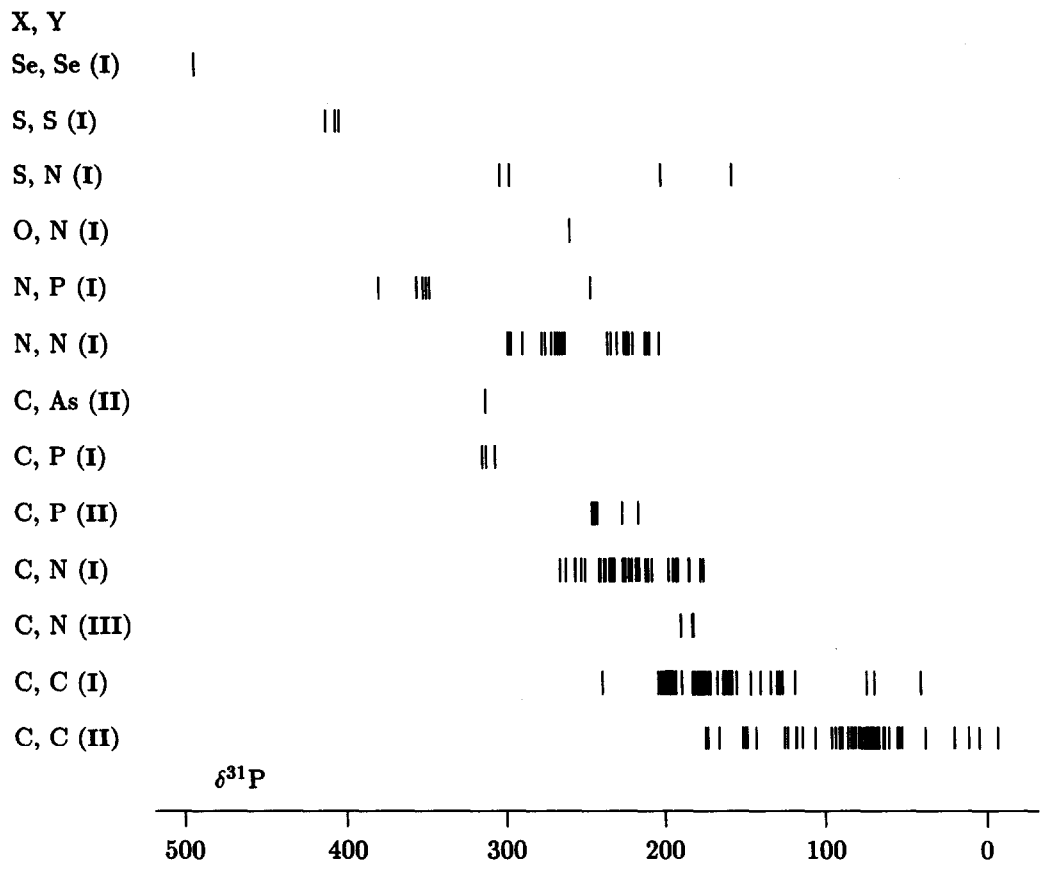
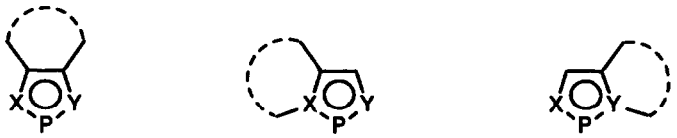
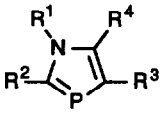


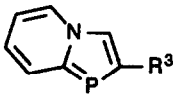
FIGURE 1 The chemical shifts $\delta^{31}P$ of the anellated fully delocalized heterophospholes and phospholes from Section 7 arranged according to the ring members X,Y adjacent to the phosphorus atom and to the position of anellation, as shown by **I**, **II** and **III**.

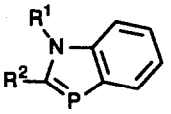


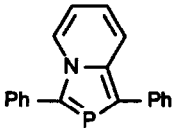
I **II** **III**

Depending on the ring members adjacent to the phosphorus atom $\delta^{31}P$ tends to higher field in the order Se,S < As,P < O,N < C. With the neighbouring atoms kept constant the phosphorus nucleus is less shielded in the anellated heterophospholes of type I than in those of type II and III (Figure 1). This is shown by the benzoderivatives of 1,3-azaphospholes, of which all three possibilities of anellation leaving the phosphorus dicoordinate are verified. 1,2- and 4,5-anellation shifts $\delta^{31}P$ to higher field, while 1,5-anellation causes a deshielding of the phosphorus nucleus, as compared to monocyclic 1,3-azaphospholes:







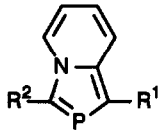


R^1-R^4	H, alkyl, aryl	alkyl, Ph	H, alkyl, Ph	
$\delta^{31}P$	86 - 106	68 - 76	65 - 76	120.9
ref.	97,107,109,110	73	52,83,86,87,104,105	48

The influence of an α-substituent on $\delta^{31}P$ is similar to that in monocyclic heterophospholes[108,111] and in acyclic two-coordinate phosphorus compounds[111,112].

In 2-phosphaindolizines $\delta^{31}P$ is affected strongly by R^2 and less by R^1, as shown by the series of 1,3-disubstituted derivatives below.

Chemical shifts $\delta^{31}P$ of 2-phosphaindolizines



R^1 =	R^2 = Ph	4-$NO_2C_6H_4$	CN	CO_2Et	COPh
Br					176.8
Ph	120.9	130.6	160.5	160.0	178.5
H		132.2		162.0	179.8
*t*Bu			161.0	162.4	
Me		136.0	165.2	165.5	183.6
PCl_2		142.4		180.4	197.2
PPhCl					199.7

While the phosphorus chemical shift of the 2-*tert*-butyl-1,3-benzodiphospholyl anion, $\delta^{31}P = 145.1$[82], fits well to the other values of line C,C (II) (Figure 1), the chemical shift of two-coordinate phosphorus in neutral 2-*tert*-butyl-1,3-benzodiphospholes, $\delta^{31}P = 263$-294, is found at considerably lower field and is not included in Figure 1. The shift indicates the loss of delocalization as the second phosphorus becomes pyramidal three-coordinate and it compares well with $\delta^{31}P$ of electron poor phosphaalkenes[112]. There is also an analogous reactivity observed for the P=C bond in these compounds (see Sections 4.1 and 4.2).

One bond P,P-coupling constants in 1*H*-1,2,3-benzazadiphospholes ($^1J_{PP}$ = 493-496 Hz)[27,28] and 3-triphenylphosphonio-1,2-benzodiphospholides ($^1J_{PP}$ = 476-480 Hz)[53] are of the same order as in diphosphenes[111,112].

$^2J_{PP}$ in 1*H*-1,3-benzodiphospholes ranges from 9 to 39 Hz[78,79,82,90]. In α-phosphino substituted heterophospholes $^2J_{PP}$ strongly depends on the substituents at the phosphorus and decreases in the order PCl_2 (130-199 Hz) > PPhCl (60-70 Hz) > $P(OMe)_2$ (46-57 Hz) > PPh_2 (2-9 Hz) (Section 7).

Solid state ^{31}P-NMR of 1,3,2-benzodithiaphospholium and 1,3,2-benzothiazaphospholium tetrachloroaluminates reveal a phosphorus chemical shift anisotropy $\Delta\delta > 500$ for all three investigated compounds. In one case the orientation of the ^{31}P chemical shift tensor was determined from dipolar chemical shift ^{31}P-NMR experiments and is in good agreement with ab initio chemical shielding calculations[113].

^{13}C- and ^{1}H-NMR data of various anellated heterophospholes and phospholes have been reported; most of them refer to anellated 1,3-azaphospholes (Section 7). Typical for the (hetero)phosphole ring are $^1J_{PC}$ = 35-73 Hz and $^2J_{PC}$ = 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 (1.0 Hz)[50] has been observed.

For anellated heterophospholes with a -P=CH- fragment $^2J_{PH}$ ranges mainly from 29 to 56 Hz and is of the same order as in *Z*-phosphaalkenes[111].

^{15}N-NMR data for 1,4,2-diazaphospholo[4,5-*a*]pyridine (N-1: δ = -127.6, $^1J_{PN}$ = 89.1 Hz; N-4: δ = -161.7, $^2J_{PN}$ = 2.0 Hz)[70], for its 3-ethoxycarbonyl derivative (N-1: δ = -124.1, $^1J_{PN}$ = 86.9 Hz; N-4: δ = -156.8, $^2J_{PN}$ = 2.2 Hz)[42], and for the $AlCl_3$-complex of 1-phenyl-1,3,2-benzodiazaphosphole (N-1: δ = -169.0, $^1J_{PN}$ = 74.4 Hz; N-3: δ = -199.3, $^1J_{PN}$ = 75.6 Hz)[20] have been reported.

5.6 *X-Ray Structure Investigations*

X-Ray crystal structure determinations of 1,3-benzazaphosphole[114], 2-(p-chlorophenyl)-1,3-benzoxaphosphole[115], 1-*tert*-butyl-3-methoxycarbonyl-2-phosphaindolizine[99], 3-cyano-2-*tert*-butyl-1,3-azaphospholo[1,2-*a*]phthalazine[9], 1,3-dimethyl-1,3,2-benzodiazaphospholium tetrachloroaluminate[23,32], 1,3,2-benzothiazaphospholium tetrachloroaluminate[23], 1,3,2-benzodithiaphospholium tetrachloroaluminate[31–34], 1,3-bis(diphenylvinylphosphonio)isophosphindolide bromide[55], 1,3-bis(triphenylphosphonio)isophosphindolide cyclopentadienyl tricarbonyltungstate[55], and potassium isophosphindolide-1,3-dione[77] have been reported. They all show planar ring systems with averaged bond distances. The angle at the phosphorus atom ranges from 88 to 100°. PC bond lengths range from 170 to 180 pm as compared to 167 pm and 185 pm for the localized double and single PC bond in phosphaalkenes[116]. PN bond lengths range from 164 to 166 pm and are in between of those for the more or less localized double (156 pm) and single bond (167 pm) in amino-iminophosphines[117]. The PS bond length in the 1,3,2-benzodithiaphospholium cation (average 172 pm) is exceptionally short[31–34].

5.7. *Quantum Chemical Calculations*

Quantum chemical calculations of different levels on various anellated heterophospholes[7,26,28,32,77,118] have been carried out (Section 7).

MNDO calculations on 4,6-diamino-1,3,5-triaza-2-phosphapentalene **10**, R^1-R^4 = H confirm the zwitterionic structure. HOMO and LUMO are localized at the anionic 1,3,2-diazaphosphole part and the cationic 1,3-diamino-2-azaallyl part of the molecule, respectively[26].

For indolizine the π-charge is highest in position 1 and 3[119] which explains their ready electrophilic substitution[10]. According to MNDO calculations, a dicoordinate phosphorus atom in position 2 lowers the π-electron density at the adjacent carbon atoms[7], in accord with the lower reactivity of 2-phosphaindolizines towards electrophiles (Section 4.6).

MINDO/3 and Extended Hückel calculations on the isophosphindolide-1,3-dione anion are found to explain the maroon colour of this species[77].

For the 1,3,2-benzodiaza-, 1,3,2-benzothiaza- and 1,3,2-benzodithiaphospholium cations the calculated HOMO-LUMO gap decreases in this order. The LUMOs are localized mainly at the phosphorus atom, which is therefore expected to be the preferred site for nucleophilic attack[32].

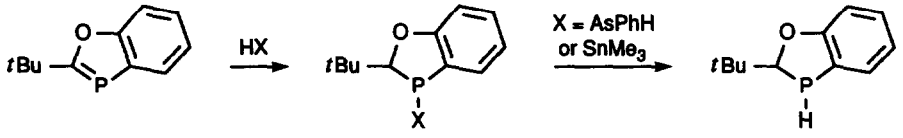
6. Reactivity

In all the anellated systems the heterophosphole or phosphole ring is the centre of reactivity. Most of the reactions involve an increase of the coordination number at the phosphorus atom: 1,2-additions to the formal P=C or P=N bond or 1,1-additions to (oxidation of) the phosphorus atom. These two types of reactions may also take place successively with either the 1,2-addition preceding the 1,1-addition or vice versa. In some cases, a 1,1-addition at the phosphorus atom may be followed by a second one, leading to zwitterionic hexacoordinate phosphorus derivatives. Electrophiles may attack a dicoordinate nitrogen atom or the phosphorus atom of an azaphosphole. At a CH or NH ring member adjacent to the phosphorus atom different substituents may be introduced by a two-step electrophilic substitution: a 1,2-addition to P=C is followed by a 1,2-elimination to give the substitution.

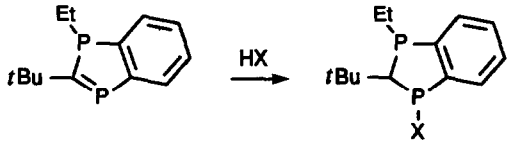
6.1 *Addition of Protic Reagents to P=C or P=N (see also* 6.6*)*

Protic reagents add to the P=C or P=N bond of the heterophosphole ring in such a way that the proton is bonded to the carbon or the nitrogen atom in accordance with the polarity of these bonds.

Addition of HX (HCl, HI, HSPh, $PhAsH_2$, Me_3SnH) to the 1,3-benzoxaphosphole **82** (R = *t*Bu, R^1 = H) leads to the 2,3-dihydro-1,3-benzoxaphospholes **112**. The addition of HCl is reversible: heating of **112**, X = Cl, with DBU regenerates **82** (R = *t*Bu, R^1 = H). In the case of phenyl arsine, the addition product **112**, X = AsPhH, under the reaction conditions loses $(AsPh)_6$ and gives the P-H-derivative **113**. The addition of trimethyltinhydride is catalyzed by AIBN and yields stereospecifically the *trans*-2,3-dihydro-1,3-benzoxaphosphole **112**, X = $SnMe_3$, which is converted to **113** by heating with more trimethyltinhydride[120].



