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Compounds containing phosphorus and boron

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ABSTRACT. This review examines the synthesis and properties of phosphorus-boron-containing compounds containing the fragments P=B, B–C–B, P–N–B, P–O–B, P–C–C–B, P–C=C–B, P=C–O–B, P–C–O–B, P–C≡C–B, and P–$(C)_n$–B, and also phosphorus-containing borohydrides, carboranes, and coordination compounds containing phosphorus- and boron-containing ligands. The interaction of heteroatomic functional groups has received special attention. Wherever possible the acquisition of new properties by the compounds as a result of these interactions has been noted.

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I. Introduction

The introduction of different heteroatom-containing groups into an organic molecule leads to the mutual enrichment of the chemistry of the corresponding classes of organic compounds. One of the most interesting examples of this type is the introduction of phosphorus atoms into organoboron compounds. Phosphorus and boron are known to have different electronic compositions (an atom with an unshared electron pair, an atom with a vacant orbital, a donor and an acceptor, a base and an acid) and have the ability to change reversibly their coordination and to form coordinate bonds with metals, while the variety of properties and types of compounds obtained may be attributed to the diversity of fragments by means of which the phosphorus- and boron-containing groups may be linked. New properties appear as a result of the mutual effect of the functional groups containing these elements. In this regard it is appropriate to examine the currently known classes of P- and B-containing compounds (PBC) and to attempt to follow the change in the interaction of the heteroatoms. In the phosphinoboranes and phosphineboranes a chemical bond is involved in this interaction. When a particular fragment is present between the P and B atoms, the effect of the heteroatomic functions is equivalent to a supplementary interaction, and the type and method of transfer of the latter are determined by several factors, i.e. the remoteness of the heteroatoms from each other, the spatial arrangement, the ability of the separating fragment to "conduct" electronic effects, etc. With such an approach different classes of P- and B-containing compounds may be combined into a single review. A study of the coordination compounds is one of the most promising avenues for the advancement of the chemistry of functionally substituted phosphorus compounds including the phosphorus-boron compounds. The introduction of boron-containing functional groups into a molecule of a phosphorus-containing ligand may lead to fundamental changes in the coordination sphere of the metal. Numerous examples of PBC coordination compounds are considered in the review.

In a study and comparison of the properties of different types of PBC such an approach may be extended also to other systems possessing two or several heteroatomic functions, for example P–Al, As–B, etc.

The currently known phosphorus-boron containing compounds may be separated into three major groups: 1) compounds in which the P and B atoms are linked by a coordinate bond, the phosphineboranes; 2) compounds containing three-coordinate P and B atoms linked directly to each other, the acyclic and cyclic monomeric phosphinoboranes; 3) compounds in which the P and B atoms are separated by some fragment, carbon atoms, heteroatoms, metal atoms, C–O and C–N fragments, etc. The present review focuses on the latter group of compounds which are presently attracting the attention of many research workers. A number of monographs and reviews have examined methods used to prepare and the properties of PBC including those in which the P and B atoms are separated by fragments.[1–7] However in these communications no reference was made to the mutual effect of heteroatom-containing groups leading to the appearance of new properties in the compounds, and in addition the relationship between the interaction of the heteroatoms and the nature of the fragments separating them has not been revealed.

To achieve these objectives the compounds presented below have been classified according to the type of the fragments which separate the phosphorus and boron atoms.

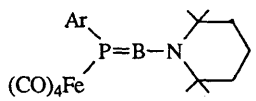
Three types of interaction between the phosphorus-boron-containing functional groups are possible, the interaction being transmitted along the bond system of the separating fragment, the trans-annular intramolecular (coordinate bond P→B), and the trans-annular intermolecular interaction (coordinate bond P→B). These interactions which are evident from the behaviour of the functional groups are determined by the coordination of the P and B atoms,

the type of fragment between them, and by the structural features of the molecule.

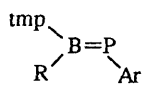
II. Compounds containing fragment P=B

The most obvious route, which can be used to obtain compounds containing the P=B fragment (boraphosphenes), is the interaction of phosphines with haloboranes or halophosphines with boron hydrides in the presence of hydrogen halide acceptors, but this route does not lead to the expected result. In this case phosphinoboranes are usually formed as dimers, trimers, or oligomers. Nevertheless the diphosphadiboretenes may be regarded as original compounds for obtaining boraphosphenes, which is confirmed by the appearance of cation radicals of the corresponding boraphosphenes in their mass spectra.[8,9]

Boraphosphenes were observed in the gas phase for the first time in the mass-spectrometer for (tmpB = PAr)$_2$ (tmp = 2,2,6-tetramethylpiperidino; Ar = 2,4,6-(*tert*-Bu)$_3$C$_6$H$_2$).[10,11] The authors[10] involved in this study suggested that they were able to identify boraphosphene as a complex with iron tetracarbonyl.