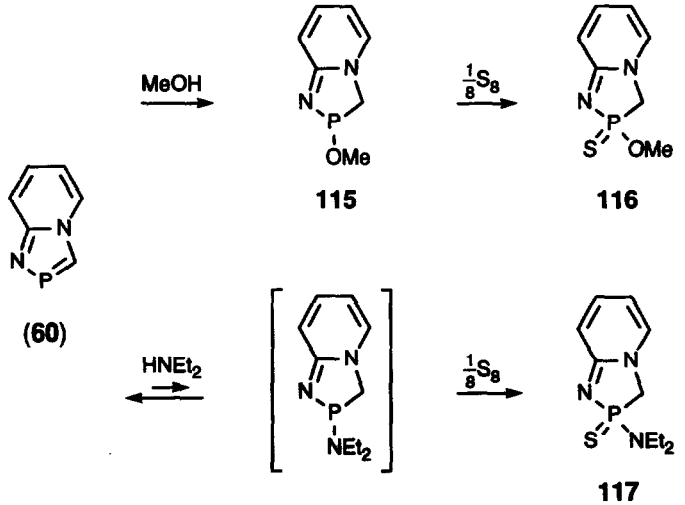
(82) 112 113



(77) 114

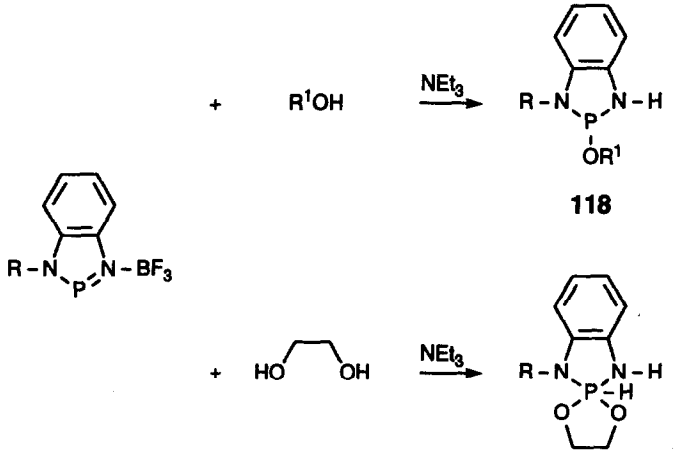
Similarly, the 1,3-benzodiphosphole **77** (R = Et, R^1 = *t*Bu) forms 1,2-addition products **114** with HCl as well as with MeOH[81,82].

1,4,2-Diazaphospholo[4,5-*a*]pyridine **60** (R^2,R^4,R^5 = H) reacts with MeOH to form the 1,2-addition product **115** which can be oxidized with sulfur to give **116**. The analogous reaction with $HNEt_2$, however, occurs only in the presence of sulfur and yields **117**[65,70].

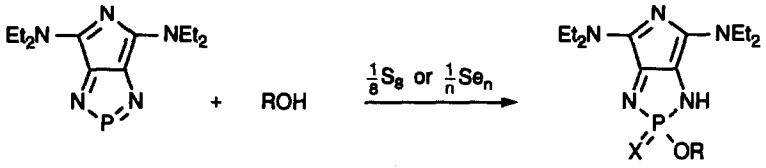


(60) 115 116 117

BF_3-complexes of 1,3,2-benzodiazaphospholes react with alcohols in the presence of NEt_3 to form 1,2-addition products **118**. In case of butanol, an intermediate 1,1-addition product could be observed. Diethylamine also gives a 1,2-addition derivative[19]. In the reaction with diols, 1,2-addition of the one hydroxy group is followed by 1,1-addition of the other to yield the spirocyclic phosphorane **119**[19].



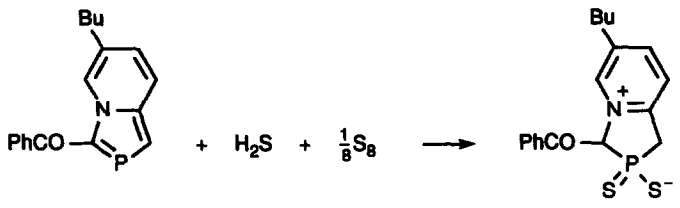
Addition of alcohols (R = Me, $CH(CF_3)_2$, 4-MeC_6H_4, 2,4,6-$Me_3C_6H_2$) to the P=N bond in 4,6-bis(diethylamino)-1,3,5-triaza-2-phosphapentalene **10** (R^1-R^4 = Et) and simultaneous oxidation by sulfur or grey selenium yield 1,2-dihydropentalene 2-sulfides **120** or 2-selenides **121**[30,121,122].



(10)

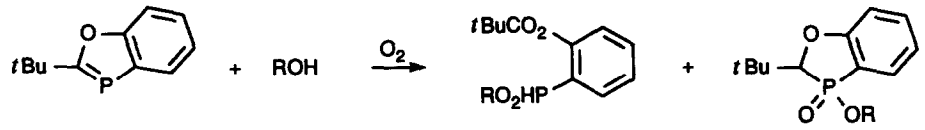
120 X = S
121 X = Se

The 2-phosphaindolizine **36** (R^1,R^4 = H, R^2 = COPh, R^3 = Bu) reacts with H_2S in the presence of sulfur in a 1,2-addition and oxidation followed by proton migration to yield the zwitterionic dithiophosphinate **122**[123]. A selenium analogue of **122** has also been obtained (see Section 4.4).



(36) 122

Reaction of 2-*tert*-butyl 1,3-benzoxaphosphole **82** (R = *t*Bu, R^1 = H) with dry oxygen in the presence of an alcohol (R = Me, Et) yields the ring-opened product **123** with both P and C oxidized, and as a side product **124** (mixture of diastereomers), in which the oxaphosphole ring is preserved.



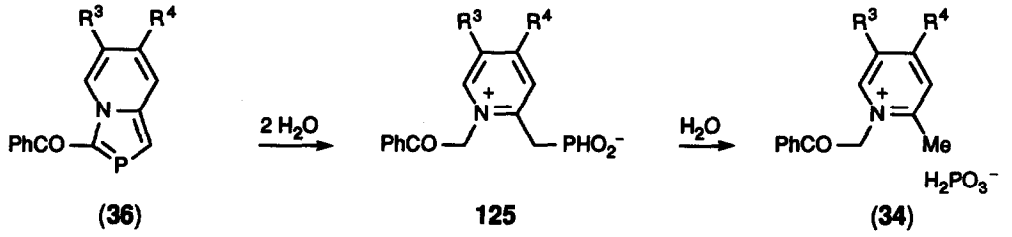
(82) 123 124

The latter is obtained also from the oxidation with 30% hydrogen peroxide in the presence of ethanol. Oxidation with dry oxygen in absence of an alcohol leads to oligomeric phosphine oxides, which probably result from the addition of O_2 to the P=C bond[124].

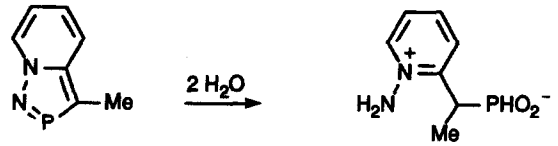
1,3-Benzazaphospholes[83] and 1,3-benzoxaphospholes[120] are resistant to hydrolysis, while 2-phosphaindolizines and diazaphospholopyridines are quite susceptible to hydrolysis and yield zwitterionic products. In these cases, the reaction with water is initiated most probably by a 1,2-addition across the P=C or P=N bond which is followed by a further addition of water leading to the cleavage of these bonds.

Reaction of the 2-phosphaindolizines **36** (R^1 = H, R^2= COPh, R^3/R^4 = H/H, H/Me, Bu/H) with water first gives the zwitterionic phosphinates **125** which are further hydrolyzed to the pyridinium salts **34**, (R^1 = H, R^2 = COPh, $H_2PO_3^-$ in place of Br^-)[7].

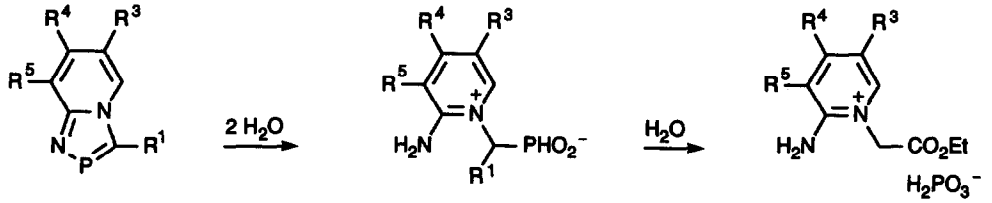
The hydrolysis of 1-methyl-1,2,3-diazaphospholo[1,5-*a*]-pyridine **25** (R^1 = Me, R^2 = H)[39] and of 1,4,2-diazaphospholo[1,5-*a*]-pyridines **27** and **60** (R^2 = H)[42,65,70] proceeds analogously and involves the cleavage of the P-N bond. The structure of **127** (R^1,R^3-R^5 = H) has been confirmed by X-ray crystal studies[70]. In the case of **127**, R^1 = CO_2Et, further hydrolysis to the pyridinium salts **128**, takes place under the reaction conditions[42].



(36) 125 (34)

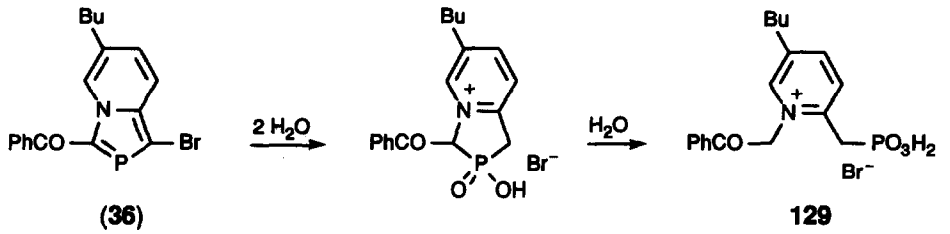


(25) 126



(27), (60) 127 128

Hydrolysis of the 1-bromo-substituted 2-phosphaindolizine **36** (R^1 = Br, R^2 = COPh, R^3 = Bu, R^4 = H) interestingly involves the debromination of C-1 coupled to the oxidation of the phosphorus atom, and yields the phosphonic acid **129**[125].



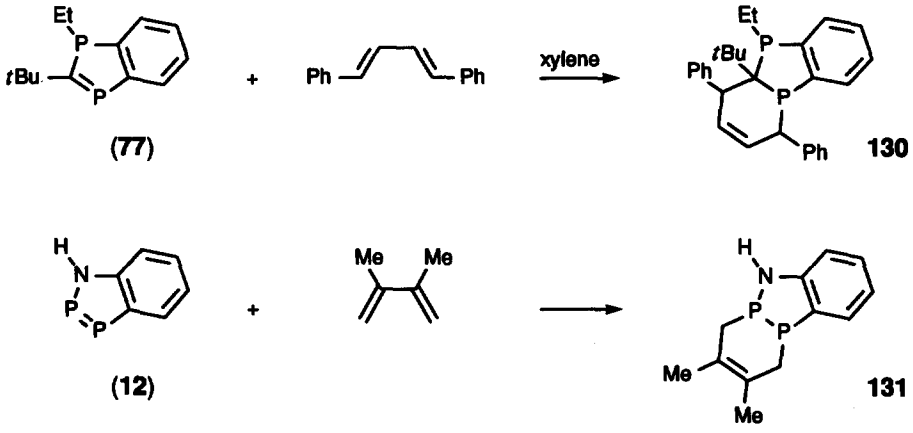
(36) 129

A similar intramolecular redox reaction has been observed in the reaction of 4-bromo-1,2,3-diazaphospholes with protic reagents[126].

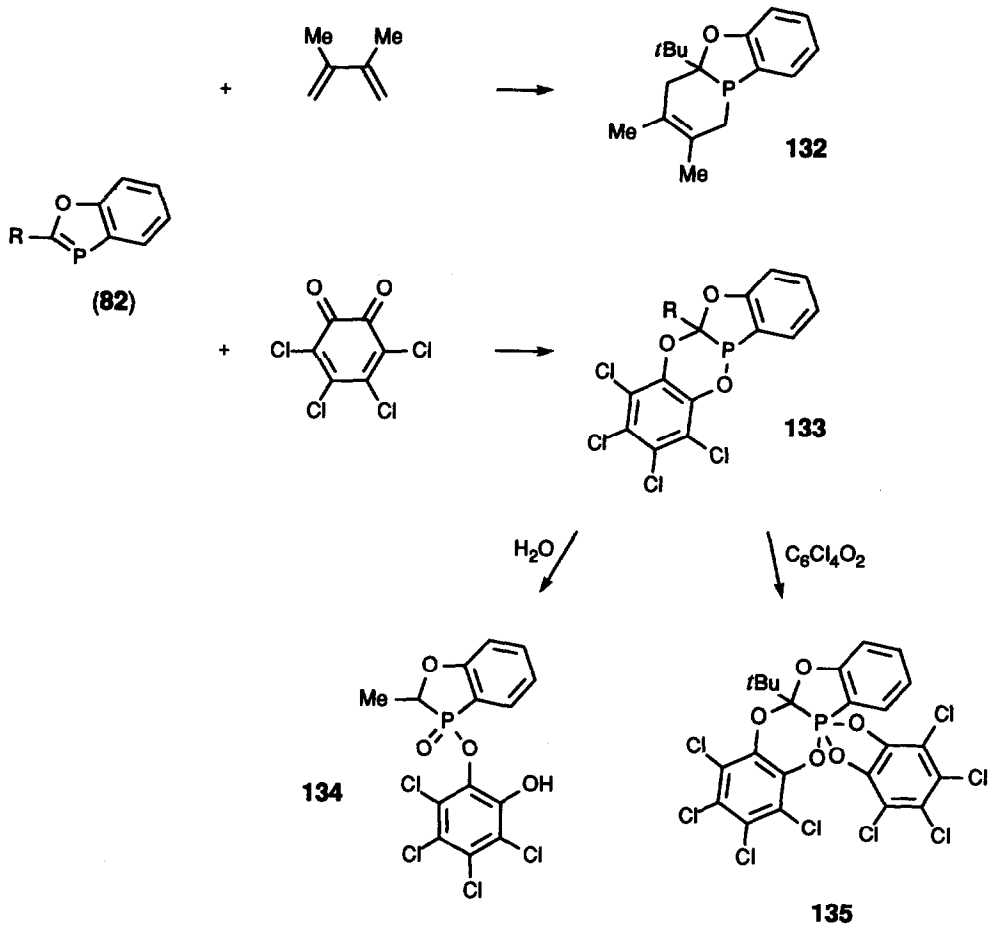
6.2 *Cycloaddition to P=C or P=N*

Like in acyclic phosphaalkenes[116,117] the P=C bond in heterophospholes can undergo cycloaddition reactions as dienophile or as dipolarophile[4,5,127]. Only a few [4+2]-Cycloadditions and no 1,3-dipolar cycloaddition of anellated heterophospholes have been reported so far, however. It is found that the reactivity of the P=C moiety is influenced by the nature of the other heteroatoms of the phosphole ring. In some cases regioselectivity has been observed.

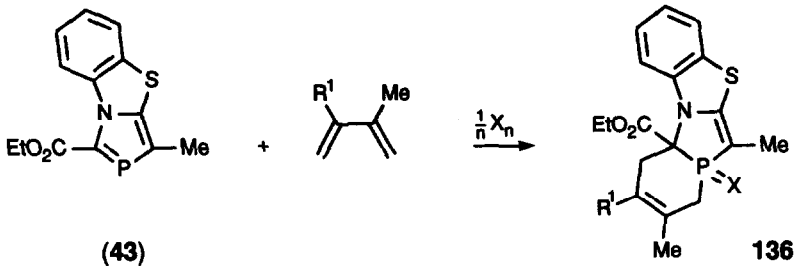
Unlike 2-phosphaindolizines[128] and 1,3-benzazaphospholes[81,82] the 1,3-benzodiphosphole **77** (R = Et, R^1 = *t*Bu) reacts with 1,4-diphenyl-1,3-butadiene to give the [4+2]-cycloadduct **130**[81,82]. Similarly, 1*H*-1,2,3-benzazadiphosphole **12** (R^1,R^2 = H) and 2,3-dimethyl-1,3-butadiene yield **131**[27].



The 1,3-benzoxaphospholes **82** (R = Me, *t*Bu, R^1 = H) react likewise and form [4+2]-cycloadducts **132** and **133** (R = Me, *t*Bu) with 2,3-dimethyl-1,3-butadiene and tetrachloro-*o*-benzoquinone, respectively. The reaction with dimethylbutadiene is stereospecific and *cis*-anellation occurs[129]. The structure of **133**, R = Me, has been confirmed by X-ray analysis[130]. With more tetrachloro-*o*-benzoquinone **133**, R = *t*Bu, undergoes a 1,1-addition at the phosphorus atom to give **135**, while **133**, R = Me, on hydrolysis yields the phosphinic acid arylester **134**[129].

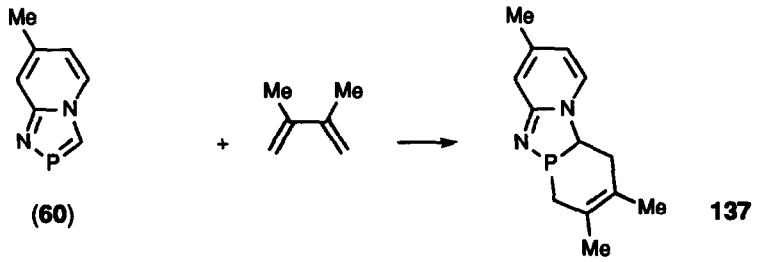


The 1,3-azaphospholo[5,1-*b*]benzothiazole **43** (R = CO_2Et) does not react with 2,3-dimethyl-1,3-butadiene or with isoprene alone. However, if the reaction is carried out in the presence of O_2, S_8, or Se_n, the [4+2]-cycloadduct **136** (R^1 = H, Me, X = O, S, Se) with pentavalent phosphorus is obtained. The reaction with isoprene occurs regioselectively[123]. It is suggested that in a first step the phosphorus is oxidized to give a transient species with a three-coordinate pentavalent phosphorus for which in case of X = S a $\delta^{31}P$ = 127.0 is observed and which subsequently undergoes cycloaddition[131]. This reaction is analogous to that of 2-phenyl-4,5-dimethyl-phosphinine with 2,3-dimethyl-1,3-butadiene in the presence of sulphur[132,133].

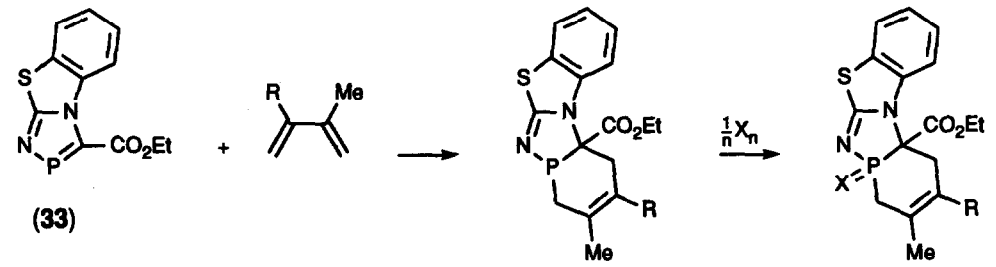


(43) **136**

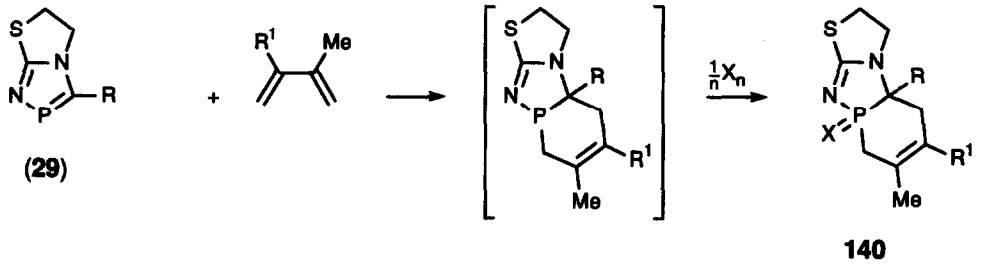
The 1,4,2-diazaphospholo[4,5-*a*]pyridine **60** (R^2,R^5 = H, R^4 = Me) yields with 2,3-dimethyl-1,3-butadiene the [4+2]-cycloadduct **137**[65]. Similarly, the [4+2]-cycloaddition of 1,4,2-diazaphospholo[5,4-*b*]benzothiazole **33** (R^1 = CO_2Et, R^2 = H) with 1,3-butadienes gives **138** (R = H, Me), which are converted to the corresponding sulfides or selenides **139** (R = H, Me, X = S, Se). 1,4,2-Diazaphospholo[5,4-*b*]thiazolines **29** (R = CO_2Me, CO_2Et) react with 1,3-butadienes only in the presence of S_8 or Se_n to give the cycloadducts **140** (R = CO_2Me, CO_2Et, R^1 = H, Me, X = S, Se). The cycloaddition of isoprene proceeds regioselectively in these cases as well[131].



(60) **137**

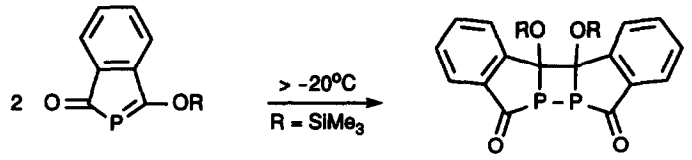


(33) **138** **139**



(29) 140

The isophosphindole derivative **72** is stable up to -20°C; at higher temperatures it undergoes head to head dimerization to form **141**[76]. The structure of the product has been confirmed by X-ray analysis[76], which corrects an earlier report suggesting head to tail dimerization[75].



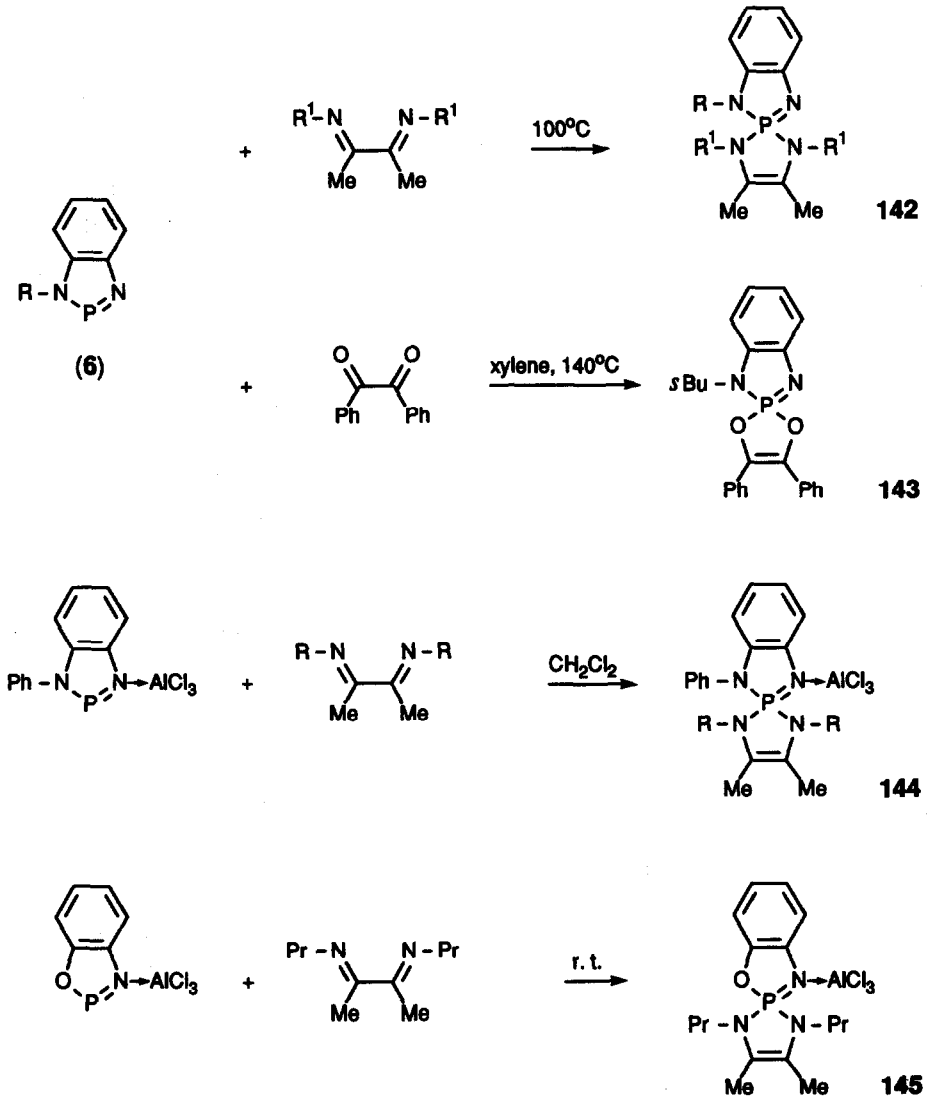
72 **141**

As mentioned earlier (Section 2.1), 1,3,2-benzodiazaphospholes do not exist as monomers at room temperature but form tetramers. Oligomerization involves nucleophilic interaction of the nitrogen atom of one monomer with the phosphorus atom of the other. A hard acceptor like BF_3 competes effectively for the nitrogen and hence stabilizes the monomeric form[17–19].

6.3 *Cycloaddition to P*

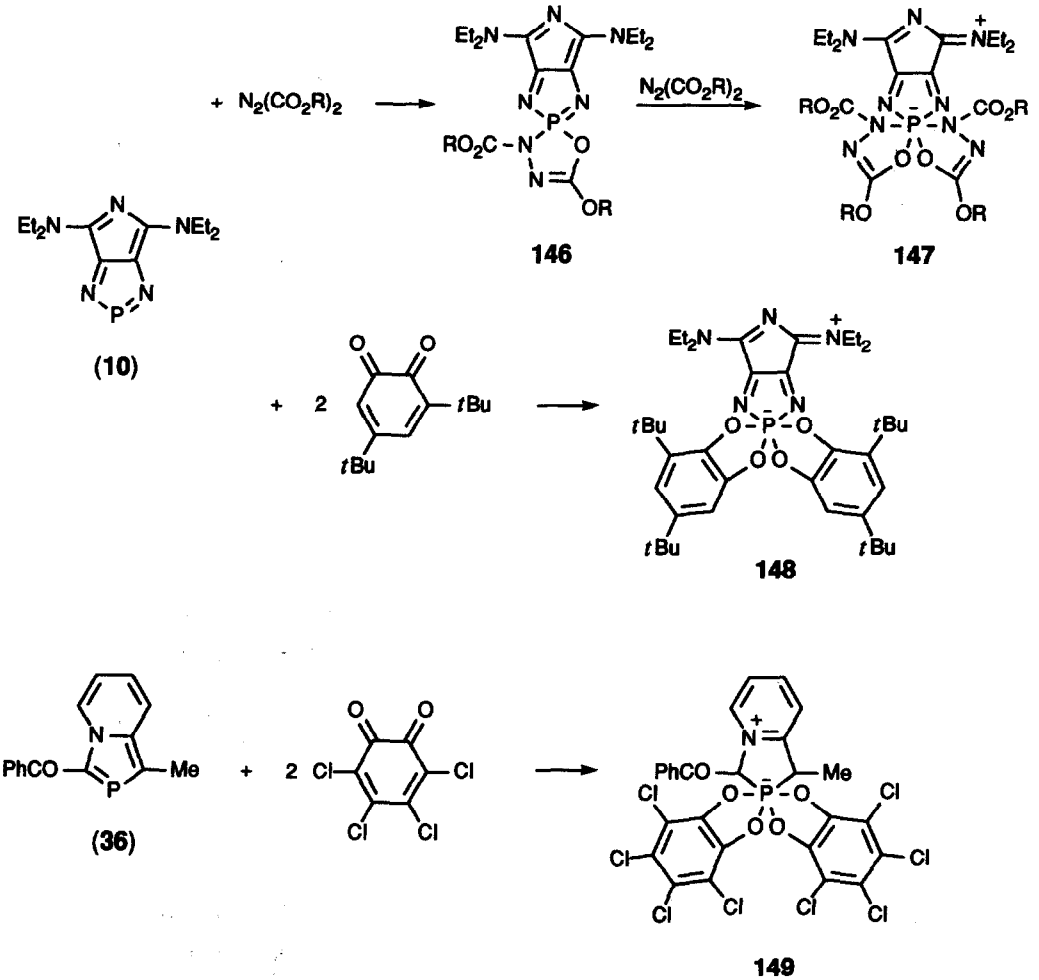
As part of the heterophosphole ring, the two-coordinate phosphorus loses much of its nucleophilic character. In most cases it will not alkylate (for an exception see Section 4.4) and will not be oxidized by oxygen, sulfur or selenium (for exceptions see Sections 4.1 and 4.2); however, it coordinates to transition metals (see Section 4.7) and undergoes 1,1-additions. The addition of α-diimines, α-diketones, *o*-quinones and azodicarboxylic esters to the phosphorus leads to the formation of a spirocyclic product and these reactions have been termed as 4+1-cycloadditions analogous to cheletropic reactions. It is found that phosphorus having high π-electron density is particularly susceptible to this type of reactions.