The dimer (tmp−PAr)$_2$ was obtained as a result of the interaction of tmpBCl$_2$ and ArP(SiMe$_3$)Li in Et$_2$O at 0 °C. Thermolysis of this compound at 250 °C yielded boraphosphene in the gas phase, which was confirmed by the mass spectra. It followed from *ab initio* calculations of a model molecule of boraphosphene H−B=P−H that the energy minimum for the boraphosphenes corresponds to a structure with a free unshared electron pair at the P atom and a P=B double bond (H−P=B−H) in contrast to the iminoboranes in which the N≡B triple bond is found (H−N≡B−B).[10] In an attempt to obtain boraphosphene by treatment of MeLi or the *tert*-BuLi compound (tmp)B(Cl)PHAr in Et$_2$O at 25 °C a new phosphide anion was found.

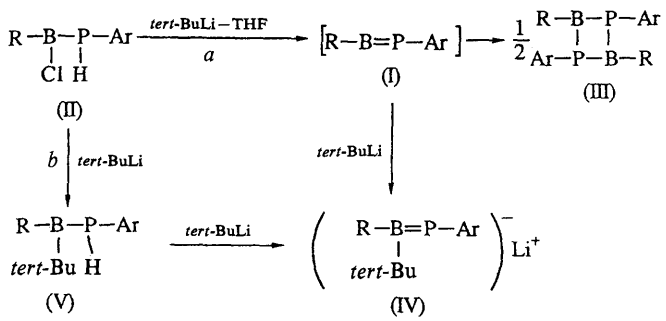


R = Me, *tert*-Bu; Ar = Ph, Mes

(Mes = 2, 4, 6-Me$_3$C$_6$H$_2$).

Thus a series of compounds containing the P=B multiple bond was synthesised. The structural parameters of double-bonded P and B atoms in complexes [Li(Et$_2$O)RPBMes$_2$] (R = Ph, C$_6$H$_{11}$, Mes) and in the ion pairs [Li(12-crown-4)$_2$][RPBMes$_2$], THF, obtained by the action of two equivalents of 12-crown-4 on these complexes have been presented for the first time.[12,13] The environment of the P and B atoms is planar, and a slight twisting is found between the planes in which the atoms lie, and there is a short bond between them (1.823 Å). The P=B bond length is significantly shorter than the known bond lengths in the borophosphines (1.96 Å). The Li ion is coordinated through the P atom. For the complexes the chemical shift in the ^{31}P NMR spectra is equal to +55−73 p.p.m. During the action of the crown ether the signal is displaced to +91−103 p.p.m.

Using chemical methods attempts were made to demonstrate the existence of compounds containing two-coordinate P and B atoms but without an ionic structure. For this the behaviour of borylphosphine in the reaction with *tert*-BuLi was studied.[14]



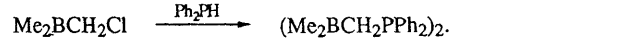
On account of the absence of compound (V) in the reaction mixture it was concluded that the reaction occurs via route *a*. Certain information is available on the reactivity of the compounds containing a double bond between the P and B atoms. Thus type (I) compounds are air-sensitive and readily react with proton donors such as water and methanol (forming in this case the type (V) structures) and also with alkyl halides and triemthylchlorosilane.[7]

Generalised data on the methods used for synthesis and on the structures of compounds containing the P=B fragment have been described.[15] In these works the synthesis and spectral data of 17 boron-phorphorus-containing compounds, relating to the synthesis of the Li(Et$_2$O)P(R)BR$_2$ type of structures, have been examined in detail. Here it is necessary to distinguish the compound with the P=B−P structure which has two different phosphorus atoms and one boron atom (δ^{31}P 32 and −117.0 p.p.m., the constant J_{P-P} is absent, J_{P-H} = 247 Hz, the P−B bond length is 1.927, and the P=B bond length is 1.810 Å). It has the shortest P=B bond.[13]

Thus of the currently known compounds containing the P=B fragment the only stable compounds are the phosphinidene borates in which the boron atom is three-coordinate. Moreover stabilisation is ensured by the bulky substituents in both heteroatoms.

III. Compounds containing the P−C−B fragment

Substances containing this fragment have long been known.[6,16] Two types of structures are possible, compounds in which the P and B atoms occur in the three-coordinate state, and substances containing a phosphonium cation and a borate anion in the molecule. Only a few representatives of the first type have been described, and furthermore they usually exist as dimers. Thus the interaction of dimethylchloromethylborane with nucleophilic reagents including phosphines has been studied.[16]



The reaction was carried out in sealed ampoules. Borylmethylenephosphine exists as the dimer in the gas phase.