1,3,2-Benzodiazaphospholes **6** (R = Et, *s*Bu, CH_2SPh), generated from their tetramers **5** (n = 4) by heating, are trapped by α-diimines (R^1 = Pr, Ph) to form spirocyclic products **142**[134]. The reaction of **6** (R = *s*Bu) with benzil proceeds analogously and yields **143**[135]. A similar reaction is found for the $AlCl_3$-complexes of 1-phenyl-1,3,2-benzodiazaphosphole and 1,3,2-benzoxazaphosphole and α-dimines to give **144** (R = Pr, Ph)[20] and **145**[134], respectively. In the case of **144** decomplexation is achieved by treatment with NEt_3[20].



In the case of electron-rich heterophospholes, double 1,1-additions of heterodienes to the phosphorus have been observed. The products are zwitterionic with the hexacoordinated phosphorus showing a characteristic upfield ^{31}P-NMR shift. 4,6-Bis(diethylamino)-1,3,5-triaza-2-phosphapentalene **10** (R^1-R^4 = Et) adds azodicarboxylic esters (R = Et, *i*Pr) to give the spirocyclic derivatives **146** and a second equivalent to give the zwitterionic compounds **147**[30,122]. With 3,5-di-*tert*-butyl-*o*-benzoquinone the 1:2-adduct **148** is formed[30,126]. **147** and **148** are obtained each as mixture of three isomers[122,126].

Similarly the 2-phosphaindolizine **36** (R^1 = Me, R^2 = COPh, R^3,R^4 = H) reacts with tetrachloro-*o*-benzoquinone in methylene chloride to form **149**[126].



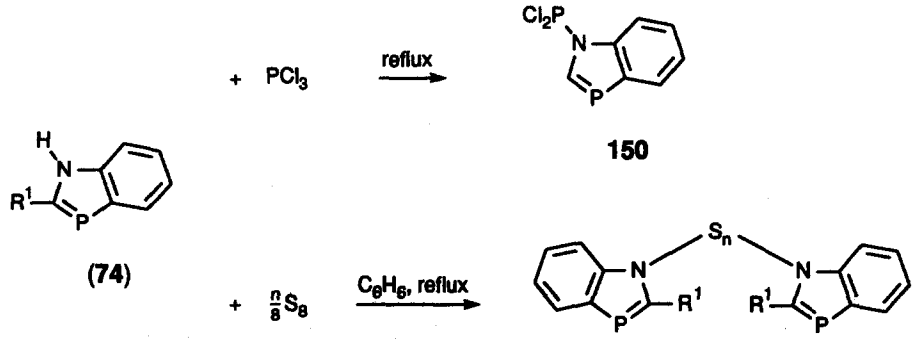
Under milder conditions (diethylether, 0°C) the 1-*tert*-butyl-3-cyano-[1,3]-azaphospholo-[1,5-*a*]pyridazine **90** (X = N, Y = CH) does not react with tetrachloro-*o*-benzoquinone, while the isomeric 1,3-azaphospholo[1,2-*a*]pyridazine **91** (X = N, Y = CH) gives a 1:2 cycloaddition

product analogous to **149**[99]. The higher reactivity of **91** is in accord with the higher π-electron density predicted by MNDO calculations for the phosphorus atom in the 1-position of phosphaindolizines as compared to the 2-position[7].

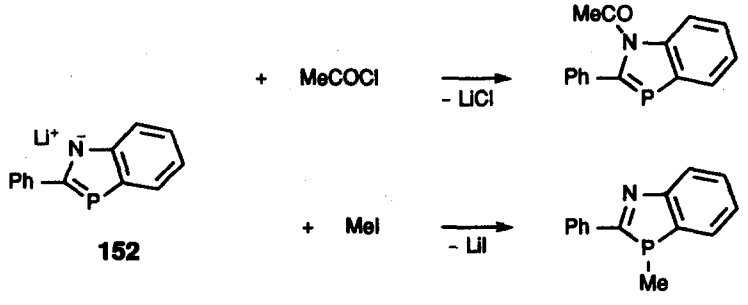
For the cycloadduct of 1-methyl-1,3-benzazaphosphole **74** (R = Me, R^1 = H) with two equivalents of tetrachloro-*o*-benzoquinone a betaine structure with a hexacoordinate phosphorus analogous to that of **149** has been assumed on the basis of ^{31}P-NMR data[129].

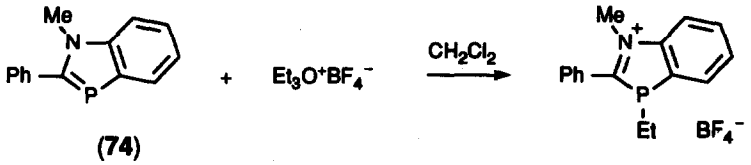
6.4 *N-Substitution, Alkylation and Coordination*

1,3-Benzazaphosphole **74** (R,R^1 = H) reacts with PCl_3 to give the *N*-dichlorophosphino derivative **150** as a red, moisture sensitive oil. When **74** (R = H, R^1 = H, SMe, Ph) is heated with sulfur, a product **151**, in which the nitrogen atoms of two molecules are bonded through a sulfur bridge is formed[83].



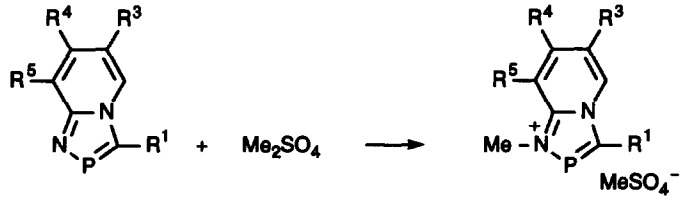
The anion **152** generated from 2-phenyl-1,3-benzazaphosphole **74** (R = H, R^1 = Ph) and lithium diethylamide shows ambident reactivity: a hard electrophile like acyl chloride attacks the nitrogen atom, while a soft electrophile like methyl iodide alkylates the phosphorus atom[83]. 1-Methyl-2-phenyl-1,3-benzazaphosphole **74** (R = Me, R^1 = Ph) is also alkylated at the phosphorus atom[136].





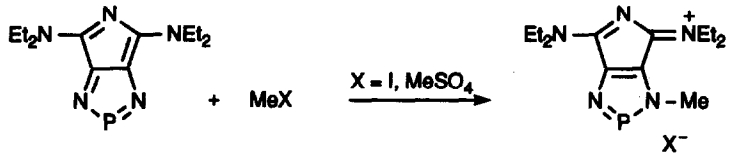
(74)

Where there is a σ^2-nitrogen available in a heterophosphole ring, alkylation occurs exclusively at this nitrogen atom. Thus 1,4,2-diazaphospholo[4,5-*a*]pyridines **27** and **60** (R^2 = H) react with dimethyl sulphate to give the *N*-methylated salts **153**[42,65]. 1,2,3-diazaphospholo[1,5-*a*]pyridines **25**[39], thiazolo[3,2-*d*][1,4,2]diazaphospholes **31**[43] and the 5,6-dihydrothiazolo[3,2-*e*][1,2,4]diazaphosphole **65**[65] behave likewise.



(27), (60) 153

4,6-Bis(diethylamino)-1,3,5-triaza-2-phosphapentalene **10** (R^1-R^4 = Et) is methylated by methyl iodide or dimethyl sulphate at the nitrogen atom of the diazaphosphole ring[26].



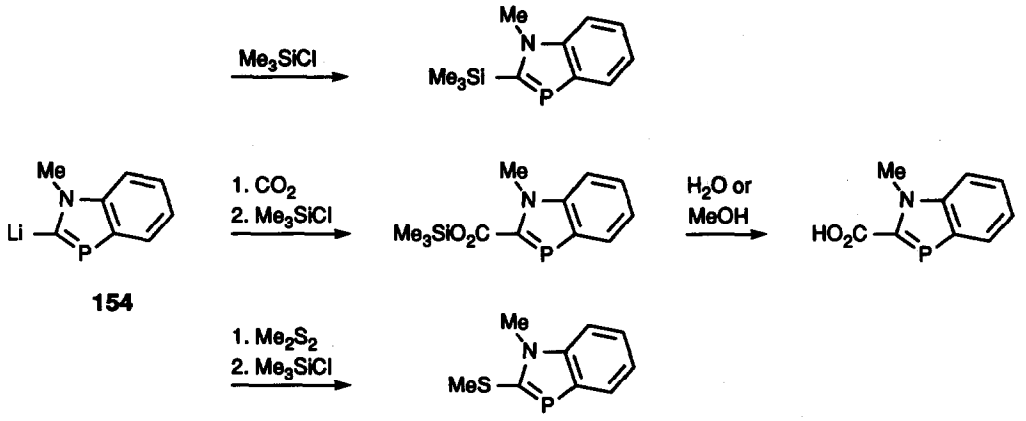
(10)

In contrast to 1-phosphaindolizines[73], 2-phosphaindolizines cannot be alkylated[7]. It has been reported that 2-*tert*-butyl-1,3-benzoxaphosphole on reacting with triethyloxonium tetrafluoroborate forms a mixture of products[120].

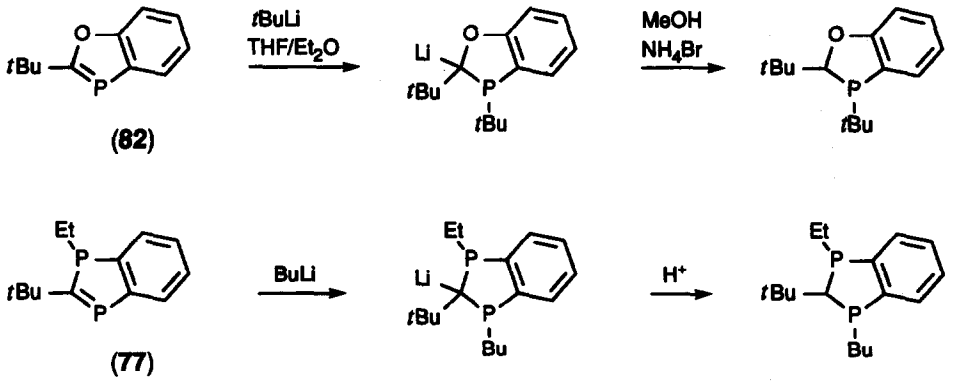
As mentioned earlier, 1,3,2-benzodiazaphospholes and 1,3,2-benzoxazaphospholes (Section 2.1) form *N*-bonded complexes with Lewis acids[17–19,21].

6.5 *C-Metallation*

Indole undergoes metallation at the nitrogen atom, while lithiation of *N*-methylindole occurs at the 2-carbon atom[137]. Likewise, 1-methyl-1,3-benzazaphosphole **74** (R = Me, R^1 = H) reacts with *tert*-butyl lithium to give besides a small quantity of the 1,2-addition product mainly the 2-lithio derivative **154**, which makes possible the synthesis of a number of 2-functional 1,3-benzazaphospholes[87,136]. No reaction occurs with phenyl lithium[87].

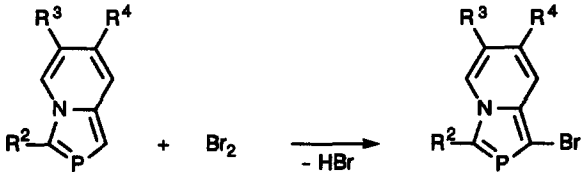


2-*tert*-Butyl-1,3-benzoxaphosphole **82** (R = *t*Bu, R^1 = H) and *t*BuLi quantitatively form the 1,2-addition product which is solvolyzed by H_2O or MeOH[120]. 1-Ethyl-2-*tert*-butyl-1,3-benzodiphosphole **77** (R^1 = Et, R^2 = *t*Bu) and butyl lithium react similarly[81].



6.6 *Electrophilic C-Substitution*

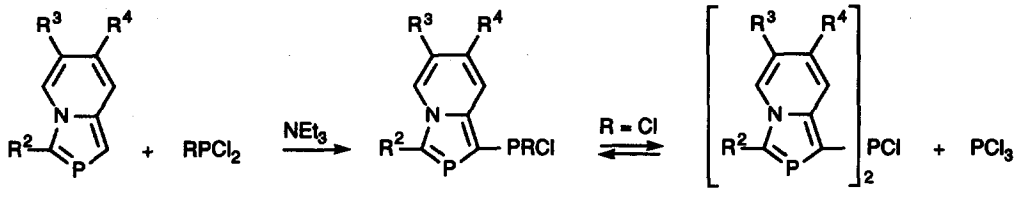
Here it is interesting to compare the reactivity of anellated heterophospholes with that of non-phosphorus analogues. The reactivity of the 1- and 3-positions in indolizine is such that in syntheses using acetic anhydride it is often impossible to prevent acetylation[10]. In contrast, 1-unsubstituted 2-phosphaindolizines fail to react with MeCOCl, PhCOCl, Me_3SiCl even on prolonged heating in the presence of triethyl amine[128]. The reduced reactivity of 2-phosphaindolizines as compared to indolizines can be attributed to a decrease in π-electron charge at the 1-position on introducing a two-coordinate phosphorus in place of 2-CH, as suggested by MNDO calculations (Section 3.7)[7]. However, 2-phosphaindolizine is still reactive towards stronger electrophiles like Br_2 and PCl_3. In contrast to indolizine which undergoes bromination to yield a mixture of several products[138], 2-phosphaindolizines **36** (R^1 = H) react with bromine to give the 1-bromo derivatives **155**, though in poor yield. Better yields could be obtained by using bromine in the presence of NEt_3 or by using *N*-bromosuccinimide[125,126].



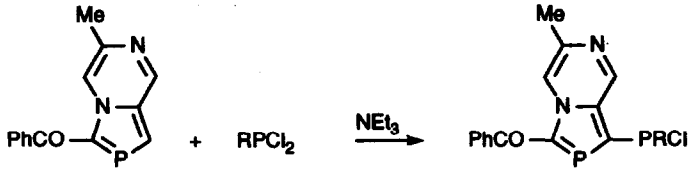
(36) **155**

This behaviour of 2-phosphaindolizines parallels that of 1,2,3-diazaphospholes, which give 4-bromo-substituted derivatives through an addition-elimination mechanism[139]. Heterophospholes and phosphinines with no replaceble α-hydrogen undergo a 1,1-addition of bromine to phosphorus[5,140].

1-Unsubstituted 2-phosphaindolizines **36** (R^1 = H) and the 7-aza-2-phosphaindolizine **40** can be phosphinylated by reacting with a chlorophosphine (PCl_3, $PhPCl_2$ and in the case of **36** (R^1 = H) also 4-(2,5-dimethyl-1,2,3-diphospholyl)PCl_2) in the presence of NEt_3[125]. Indolizines show a similar behaviour[141].

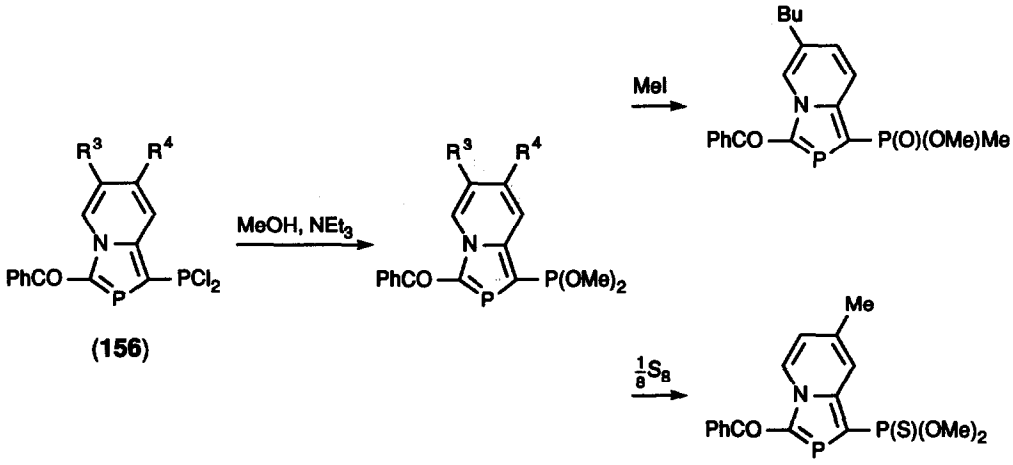


(36) **156** **157**



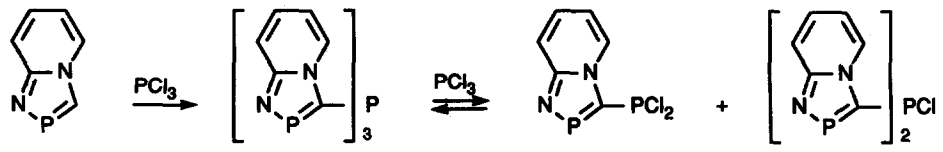
40

The 1-dichlorophosphino-2-phosphaindolizines **156**, R = Cl, tend to disproportionate in PCl_3 and the bis(2-phosphaindolizinyl)chlorophosphines **157**[125]. Methanolysis of **156** (R = Cl, R^2 = COPh, R^3/R^4 = H/Me, Bu/H) yields a 1-dimethoxyphosphino derivative (R^3/R^4 = H/Me, Bu/H), which undergoes MeI-catalyzed Arbuzov rearrangement and which is oxidized by sulfur at the exocyclic phosphorus atom[125]. All these reactions do not affect the dicoordinate phosphorus.



(156)

In analogy to 1-azaindolizine[142], 1,4,2-diazaphospholo[4,5-*a*]pyridine **60** (R^2,R^4,R^5 = H) undergoes substitution reactions with chlorophosphines in 3-position and yields with PCl_3 the tris(diazaphospholyl)phosphine **158**.



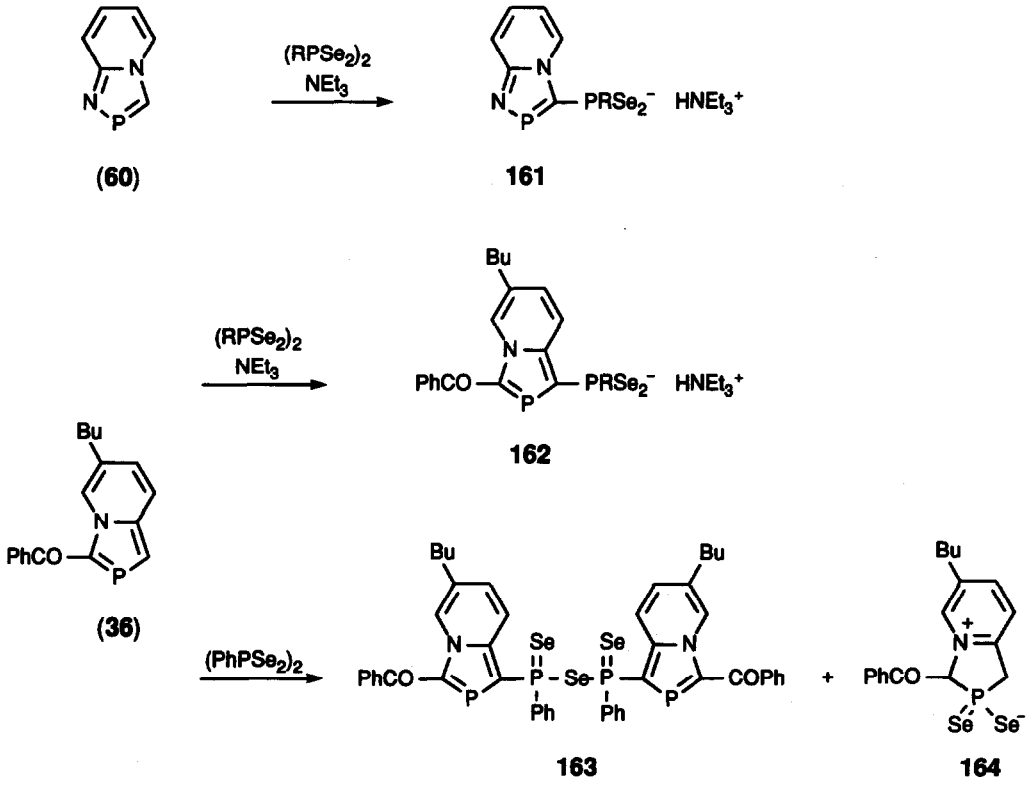
(60) **158** **159** **160**

The latter enters a substituent exchange with PCl_3 and an equilibrium is set up between the three products **158**, **159**, **160** and PCl_3[65]. This equilibrium, which involves the cleavage of P-C bonds, is mobile at room temperature[65], while the substituent exchange between triphenylphosphine and PCl_3 requires temperatures of 200°C and more[143]. The mobility is attributed to the addition/elimination mechanism operating in this case[65].

158 is oxidized by air oxygen, sulfur or grey selenium at the three-coordinate phosphorus atom[65].

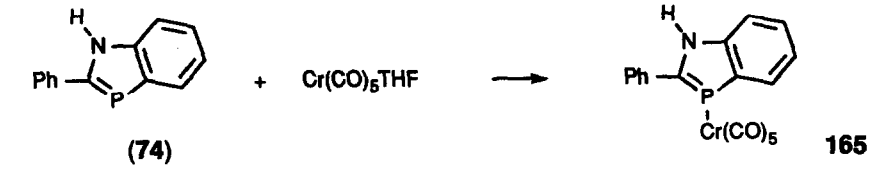
1-(Dichlorophosphino)-5,6-dihydro-1,3-azaphospholo[5,1-*b*]thiazole **29**, R = PCl_2, is obtained directly from the reaction of the corresponding thiazolium salt with two equivalents PCl_3 in the presence of NEt_3 (Section 2.1)[50].

The reaction of 1,4,2-diazaphospholo[4,5-*a*]pyridine **60** (R^2,R^4,R^5 = H) and 3-phenacyl-6-butyl-2-phosphaindolizine **36** (R^1,R^4 = H, R^2 = COPh, R^3 = Bu) with selenophosphonic acid anhydrides $(RPSe_2)_2$ (R = Ph, 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$) in the presence of NEt_3 leads to the triethylammonium selenophosphinates **161** and **162**, respectively. In the absence of NEt_3, however, the seleno anhydride **163** is obtained as a mixture of two diastereomers along with the zwitterionic selenophosphinate **164**[123].

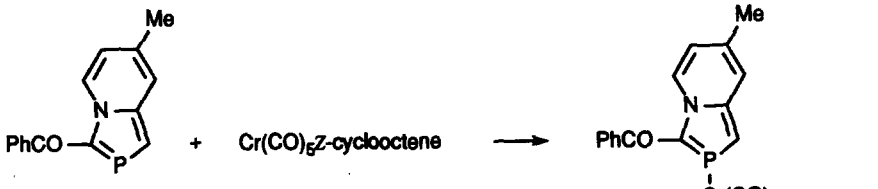


6.7 *Coordination to Transition Metals*

2-Phenyl-1,3-benzazaphosphole **74** (R = H, R^1 = Ph) and 2-phenacyl-7-methyl-2-phosphaindolizine **36** (R^1,R^3 = H, R^2 = COPh, R^4 = Me) form *P*-coordinated $Cr(CO)_5$-complexes **165**[83] and **166**[7]. Complex formation is accompanied by a downfield shift of the ^{31}P-NMR signal by $\Delta\delta$ = 4.4 and 7.5, respectively.

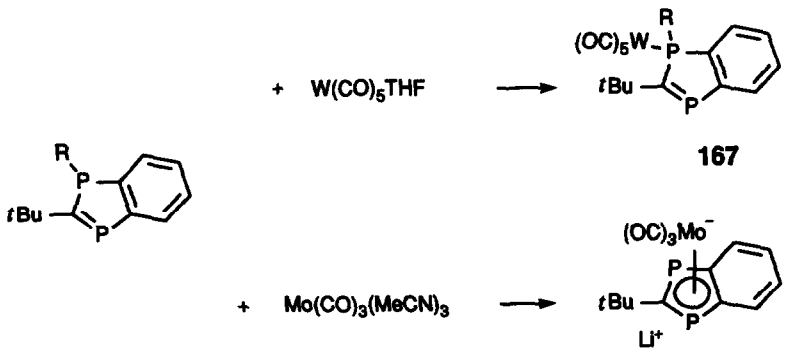


(74) **165**



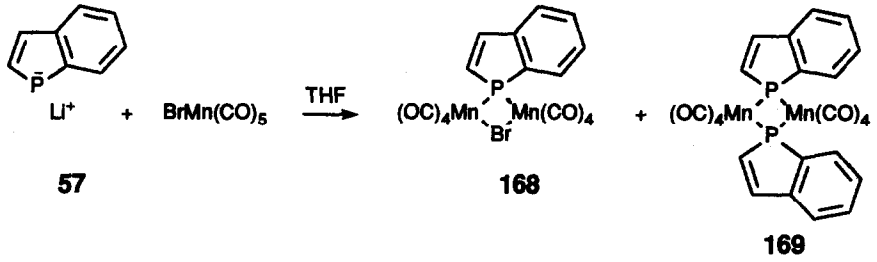
(36) **166**

1-Ethyl- as well as 1-lithio-2-*tert*-butyl-1,3-benzodiphosphole form η^1-complexes **167** (R = Et, Li) with $W(CO)_5$ in which the metal is bonded to the three-coordinate phosphorus atom[81,82]. Towards $Mo(CO)_3$ the benzodiphospholyl anion acts as an η^5-ligand[81,82].



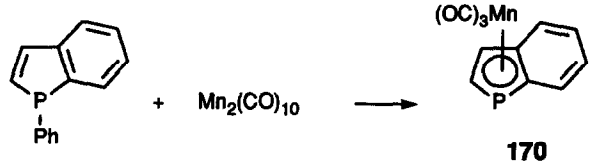
167

The phosphindolyl anion **57** shows ligand properties similar to that of the pyrrolyl anion. It reacts with bromomanganese pentacarbonyl to form a mixture of the two complexes **168** and **169**[62].



57 **168** **169**

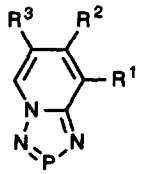
The η^5-phosphindolyl-manganese tricarbonyl complex **170** could be obtained directly from the reaction of 1-phenylphosphindole with dimanganese decacarbonyl[62].