Much more work has been done on the synthesis of boratomethylenephosphonium betaines. The method used to obtain such compounds is based on the reaction of phosphorus ylides with halogen boranes[17–22] or boron hydrides.[22–27]

$$R_3P{=}CHR' + BX_3 \longrightarrow R_3\overset{+}{P}{=}CHR'{-}\overset{-}{B}X_3,$$

R = Me, Et, Ph, R' = H, Alk, X = Hal;

$$Ph_3P{=}CHR' + B_2H_6 \xrightarrow[0°C]{Et_2O} Ph_3\overset{+}{P}\underset{\displaystyle R^1}{CH}\overset{-}{B}H_3;$$

$$Ph_3P{=}CH_2 + H_2RB{\leftarrow}NEt_3 \xrightarrow[-NEt_3]{C_6H_6,\ 80°C} Ph_3\overset{+}{P}CH_2\overset{-}{B}RH_2.$$

The borate alkylidene phosphonium betaines are of interest in that as a result of intramolecular regroupings they may give rise to a phosphine complex with borane in which the alkylidene fragment of the molecule is found to be at the boron atom. This regrouping is used in organic syntheses.[28–30]

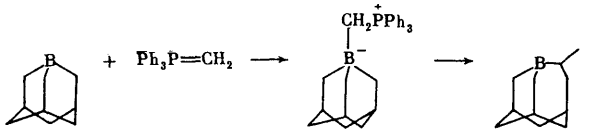
$$R^1CH{=}PPh_3 \xrightarrow{BH_3THF} R^1\underset{\displaystyle \overset{-}{B}H_3}{CH}{-}\overset{+}{P}Ph_3 \longrightarrow$$

$$\longrightarrow R^1CH_2{-}H_2B{\leftarrow}PPh_3 \xrightarrow[-R^5\overset{+}{P}Ph_3\overset{-}{I}]{R^2HC{=}CR^3R^4,\ R^5I}$$

$$\longrightarrow R^1CH_2B\left(\underset{R^2}{CH}{-}\underset{R^3}{\overset{R^4}{\overset{|}{C}}}H\right)_2 \xrightarrow[3)H_2O_2/NaOH]{1)\ Cl_2CHOMe,\ 2)LiOCEt_3}$$

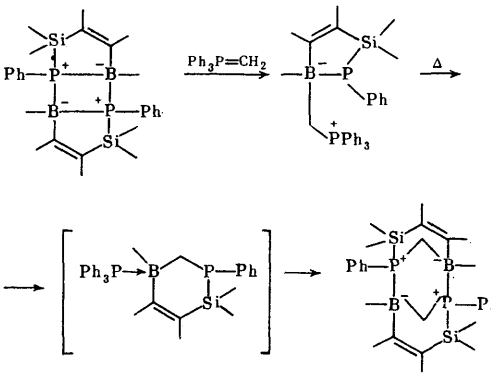
$$\longrightarrow R^1CH_2{-}\underset{HO}{C}\left(\underset{R^2}{CH}{-}\underset{R^3}{\overset{R^4}{\overset{|}{C}}}H\right)_2.$$

An analogous regrouping has been acheived for boradamantane derivatives. On interaction of triphenylphosphine ylide with boradamantane the corresponding phosphonium salt is formed which regroups with a change of the boradamantyl framework into the homodamantyl framework. After triphenylphosphine is removed, 4-alkyl-3-borohomoadamanatane separates out.[31]



The X-ray diffraction analysis of borataphosphonium betaine formed in this reaction shows that certain geometric parameters in the P atom environment differ significantly from the corresponding characteristics of the phosphonium systems and are intermediate between the values observed in them and in the ylide molecules.[32]

The regrouping of the borataalkylenephosphonium salts may involve two phosphorus atoms.[33] In this case one $\overset{+}{P}{-}C{-}\overset{-}{B}$ fragment is disrupted and a new fragment is formed.



By substitution of boron hydride by the haloboranes in reactions with phosphorus ylides it is possible to obtain borylalkylidene phosphoranes,[34] i.e. compounds containing the P=C–B fragment.

$$R'CH{=}PPh_3 \xrightarrow{R^2_2BCl} R'\underset{\displaystyle Ph_3P^+}{CH}{-}\underset{\displaystyle Cl}{\overset{-}{B}}R^2_2 \rightleftharpoons R'\underset{\displaystyle Ph_3P^+}{CH}{-}BR^2_2Cl^- \longrightarrow$$

$$\xrightarrow[-\,R'CH_2{-}\overset{+}{P}Ph_3Cl^-]{R'CH{=}PPh_3} R'\underset{\displaystyle \overset{\|}{PPh_3}}{C}{-}BR^2_2 \longleftrightarrow R'\underset{\displaystyle {}^+PPh_3}{C}{=}\overset{-}{B}R^2_2.$$