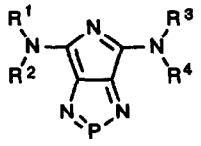
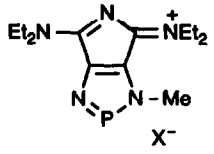
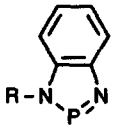
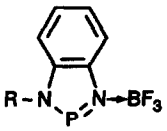


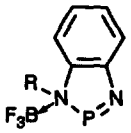
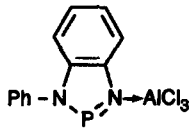
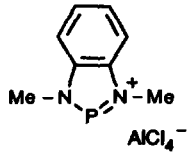
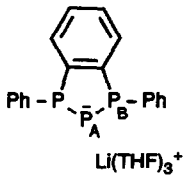
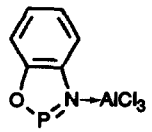
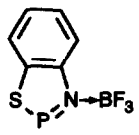
170

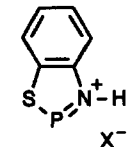
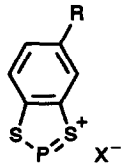
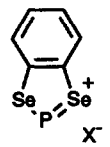
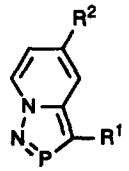
7. List of Anellated Heterophospholes and σ^2-Phospholes

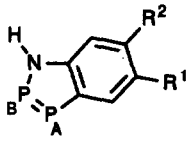
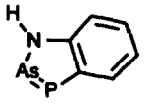
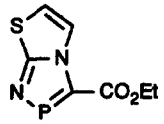
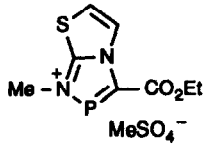
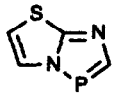
The known anellated σ^2-heterophospholes and σ^2-phospholes are listed below, together with the method of synthesis and relevant physical data. (Coupling constants J in Hz, melting and boiling points in °C, the subscript at the latter indicates the pressure in mbar.)

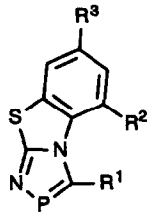
			Synthesis	m.p. (b.p.)	δ^{31}P (J_{PP})	other data
			2.1[15]	84-85[15]	291.5[15]	^{1}H-, ^{13}C-NMR[15]
						
R^1	R^2	R^3				
H	H	H	2.1[14]	132-133[14]	268.1[14]	^{1}H-, ^{13}C-NMR, MNDO[14]
Me	H	H	2.1[14]	126-127[14]	265.0[14]	^{1}H-, ^{13}C-NMR[14]
H	Me	H	2.1[14]	134-136[14]	269.7[14]	^{1}H-, ^{13}C-NMR[14]
H	H	Me	2.1[14]	180-182[14]	267.0[14]	^{1}H-, ^{13}C-NMR[14]
CN	Me	H	2.1[15]		271.3[15]	
CN	Ph	H	2.1[15]	215-216[15]	273.5[15]	^{1}H-NMR[15]

				Synthesis	m.p. (b.p.)	$\delta^{31}P$ (J_{PP})	other data
							
R^1	R^2	R^3	R^4				
Me	Me	Me	Me	2.1[25,26]	249-250[25,26]	300[25,26]	^{1}H-, ^{13}C-NMR[25,26] IR[25,26], X-Ray[26] MNDO[26]
Me	Me	Et	Et	2.1[26]		300.8[26]	
Me	Me	-$(CH_2)_5$-		2.1[26]		299.6[26]	
Et	Et	Et	Et	2.1[25,26]	82-83[25,26]	301.0[25,26]	^{1}H-, ^{13}C-NMR[25,26] UV[25,26]
-$(CH_2)_5$-		-$(CH_2)_5$-		2.1[26]	dark red oil[26]	298.9[26]	^{13}C-NMR[26]
Me	CH_2Ph	Me	CH_2Ph	2.1[26]	183-185[26]	300.8[26]	^{1}H-, ^{13}C-NMR[26]
						300.5[26]	^{1}H-NMR[26]
						300.2[26]	^{1}H-NMR[26]
		X					
		I		6.4[26]	153-155[26]	279.7[26]	^{1}H-NMR[26]
		$MeSO_4$		6.4[26]	86-88[26]	277.5[26]	^{1}H-, ^{13}C-NMR[26]
		R					
		H		2.1[19]		238[18,19]	
		Et		2.1[19]		232[18,19]	
		Pr		2.1[17,19]		236[17,19]	
		*i*Pr		2.1[17,19]		228[17,19], 232[18]	
		*s*Bu		2.1[17,19]		225.8[17,19]	
		$(CH_2)_2CHMe_2$		2.1[19]		232[19]	
		CH_2Ph		2.1[17,19]		228[17,19]	
		Ph		2.1[20]		229[20]	
		R					
		H		6.4[19]		222[19]	
		Pr		6.4[17,19]	147[18], 145[19]	226[18,19], 214.7[17]	
		*i*Pr		6.4[17,19]	132[18,19]	225.6[18,19], 214.2[17]	
		*s*Bu		6.4[18,19]	104[18,19]	226.7[18,19], 214.1[17]	
		$(CH_2)_2CHMe_2$		6.4[19]		226[19]	
		CH_2Ph		6.4[17,19]	122[18,19]	224.8[18,19], 225[21] 211.7[17], 212[21]	
		Ph		6.4[17,19]		205.9[17-19]	

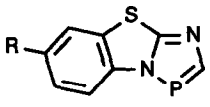
		Synthesis	m.p. (b.p.)	$\delta^{31}P$ (J_{PP})	other data
	R				
	Pr	6.4[17]		226[17]	
	*i*Pr	6.4[17]		225.6[17]	
	*s*Bu	6.4[17]		226.7[17]	
	CH_2Ph	6.4[17,21]		224.8[17], 225[21]	
		6.4[20]		200.9[20]	^{15}N-, ^{27}Al-NMR[20]
		2.1[23]		212[31]	X-Ray[23]
		2.1[29]		-174.0[A], 31.4[B] (368.5)[29]	X-Ray[29]
		6.4[18]		262[18]	
		6.4[18]	191[18]	160[18]	

			Synthesis	m.p. (b.p.)	$\delta^{31}P$ (J_{PP})	other data
	X					
	$AlCl_4$		2.1[31]	123-125[31]	306[31]	^1H-, ^{13}C-NMR[31] ^{27}Al-NMR, IR[31] MS, X-Ray[31] STO-3G[31] MCD, PPP[144]
			2.1[30]		317[108,30]	
	$AlCl_3Br$		2.1[31]		300[31]	^{27}Al-NMR[31]
	R	X				
	H	$AlCl_4$	2.1[32,33]	80(dec.)[32,33]	408[33]	^1H-, ^{13}C-NMR[33] IR, MS[33] X-Ray[31–33] MCD, PPP[144] STO-3G[31]
	Me	$AlCl_4$	2.1[33]	106-108(dec.)[33]	414[33]	^1H-, ^{13}C-NMR[33] IR, MS[33] MCD, PPP[144]
	Me	$AlClBr_3$	2.1[33]	75-78(dec.)[33]	406[33]	^1H-NMR, IR[33] MS[33]
	Me	$MoCl_6$	2.1[33]			IR[33]
					495[31]	
	R^1	R^2				
	H	H	2.1[39]	syrupy[39]	236.3[39]	^1H-, ^{13}C-NMR[39]
	H	Me	2.1[39]	74-76[39]	237.6[39]	^1H-, ^{13}C-NMR[39]
	Me	H	2.1[39]	80-83[39]	239.5[39]	^1H-, ^{13}C-NMR[39] MS[39]
	P^BCl_2	H	2.1[39]	114-116[39]	249.2, 157.0[B 39]	

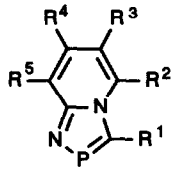
			Synthesis	m.p. (b.p.)	$\delta^{31}P$ (J_{PP})	other data
	R^1	R^2				
	H	H	2.1[27,28]	72-75[27]	246[A], 354[B] (493)[27]	^{13}C-NMR, MS[27]
					248[A], 352[B] (496)[28]	PE, MNDO[28]
	Me	H	2.1[28]		246[A], 358[B] (494)[28]	
	Cl	H	2.1[28]		245[A], 350[B] (494)[28]	
	H	Me	2.1[28]		248[A], 382[B] (496)[28]	
	H	Cl	2.1[28]		247[A], 349[B] (494)[28]	
			2.1[28]		315[28]	MS[28]
			2.1[43]	104-106[43]	252.6[43]	^{1}H-, ^{13}C-NMR[43]
			6.4[43]		252.6[43]	^{1}H-, ^{13}C-NMR[43]
			2.2[30]		192.3[30]	^{1}H-, ^{13}C-NMR[30]



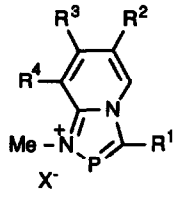
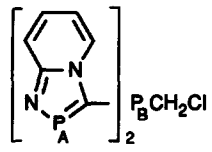
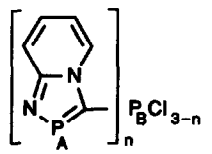
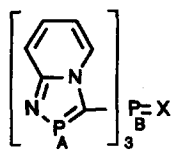
R^1	R^2	R^3	Synthesis	m.p. (b.p.)	$\delta^{31}P$ (J_{PP})	other data
H	H	H	2.2[72]		223.4[72]	^{1}H-, ^{13}C-NMR[72]
H	H	OMe	2.2[72]		219.4[72]	^{1}H-, ^{13}C-NMR[72]
H	Me	H	2.2[72]	116-117[72]	220.4[72]	^{1}H-, ^{13}C-NMR[72]
CO_2Me	H	H	2.1[43]	153-155[43]	258.6[43]	^{1}H-NMR[43]
CO_2Et	H	H	2.1[43]	112-113[43]	259.1[43]	^{1}H-NMR[43]
COPh	H	H	2.1[43]		268.7[43]	
CO_2Et	H	OMe	2.1[43]	118-121[43]	255.0[43]	^{1}H-NMR[43]
COPh	H	OMe	2.1[43]		264.9[43]	

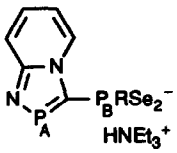
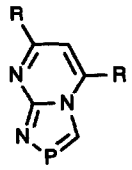
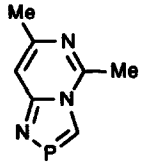
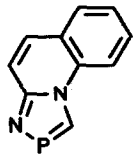
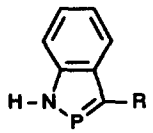
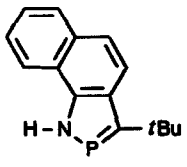


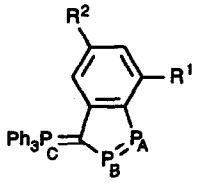
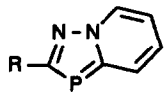
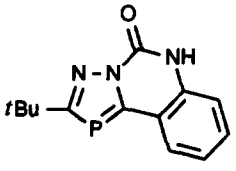
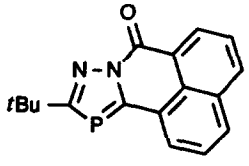
R			
H	2.2[72]	184.8[72]	^{1}H-, ^{13}C-NMR[72]
OMe	2.2[72]	184.6[72]	^{1}H-, ^{13}C-NMR[72]

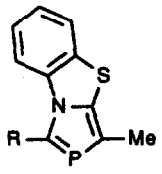


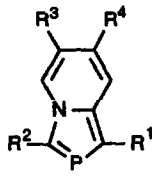
R^1	R^2	R^3	R^4	R^5				
H	H	H	H	H	2.2[65,70]	44-46[70]	195.0[65,70]	^{1}H-, ^{13}C-NMR[70] ^{15}N-NMR[70,145]
H	H	H	Me	H	2.2[30]		195.1[30]	^{1}H-, ^{13}C-NMR[30]
H	H	Me	H	H	2.2[30]		194.3[30]	^{1}H-, ^{13}C-NMR[30]
H	H	H	H	Me	2.2[30]		194.8[30]	^{1}H-, ^{13}C-NMR[30]
CO_2Et	H	H	H	H	2.1[42]	78-79[42]	234.7[42]	^{1}H-, ^{13}C-NMR[42] ^{15}N-NMR[42]
CO_2Et	H	Me	H	H	2.1[42]	76-78[42]	237.5[42]	^{1}H-, ^{13}C-NMR[42]
CO_2Et	H	H	Me	H	2.1[42]	91-93[42]	233.7[42]	^{1}H-, ^{13}C-NMR[42]
CO_2Et	Me	H	H	H	2.1[42]	76-77[42]	234.8[42]	^{1}H-, ^{13}C-NMR[42]
P^BPh_2	H	H	H	H	6.6[30]		227.3, -37.8[B] (2)[30]	
P^BPh_2	H	Me	H	H	6.6[30]		228.1, -37.9[B] (5)[30]	

					Synthesis	m.p. (b.p.)	$\delta^{31}P$ (J_{PP})	other data
								
X	R^1	R^2	R^3	R^4				
$MeSO_4$	H	H	H	Me	6.4[65]		186.7[65]	
Cl	H	H	H	2-C_5H_4N	2.2[30]		178.2[30]	
$MeSO_4$	CO_2Et	H	H	Me	6.4[42]		214.5[42]	^{1}H-, ^{13}C-NMR[42]
$MeSO_4$	CO_2Et	Me	H	Me	6.4[42]		212.9[42]	^{1}H-, ^{13}C-NMR[42]
$MeSO_4$	CO_2Et	H	Me	Me	6.4[42]		218.4[42]	^{1}H-, ^{13}C-NMR[42]
					6.6[30]		232.4^A, -54.2^B (2)[30]	
P^B-sulfide					6.6[30]		237.8^A, 16.1^B (24.9)[30]	
				n				
				1	6.6[65]		243.6^A, 123.1^B (166.1)[65]	
				2	6.6[65]		237.5^A, 24.3^B (69.7)[65]	
				3	6.6[65]		235.2^A, -74.1^B (5.4)[65]	
				X				
				O	6.6[65]		242.8^A, -2.0^B (44.9)[65]	
				S	6.6[65]		240.5^A, -3.4^B (40.3)[65]	
				Se	6.6[65]		239.7^A, -26.4^B (36.7)[65]	

		Synthesis	m.p. (b.p.)	$\delta^{31}P$ (J_{PP})	other data
	R				
	Ph	6.6[146]	165-167(dec.)[146]	228.9^{A}, -9.3^{B} (35.0)[146]	^{1}H-, ^{13}C-NMR[146]
	4-MeOC$_6$H$_4$	6.6[146]	168-170(dec.)[146]	225.1^{A}, -10.6^{B} (32.0)[133]	^{1}H-, ^{13}C-NMR[146]
	R				
	H	2.2[30]		197.0[30]	^{1}H-NMR[30]
	Me	2.2[65]		197.2[65]	^{1}H-, ^{13}C-NMR[30]
		2.2[30]		200.2[30]	^{1}H-, ^{13}C-NMR[30]
		2.2[30]		187.3[30]	^{1}H-, ^{13}C-NMR[30]
	R				
	Me	4.2[105]	oil[105]	194.4[105]	^{1}H-, ^{13}C-NMR[105] MS[105]
	*t*Bu	4.2[104]	86[104]	210.3[104]	^{1}H-, ^{13}C-NMR[104] IR[104]
		4.2[104]	135[104]	180.1[104]	^{1}H-, ^{13}C-NMR[104] IR[104]

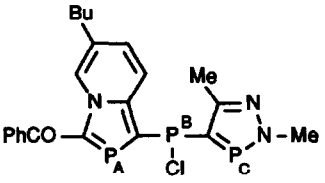
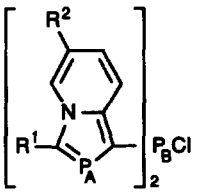
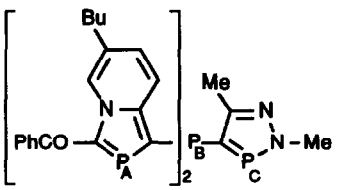
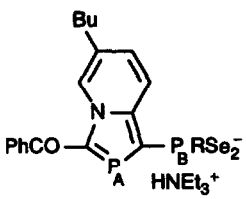
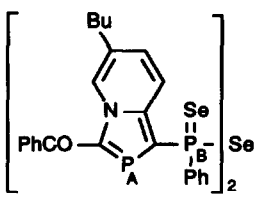
			Synthesis	m.p. (b.p.)	$\delta^{31}P$ (J_{PP})	other data
	R^1	R^2				
	H	H	2.1[53]		229.4[A], 317.1[B] 14.9[C], (480.2[AB] 6.1[AC], 87.5[BC])[53]	^{1}H-, ^{13}C-NMR[53]
	H	Me	2.1[53]		218.8[A], 309.2[B] 14.4[C], (477.6[AB] 4.5[AC], 87.0[BC])[53]	
	Me	H	2.1[53]		229.1[A], 314.7[B] 14.0[C], (476.1[AB] 6.1[AC], 87.0[BC])[53]	
	R					
	Me		3.1[73]	30-31[73]	63.0[73]	^{1}H-, ^{13}C-NMR[73] MS[73]
	*i*Pr		3.1[73]	yellow oil[73]	57.4[73]	^{1}H-, ^{13}C-NMR[73] MS[73]
	*t*Bu		3.1[73]	yellow oil[73]	54.6[73]	^{1}H-, ^{13}C-NMR[73] MS[73]
	Ph		3.1[73]	96-97[73]	57.5[73]	^{1}H-, ^{13}C-NMR[73] MS[73]
	OCOMe		3.1[74]	117-119[74]	22.1[74]	IR, MS[74]
	OCOPh		3.1[74]	115-117[74]	22.3[74]	^{13}C-NMR, IR[74] MS[74]
	OH		3.1[74]	219-220[74]		IR, MS[74]
	$OSiMe_3$		3.1[74]	34-36[74]	13.6[74]	^{13}C-NMR, MS[74]
			4.1[96]	118[96]	83.9[96]	^{1}H-NMR, IR[96]
			4.1[95,96]	167[95,96]	98.2[95,96]	^{1}H-NMR[96] ^{13}C-NMR[95,96] IR[96]

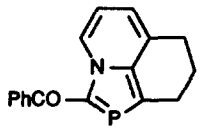
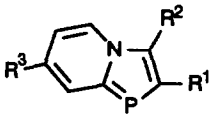
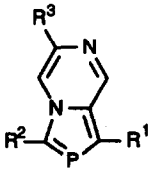
		Synthesis	m.p. (b.p.)	$\delta^{31}P$ (J_{PP})	other data
	R				
	CO_2Et	2.1[50]	99-100[50]	184.8[50]	^1H-, ^{13}C-NMR[50]
	COPh	2.1[50]	146-147[50]	202.6[50]	^1H-, ^{13}C-NMR[50]
	CN	2.1[50]	106-108[50]	191.6[50]	^1H-, ^{13}C-NMR[50]

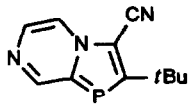
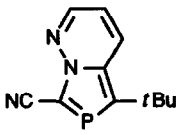
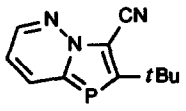
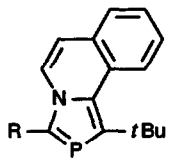
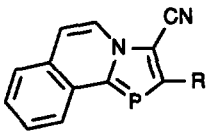
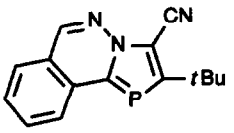
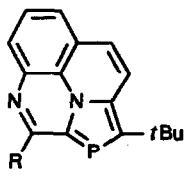


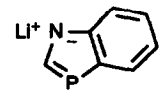
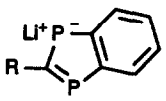
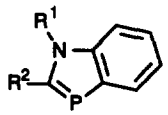
R^1	R^2	R^3	R^4				
H	COPh	H	H	2.1[7]	114-119[7]	179.8[7]	^1H-, ^{13}C-NMR[7]
H	CO_2Et	H	H	2.1[7]	orange oil[7]	162.0[7]	^1H-, ^{13}C-NMR[7]
H	4-$NO_2C_6H_4$	H	H	2.1[7]		132.2[7]	^1H-, ^{13}C-NMR[7]
H	COPh	H	Me	2.1[7]	117-118[7]	184.4[7]	^1H-, ^{13}C-NMR[7]
	P-$Cr(CO)_5$ complex			6.7[7]		191.9[7]	IR[7]
H	CO_2Et	H	Me	2.1[7]	34[7]	163.3[7]	^1H-, ^{13}C-NMR[7]
H	COPh	Bu	H	2.1[7]	51-52[7]	180.0[7]	^1H-, ^{13}C-NMR[7]
H	CN	H	Me	2.1[48]	136-137[48]	165.8[48]	^1H-NMR[48]
H	CO_2Et	Bu	H	2.1[48]	oil[48]	160.7[48]	^1H-NMR[48]
Me	COPh	H	H	2.1[7]	124-125[7]	183.6[7]	^1H-, ^{13}C-NMR[7]
Me	CO_2Et	H	H	2.1[7]	71-73[7]	165.5[7]	^1H-, ^{13}C-NMR[7]
Me	4-$NO_2C_6H_4$	H	H	2.1[7]	188-189[7]	136.0[7]	^1H-, ^{13}C-NMR[7]
Me	CN	H	H	2.1[7]	151-152[7]	165.2[7]	^1H-, ^{13}C-NMR[7]
Ph	COPh	H	H	2.1[7]	135-136[7]	178.5[7]	^1H-, ^{13}C-NMR[7]
Ph	CO_2Et	H	H	2.1[7]	73-75[7]	160.0[7]	^1H-, ^{13}C-NMR[7]
Ph	4-$NO_2C_6H_4$	H	H	2.1[7]	171-178[7]	130.6[7]	^1H-, ^{13}C-NMR[7]
Ph	CN	H	H	2.1[7]	158-159[7]	160.5[7]	^1H-, ^{13}C-NMR[7]
Ph	Ph	H	H	2.1[48]	120-121[48]	120.9[48]	^1H-NMR[48]
4-ClC_6H_4	4-$NO_2C_6H_4$	H	H	2.1[48]	210-212[48]	128.8[48]	^1H-NMR[48]
*t*Bu	CO_2Me	H	H	4.1[99]	132 ($150\text{-}160_{0.05}$)[99]	162.7[99]	^1H-, ^{13}C-NMR[99] X-Ray[99]
*t*Bu	CO_2Et	H	H	4.1[9]	148 ($160\text{-}170_{0.05}$)[99]	162.4[9]	^{13}C-NMR[9] ^1H-NMR, MS[99]
*t*Bu	CN	H	H	4.1[9]		161.0[99]	^1H-, ^{13}C-NMR[99]
*t*Bu	CN	H	Me	4.1[9]		162.0[99]	^1H-, ^{13}C-NMR[99]
*t*Bu	CN	H	*t*Bu	4.1[9]		162.1[99]	^1H-, ^{13}C-NMR[99]

				Synthesis	m.p. (b.p.)	$\delta^{31}P$ (J_{PP})	other data
*t*Bu	CN	H	O*i*Pr	4.1[9]		162.7[99]	
*t*Bu	CN	H	CO_2Me	4.1[9]		165.1[99]	^1H-, ^{13}C-NMR[99]
*t*Bu	CN	H	CN	4.1[9]		169.2[99]	^1H-, ^{13}C-NMR[99]
*t*Bu	CN	H	COPh	4.1[9]		164.9[99]	^1H-, ^{13}C-NMR[99]
Br	COPh	H	H	6.6[125]	137-140(dec.)[125]	176.8[125]	^1H-NMR[125]
Br	COPh	H	Me	6.6[125]	152-154[125]	177.9[125]	^1H-, ^{13}C-NMR[125]
Br	COPh	Bu	H	6.6[125]	79-81[125]	175.0[125]	^1H-, ^{13}C-NMR[125]
Br	CO_2Et	H	Me	6.6[125]	76-77[125]	161.0[125]	^1H-NMR[125]
Br	CO_2Et	Bu	H	6.6[125]	syrupy[125]	157.1[125]	^1H-, ^{13}C-NMR[125]
Br	CN	H	Me	6.6[125]	137-138[125]	160.5[125]	^1H-NMR[125]
P^BCl_2	COPh	H	H	6.6[125]	115(dec.)[125]	197.2, 158.8[B] (169.2)[125] 197.1, 159.5[B] (165.0)[125]	^1H-, ^{13}C-NMR[125]
P^BCl_2	COPh	H	Me	6.6[125]	119-121[125]	200.7, 155.0[B] (180.4)[125]	
P^BCl^2	COPh	Bu	H	6.6[125]		195.6, 159.1[B] (173.9)[125]	
P^BCl_2	CO_2Et	H	H	6.6[125]		180.4, 161.2[B] (159.8)[125]	
P^BCl_2	CO_2Et	H	Me	6.6[125]		180.3, 162.1[B] (158.7)[125]	
P^BCl_2	4-$NO_2C_6H_4$	H	H	6.6[125]		142.4, 164.3[B] (130.0)[125]	
P^B(Ph)Cl	COPh	H	H	6.6[125]		199.7, 74.6[B] (57.0)[125]	
P^B(Ph)Cl	COPh	Bu	H	6.6[125]		198.8, 74.8[B] (60.9)[125]	
$P^B(OMe)_2$	COPh	H	Me	6.6[125]		200.7, 158.2[B] (34.2)[125]	
$P^B(OMe)_2$	COPh	Bu	H	6.6[125]		197.5, 159.2[A] (33.5)[125]	
$P^BS(OMe)_2$	COPh	H	Me	6.6[125]		206.4, 85.3[B] (87.9)[125]	
$P^BO(OMe)_2Me$	COPh	Bu	H	6.6[125]		203.9, 24.0[B] (79.3)[125]	

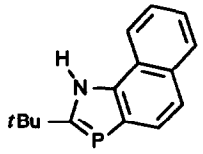
			Synthesis	m.p. (b.p.)	$\delta^{31}P$ (J_{PP})	other data
			6.6[125]	oil[125]	201.5[A], 59.6[B] 247.2[C], (50.3[AB] 15.2[AC], 8.2[BC])[125]	^{1}H-, ^{13}C-NMR[125]
	R^1	R^2				
	COPh	H	6.6[125]		199.2[A], 68.0[B] (47.3)[125] 198.3[A], 69.4[B] (46.1)[125]	
	COPh	Bu	6.6[125]		197.9[A], 69.2[B] (51.3)[125]	
	CO_2Et	H	6.6[125]		181.8[A], 69.7[B] (42.3)[125]	
			6.6[125]		202.3[A], -61.4[B] 247.2[C], (10.4[AB] 15.2[AC], 8.2[BC])[125]	
	R					
	Ph		6.6[123,146]	78-95(dec.)[146]	201.9[A], -0.4[B] (82.4)[146]	^{1}H-, ^{13}C-NMR[146] ^{77}Se-NMR[146]
	4-$MeOC_6H_4$		6.6[146]	93-96[146]	201.0[A], -1.4[B] (82.4)[146]	^{1}H-, ^{13}C-NMR[146] ^{77}Se-NMR[146]
	4-$Me_2NC_6H_4$		6.6[146]	123-126[146]	200.6[A], -1.2[B] (80.9)[146]	^{1}H-, ^{13}C-NMR[146] ^{77}Se-NMR[146]
			6.6[123]		204.6[A], 25.7[B] (N = 68.0)[146] 200.2[A], 26.2[B] (N = 74.0)[146]	

			Synthesis	m.p. (b.p.)	$\delta^{31}P$ (J_{PP})	other data
			2.1[7]	116-118[7]	174.0[7]	^1H-, ^{13}C-NMR[7]
						
R^1	R^2	R^3				
Me	H	H	3.1[73]	69-71[73]	76.2[73]	^1H-, ^{13}C-NMR[73] MS[73]
*t*Bu	H	H	3.1[73]	yellow oil[73]	69.5[73]	^1H-, ^{13}C-NMR[73] MS[73]
Ph	H	H	3.1[73]	146-147[73]	68.7[73]	^1H-, ^{13}C-NMR[73] MS[73]
*t*Bu	CN	H	4.1[9,99]		75.1[99]	^1H-, ^{13}C-NMR[99]
*t*Bu	CN	Me	4.1[9,99]		69.0[99]	^1H-, ^{13}C-NMR[99]
*t*Bu	CN	*t*Bu	4.1[9,99]		72.0[99]	^1H-, ^{13}C-NMR[99]
*t*Bu	CN	CO_2Me	4.1[9,99]		92.5[99]	^1H-, ^{13}C-NMR[99]
*t*Bu	CN	COPh	4.1[9,99]		93.3[99]	^1H-, ^{13}C-NMR[99]
*t*Bu	CN	CN	4.1[99]		95.7[99]	^1H-, ^{13}C-NMR[99]
						