The borylalkylidene phosphoranes are of interest in regard to the synthesis of organic compounds which are not readily available. In this case the reactions may be carried out without the release of the PBS.[35]

$$Ph_3P{=}CH_2 + Cl{-}B\underset{O}{\overset{O}{\diagup\diagdown}}(CH_2)_3 \xrightarrow[-(iso\text{-}Pr)_2NH,LiCl]{(iso\text{-}Pr)_2NLi}$$

$$\longrightarrow \left[Ph_3P{=}CHB\underset{O}{\overset{O}{\diagup\diagdown}}(CH_2)_3\right] \xrightarrow{PhCH{=}O} PhC{\equiv}C{-}CPh.$$

Not isolated

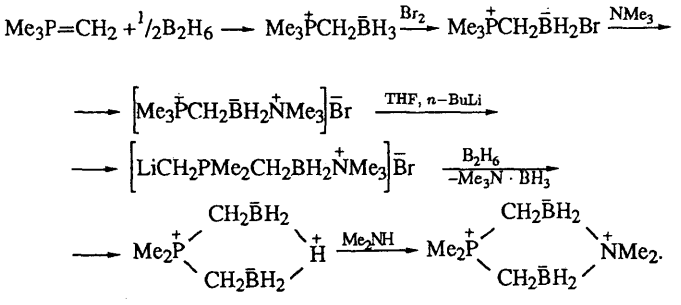
The same authors also obtained a diylideborane according to the following scheme:[36]

$$R^1{-}\underset{\displaystyle R^2}{C}{=}PPh_3 + R^3BCl_2 \xrightarrow[2)\ 25\ °C,\ 5\ h]{1)\ -78\ °C,\ Et_2O} R^1{-}\underset{\displaystyle Ph_3P^+}{\overset{R^2}{C}}{-}\overset{-}{\underset{\displaystyle Cl}{B}}{-}R^3 \xrightarrow{R^1=H}$$

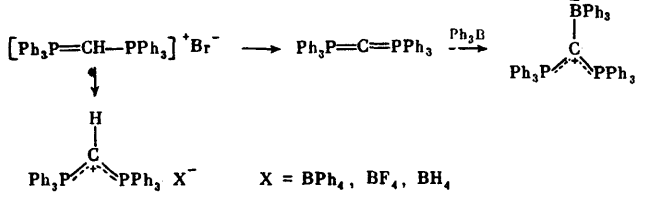
$$\longrightarrow R^2{-}\underset{\displaystyle {}^+PPh_3}{\overset{Cl}{\overset{|}{C}}}{-}\overset{-}{B}{-}R^3 \longrightarrow \begin{matrix} Ph_3P{=}C \\ \\ Ph_3P{=}C \end{matrix}\begin{matrix} R^2 \\ \diagdown \\ B{-}R^3 \\ \diagup \\ R^2 \end{matrix} + \left[Ph_3PCH_2R^2\right]^+Cl^-.$$

On account of the ability of the borylalkylidene phosphoranes to react with the proton donors and bromine it is possible to obtain deuterated and brominated phosphorus ylides, which in turn provide a means to achieve the stereoselective synthesis of deuterated and bromo-substituted vinyl compounds according to the Wittig reaction.[37]

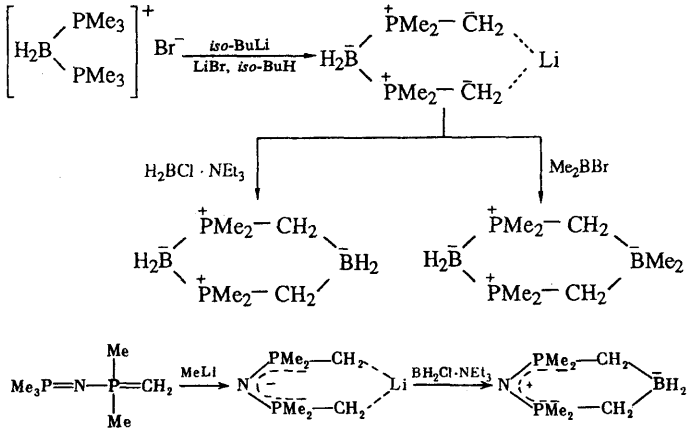
Two novel and unusual heterocycles containing P–C–B fragments were synthesised according to the following scheme:[38]



On account of the ability of the P and B atoms to change their coordination and to form ionic structures it is possible to obtain a diversity of compounds. Thus in the PBC series containing the P–C–B fragment compounds having a mesoionic structure are known.[39,40]

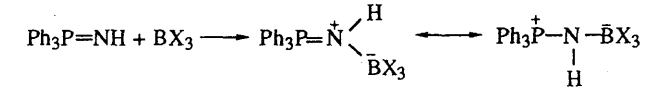


The synthesis of new heterocyclic systems containing P and B atoms in the four-coordinate state, borata-*bis*-(dimethylphosphoniamethylene) borate and nitrido-*bis*-(dimethylphosphoniamethylene)-borate has been studied.[40]

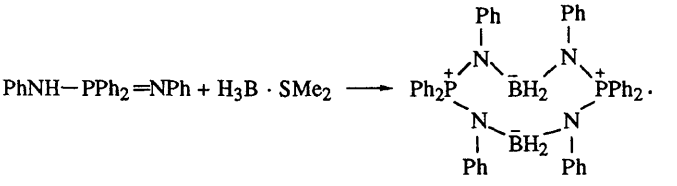


IV. Compounds containing fragment P–N–B

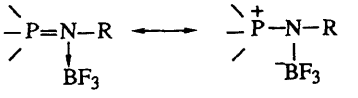
PBS containing such a fragment are most numerous among compounds in which the P and B atoms are separated by one atom. Such compounds were described a considerable time ago. Substances containing 3- or 4-coordinate P and B atoms depending on the original reagents and the synthetic route have been obtained. Thus betaines, which may be presented as two boundary mesomeric structures, were obtained from iminophosphoranes and boranes, triphenylborane or trifluoroborane.[41,42]



On interaction with a borane complex containing diethylsulphide the amino(imino)phosphoranes form a diazaboraphosphetidine dimer in which there are two atoms of four-coordinate boron and two phosphonium centres:[43]

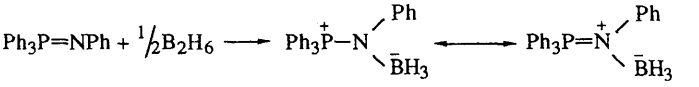


The structures of phenyl-, *p*-fluorophenyl-, and benzylamino-triphenylphosphorane complexes with boron trifluoride have been studied by i.r. and ^{31}P NMR spectroscopy.[44]



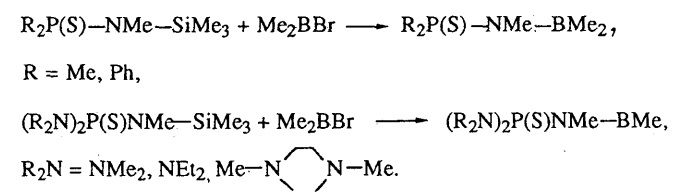
The complexes have the phosphorane structure towards which the phosphonium salt structure makes a significant contribution.

Phenyliminophosphorane forms a complex with diborane and the composition of this complex may also be presented as two resonance structures.[42]



It will be found impossible subsequently to describe the structure of the compounds containing the P–N–B fragment as a simple structure, which can be attributed to the ability of the heteroatoms of the P–N–B system to change reversibly their coordination and to the possibility of charge delocalisation at several atoms.

Borylaminophosphine sulphides are formed on substitution of the trimethylsilyl group in the silyaminophosphine sulphides during the action of bromoboranes.[45]



Use of lithium amides increases the yield to 90%.[45,46]

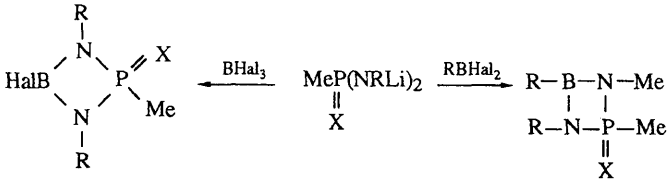
$$Me_2P(S)NRLi + Me_2BBr \longrightarrow Me_2P(S)NRBMe_2,$$

R = H, Me,

$$MeP(X)(NRLi)_2 \xrightarrow{2R_2BHal} MeP(X)(NR{-}BR_2)_2,$$

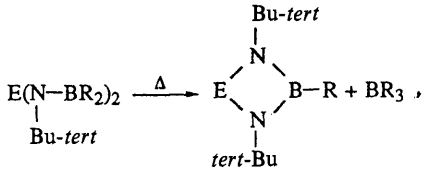
X = O, S; R = H, Me, Et.

It is noteworthy that of the boron dihalides or trihalides it has not been possible to obtain *bis*-(borylamino)methylphosphine sulphides or oxides, since cyclisation to diazaboraphosphetidines occurs.[46]



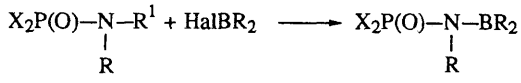
X = O, S.