R^1	R^2	R^3				
H	COPh	Me	2.1[7]	120-130[7]	181.5[7]	^1H-, ^{13}C-NMR[7]
*t*Bu	CN	H	4.1[9,99]		163.8[99]	^1H-, ^{13}C-NMR[99]
P^BCl_2	COPh	Me	6.6[125]		197.8, 152.0[B] (152.0)[125]	
$P^B(Ph)Cl$	COPh	Me	6.6[125]		200.0, 67.3[B] (56.8)[125]	

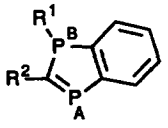
		Synthesis	m.p. (b.p.)	$\delta^{31}P$ (J_{PP})	other data
		4.1[9,99]		91.7[99]	^1H-, ^{13}C-NMR[99]
		4.1[9,99]		148.7[99]	^1H-, ^{13}C-NMR[99]
		4.1[9,99]		76.8[99]	^1H-, ^{13}C-NMR[99]
	R				
	CO_2Me	4.1[99]	158 ($170\text{-}180_{0.005}$)[99]	163.5[99]	^1H-, ^{13}C-NMR[99]
	CO_2Et	4.1[99]		162.0[99]	^1H-, ^{13}C-NMR[99]
	R				
	*t*Bu	4.1[9,99]	195(dec.)[99]	76.7[99]	^1H-, ^{13}C-NMR[99]
	CMe_2Et	4.1[9,99]	189(dec.)[99]	88.1[99]	^1H-, ^{13}C-NMR[99] MS[99]
		4.1[9,99]	228(dec.)[99] ($200_{0.05}$)[99]	73.0[99]	^1H-, ^{13}C-NMR[99] MS[99], X-Ray[9]
	R				
	Me	4.1[99]	234.6(dec.)[99]	108.2[99]	^1H-, ^{13}C-NMR[99] MS[99]
	Ph	4.1[99]	184(dec.)[99]	115.9[99]	^1H-, ^{13}C-NMR[99] MS[99]

		Synthesis	m.p. (b.p.)	$\delta^{31}P$ (J_{PP})	other data
		6.4[83]	orange red[83]		
					
R					
Me		3.2[82]		153.4[82]	
*t*Bu		3.2[82]		145.1[82]	
	P^B-W(CO)$_5$ complex	6.7[82]	124-125[82]	176.8, 18.7[B 82]	IR[82] $^1J_{PW}$ = 186.9 Hz[82]
	η^5-Mo(CO)$_3$ complex	6.7[82]	oil[82]	19.1[82]	IR[82]
Ph		3.2[82]		151[82]	
2,4,6-$Me_3C_6H_2$		3.2[82]		152[82]	
$OSiMe_3$		3.2[78]		120.0[78]	
NPhLi		3.2[78,79]		83.5[78,79]	
					
R^1	R^2				
H	H	3.2[86]	102-103[86]	77.2[86]	^{1}H-, ^{13}C-NMR[86] UV, MS[86]
H	Me	3.2[83,86] 4.2[105]	116-117[83,86]	69.8[83,86] 71.4[105]	^{1}H-NMR[83,86,105] ^{13}C-NMR[83,86] UV, MS[83,86]
H	Ph	3.2[83,86]	127-129[83,86]	72.1[83,86]	^{1}H-, ^{13}C-NMR[83,86] UV, MS[83,86]
	P-Cr(CO)$_5$ complex	6.7[83]	111[83]	76.5[83]	IR[83]
H	$NHPh$	3.2[80]	144-145[80]	6.7[80]	UV[80]
H	NMe_2	3.2[83]	89-91[83]	-4.6[83]	^{1}H-NMR[83]
H	*t*Bu	2.1[52]	132-133[52]	65.7[52]	^{1}H-NMR[52,104] ^{13}C-NMR[104]
		4.2[104]		66.3[104]	
Me	H	3.2[87]	(77-80$_{0.06}$)[87]	72.6[87]	^{1}H-, ^{13}C-NMR[87] UV, MS[87], PE[106] MNDO, CNDO/S[106]

		Synthesis	m.p. (b.p.)	$\delta^{31}P$ (J_{PP})	other data
Me	Me	3.2[87]	78-80 ($108\text{-}110_{0.02}$)[87]	69.3[87]	^{1}H-, ^{13}C-NMR[87] UV[87]
Me	Ph	3.2[87]	100-105 ($150\text{-}155_{0.01}$)[87]	76.0[87]	^{13}C-NMR, UV[87]
Me	*t*Bu	3.2[87]	38-40 ($110\text{-}115_{0.01}$)[87]		^{1}H-, ^{13}C-NMR[87] UV[87]
Me	CO_2SiMe_3	6.5[87]	55-60 ($100\text{-}106_{0.01}$)[87]	125.5[87]	^{13}C-NMR, IR[87]
Me	$SiMe_3$	6.5[87]	($98\text{-}100_{0.01}$)[87]	120.5[87]	^{1}H-, ^{13}C-NMR[87] IR[87]
Me	CO_2H	6.5[87]	200[87]	127.4[87]	IR, UV[87]
Me	Li	6.5[87]			^{13}C-NMR[87]
Me	SMe	6.5[136]	28-30[136]	65.5[136]	^{1}H-NMR, UV[136]
COMe	Ph	6.4[83]	145-150(dec.)[83]	72.7[83]	^{1}H-NMR, IR[83]
P^BCl_2	H	6.4[83]	dark red oil[83]	72.5, 160.3[B 83]	
$S_{n/2}$	Ph	6.4[83]	>100 (dec.)[83]	73.6[83]	

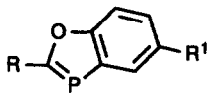


		4.2[104]		74.4[104]	^{1}H-NMR[104]

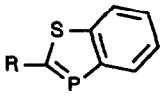
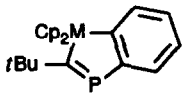
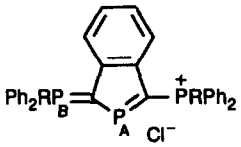
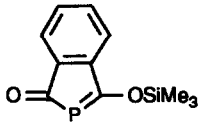
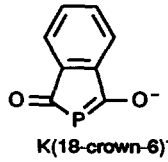


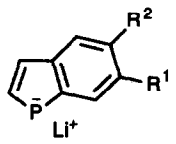
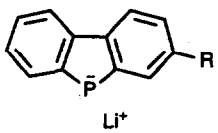
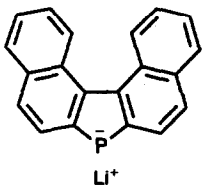
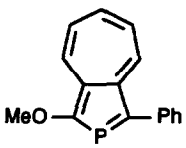
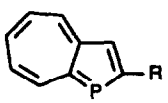
R^1	R^2				
H	*t*Bu	3.2[82]		263.1[A], -84.9[B] (23.3)[82]	
Me	NMe_2	3.2[90]	($135\text{-}137_{0.003}$)[90]	103.5[A], 2.4[B] (26.9)[90]	^{13}C-NMR, MS[90]
Et	*t*Bu	3.2[82]	($123_{0.001}$)[82]	270[A], 29.6[B] (9.7)[82]	^{13}C-NMR, UV[82] MS[82]
	P^B-sulfide	3.2[82]		274.6[A], 65.6[B] (53.2)[82]	
	P^B-$W(CO)_5$ complex	6.7[82]	149-151[82]	292.7[A], 37.9[B] (44.4)[82]	IR[82] $^{1}J_{PW}$ = 186.9 Hz[82]

		Synthesis	m.p. (b.p.)	$\delta^{31}P$ (J_{PP})	other data
Et	NMe_2	3.2[90]	$(138\text{-}140_{0.003})$[90]	114.8^A, 19.9^B (24.4)[90]	^{13}C-NMR, MS[90]
CO*t*Bu	*t*Bu	3.2[82]	$(113_{0.007})$[82]	294^A, 37.8^B (17.1)[82]	IR[82]
$SiMe_3$	*t*Bu	3.2[82]		265^A, -1^B (24.6)[82]	
P^CPh_2	*t*Bu	3.2[82]		270^A, 33^B 8.9^C, $(26.6^{AB}$ 9^{AC}, $350^{BC})$[82]	
*t*Bu	H	3.2[82]		288.7^A, 55.6^B (14.7)[82]	
*t*Bu	$SiMe_3$	3.2[82]		271^A, 31^B (9.8)[82]	
*t*Bu	P^CPh_2	3.2[82]		285.7^A, 81.8^B -15.6^C [82]	
$SiMe_3$	$OSiMe_3$	3.2[78]	yellow oil 120 (dec.)[78]	177^A, -8^B (39)[78]	
$SiMe_3$	$NPhSiMe_3$	3.2[79]	oil[79]	178.1^A, -6.6^B (26.0)[79]	^1H-, ^{13}C-NMR[79]



R	R^1				
Me	H	3.2[84]	$(41\text{-}42_{0.15})$ (63_{3-4})[84]	85.3[84]	^1H-, ^{13}C-NMR[84] UV[84], PE[106] MNDO, CNDO/S[106]
Et	H	3.2[84]	$(73\text{-}76_{4-5})$[84]	81.4[84]	^1H-NMR[84]
*t*Bu	H	3.2[84,85]	$(53\text{-}55_{0.02})$ $(43\text{-}45_{0.01})$[84]	76.4[84,85]	^1H-, ^{13}C-NMR[84,85] UV, MS[85], PE[106] MNDO, CNDO/S[106]
*t*Bu	Me	3.2[84]	$(57\text{-}59_{0.01})$[84]	77.0[84]	^1H-NMR, UV[84]
Ph	H	3.2[84]	82-83 $(124\text{-}126_{0.09})$[84]	86.3[84]	^{13}C-NMR, UV[84]
4-ClC_6H_4	H	3.2[84]	97-98[84]	88.5[84]	UV[84]
4-$MeOC_6H_4$	H	3.2[84]	100-101[84]	78.1[84]	^1H-NMR, UV[84]

		Synthesis	m.p. (b.p.)	$\delta^{31}P$ (J_{PP})	other data
	R				
	H	3.2[91]	(154-155$_{0.1}$)[91]	79.9[91]	^{1}H-, ^{13}C-NMR[91]
	Me	3.2[91]	(135$_{0.1}$)[91]	70.6[91]	^{1}H-NMR[91]
	Ph	3.2[91]	(165-168$_{0.4}$)[91]	56.3[91]	
	M				
	Ti	4.1[103]	107(dec.)[103]	170.4[103]	^{1}H-, ^{13}C-NMR[103] MS[103]
	Zr	4.1[103]	127(dec.)[103]	186.3[103]	^{1}H-, ^{13}C-NMR[103] MS[103]
	R				
	Me	2.1[55]	>250(dec.)[55]	228.5^A, 11.7^B (92.7)[55]	^{1}H-, ^{13}C-NMR[55]
	C_2H_3	2.1[55]		229.6^A, 18.2^B (84.0)[55]	^{1}H-NMR, X-Ray[55]
	2-C_4H_3S	2.1[55]	>250(dec.)[55]	241.7^A, 9.2^B (97.7)[55]	^{1}H-, ^{13}C-NMR[55]
	2-C_5H_4N	2.1[55]	>250(dec.)[55]	245.4^A, 9.2^B (90.0)[55]	^{1}H-, ^{13}C-NMR[55]
	Ph	2.1[54]	302(dec.)[54]	241.8^A, 16.8^B (91.4)[54]	^{13}C-NMR[54] X-Ray of $CpW(CO)_3^-$-salt[55]
P-AuCl complex, $CF_3SO_3^-$-salt		6.7[55]	>200[55]	186.7^A, 12.4^B (65.2)[55]	^{1}H-NMR, MS[55] X-Ray[55]
		3.1[75,76]		71.7[76] 76.6[75]	^{1}H-NMR[75], IR[75,76] UV[75]
		3.1[77]	159-161[77]	43.4[77]	^{1}H-, ^{13}C-NMR[77] IR, UV, X-Ray[77] MINDO/3[77] Extd. Hückel[77]

		Synthesis	m.p. (b.p.)	$\delta^{31}P$ (J_{PP})	other data
					
R^1	R^2				
H	H	2.1[62]		40[62]	
	η^5-Mn(CO)$_3$ complex	6.7[62]	45[62]	-54.7[62]	^{1}H-NMR[62] IR, MS[62]
	P-Mn$_2$(CO)$_8$Br$^+$ complex	6.7[62]	146(dec.)[62]	-36[62]	^{1}H-NMR[62] IR, MS[62]
	P-Mn(CO)$_4^+$ dimer complex	6.7[62]	250(dec.)[62]		^{1}H-NMR[62] IR, MS[62]
Ph	Bu	2.1[147]			
	R				
	H	2.1[63]			
	Me	2.1[55]			
		2.1[64]			
		2.1[102]	85-87[102]	177.9[102]	^{1}H-NMR, UV[102]
	R				
	H	2.1[57]	71.5 ($40_{0.1}$)[57]	174.8[57]	^{1}H-, ^{13}C-NMR[57] UV, MS[57]
	CH_2Ph	2.1[56]	(120-125$_{0.01}$)[56]	168.3[102]	^{1}H-NMR, UV[56] MS[56]

8. Concluding Remarks and Acknowledgements

A recent paper[20] reports anew about the reaction mentioned at the very beginning of this Report. As it turns out, the authors then were not too far from truth and derivatives of 1,3,2-benzodiazaphospholes can indeed be obtained this way. Our knowledge of anellated (hetero)phospholes has greatly developed since then, but the topic is still a frontier area of research in organophosphorus chemistry. More syntheses and more systems will certainly be added.

The reactivity of these compounds has been little explored so far and much more remains to be investigated. It is already apparent, however, that the compounds offer many possibilities and as some of them are readily accessible, their reactions may well become of practical use. It is hoped that this Report will stimulate further work in this areas.

We take this opportunity to thank the Department of Science and Technology, Government of India, New Delhi, for sanctioning a project (to R.K.B.), the Alexander von Humboldt Foundation, Bonn, for a fellowship which greatly helped the joint research of the Munich and the Jaipur group to come into existence, and the Volkswagen Foundation, Hannover, for generous financial support to this cooperation.

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