Certain authors have noted that formation of borylaminophosphine sulphides does not occur on interaction of thiochlorophosphines and silylated aminoboranes.[45] In subsequent studies these authors extended the range of starting reagents,[46–50] using boron trihalides,[46,47] dichloro(silylamino)phosphine sulphide, and lithium phosphamides. Three methods used to synthesise borylaminophosphine sulphides were analysed,[48] and their degradation routes on thermolysis were studied.[47,49] It was shown that 1,3,2,4-diazaboraphosphetidines are formed, when a bulky substituent (*tert*-Bu) is present at the atom.



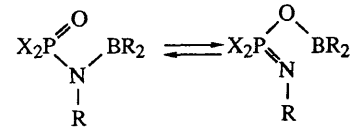
E = PPh, PMe.

A series of phosphoryl aminoboranes obtained by substitution of the hydrogen, silyl group, or lithium at the nitrogen atom in the corresponding oxides of aminophosphines or aminochlorophosphines by the boryl group has been described.[50]



X = Cl, Me, NMe_2; R = Me, Et, Cl, Br; R^1 = H, Li, $SiMe_3$.

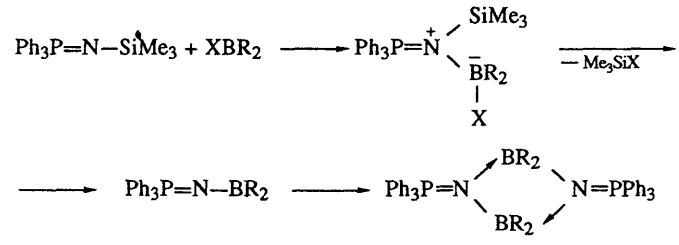
These compounds exist in solutions (X = R = NMe_2) as monomers. When X = Cl or NMe_2 and When R = Me borotrophic tautomerism was observed.



These authors later described the synthesis of borated iminophosphoranes,[51] which were previously obtained during thermal transformations of the triphenylboron complex with iminotriphenylphosphorane.[41]

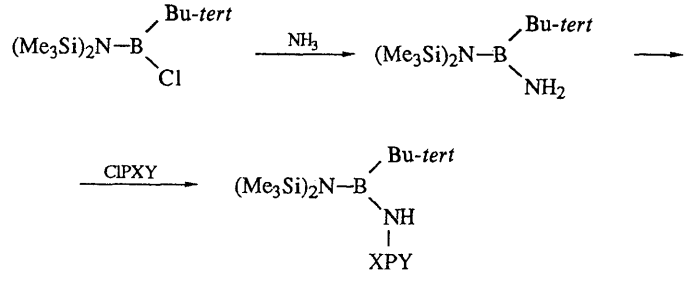
$$Ph_3P{=}\overset{+}{N}H{-}\overset{-}{B}Ph_3 \xrightarrow[-C_6H_6]{\Delta} Ph_3P{=}N{-}BPh_2.$$

Using the same method, the substitution of the silyl group at the nitrogen atom by the boryl group in the reaction with boron halides, it was possible to obtain a series of borated iminophosphoranes, which underwent association into dimers in the solutions but which were monomeric in the gas phase.



X = F, Cl, Br; R = F, Cl, Br, *n*-Bu, Ph.

Although these authors do not recommend the use of silylated aminoboranes and the acid chlorides of phosphorous-containing acids to obtain compounds containing the P–N–B fragment,[45–50] such a synthetic route has previously been described,[52] and the yield of the compounds was 40–90%.



X, Y = NMe_2, Ph, CH_2SiMe_3, $N(SiMe_3)_2$, Cl.

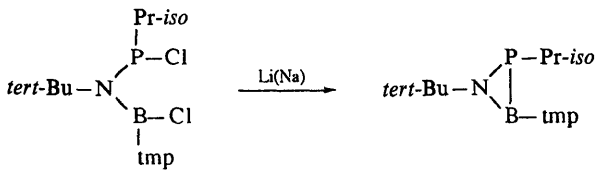
Fluoro(amino)phosphines and their sulphides with halides give phosphinoaminoboranes,[53,54] and derivatives of *tris*, *bis*, and monophosphinoaminoboranes may be obtained depending on the number of halogen atoms at the boron and the ratios of the reagents.

$$F_2PNH_2 + BF_3 \longrightarrow F_2B{-}NH{-}PF_2,$$

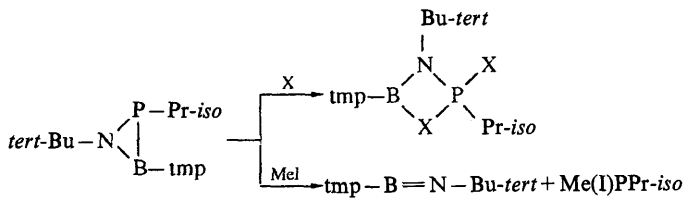
$$nF_2(S)PNH_2 + Cl_nBPh_{3-n} \longrightarrow (F_2(S)PNH)_nBPh_{3-n}$$

$n = 2, 3.$

The most characteristic property of the borylaminophosphine derivatives is their ability to form heterocyclic structures. Cyclisation may arise by the action of some reagent owing to the detachment of the halogen atoms.[55]

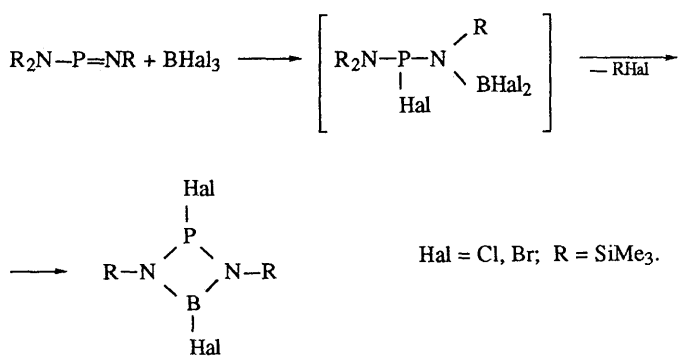


Breakage of the three-membered ring formed by the action of S(Se) or methyl iodide occurs at the P—B bond:



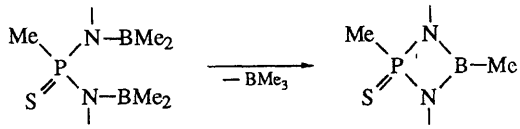
X = S, Se.

The formation of the four-membered ring, diazaboraphosphetidine, may arise as a result of intramolecular cyclisation in the N-boryl(sily)aminophosphines.[56]

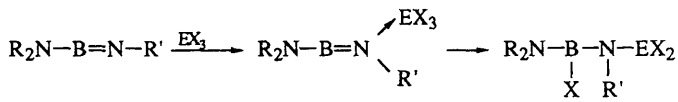


Hal = Cl, Br; R = $SiMe_3$.

Intramolecular cyclisation may appear not only because of the detachment of the halosilane, as in the above example, but also owing to the release of trialkylborane.[57,58]



Compounds containing the P—N—B fragment in the molecule have been obtained as a result of the addition of halogenphosphines to two-coordinate boron compounds, amino-iminoboranes. This is a general method and halogenarsines, halogenstibines, and also the $E(OMe)_3$ or $E(OMe_2)_3$ type of derivatives, where E = P, As, Sb, may be used in this reaction. The reaction initially involves complex formation at the imonium atom, after which hetero-aminoboranes are formed,[59,60] as a result of the migration of the substituent from the phosphorus atom (arsenic, tin) to the boron atom.

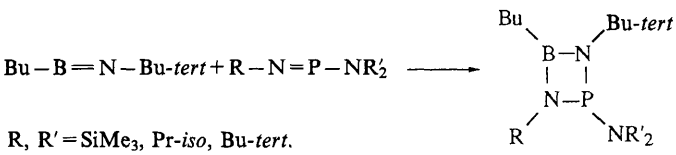


E = P, As, Sb; X = Cl, Br, F, OMe, NMe_2;

R' = Alk, Ar; R_2 =

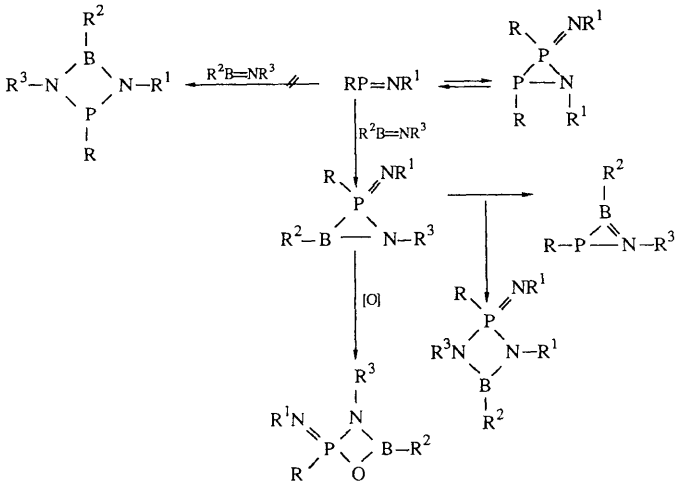


The borylaminophosphines may be synthesised by using compounds containing P and B atoms with low coordination numbers. The method is based on the cycloaddition reaction of iminoboranes and iminophosphenes. It has been shown that depending on the radicals the reaction may occur either as a [2 + 2]-cycloaddition, or as a [2 + 1]-cycloaddition. Thus the iminoborane Bu—B=N—Bu-*tert* and aminoiminophosphene react via [2 + 2]-cycloaddition giving rise to diazaboraphosphetidine.[61]

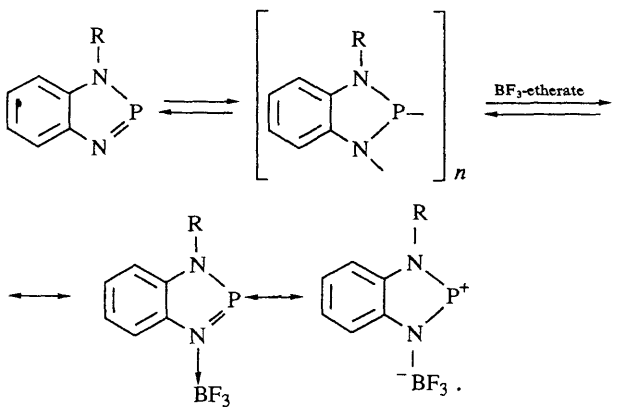


R, R' = $SiMe_3$, Pr-*iso*, Bu-*tert*.

Otherwise the reaction proceeds at the P and B atoms in the case of the alkyl substituents. The iminophosphene RP = NR· undergoes autocyclisation and an iminophosphorane is obtained. When it interacts with iminoborane, [2 + 2]-cycloaddition does not occur, while a reaction analogous to autocyclisation of iminophosphene is acheived. The azaboraphosphyrene formed readily oxidises with the disruption of the P—B bond, giving rise to oxazaboraphosphetidine or it undergoes disproportionation.[62]

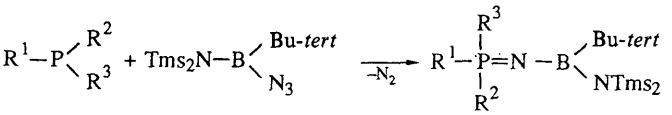


1,3-Diazaphosphols existing as oligomers or tetramers undergo monomerisation by the action of boron trifluoride etherate with the formation of the complexes[63]

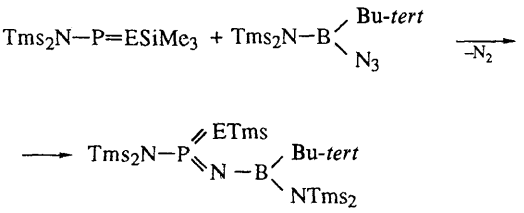


It is proposed that the complex may be described by two boundary structures.

Yet another example of the diversity of the original reagents which may be used to synthesise PBC containing the P–N–B fragment is the interaction of azidoboranes with phosphines leading to the formation of boryliminophosphoranes, and depending on the type of the original phosphorus-containing reagent a four- or three-coordinate phosphorane containing the P=N–B fragment is formed.[64]



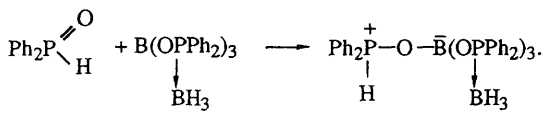
$R^1 = Ph$; $R^2 = Me, NMe_2$; $R^3 = NMe_2, NTms_2$.



E = CH, N.

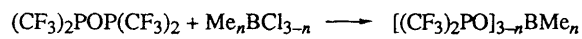
V. Compounds containing fragment P–O–B

Compounds containing fragment P–O–B have been known since 1951.[65,66] The reactions of phosphoric acid esters with various boron hydrides have been examined in earlier reviews.[67,68] In the P–O–B system the P atom preserves its ability to form complexes with boranes. Thus the compound containing four-coordinate P and B atoms in the P–O–B fragment have been obtained by the following scheme:



The structure of the betaine has been confirmed by X-ray diffraction studies.[68]

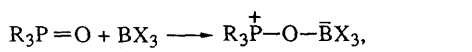
Borophosphinites containing strong electron-acceptor substituents have been obtained on disruption of the phosphinite fragment by the action of halogenboranes.[69]



$n = 0, 1, 2$.

The authors note the stability of the borphosphinites to the Arbuzov reaction type of regrouping. Trifluoromethyl groups such as strong electron acceptors increase the acidity of the boron atom as a result of which all three borophosphinites form complexes with dimethyl ether.

Compounds with the P–O–B fragments in which P and B atoms are in the four coordinate state can be obtained by the action of halogenboranes or phosphine[70] or aminophosphine oxides.[71,72]



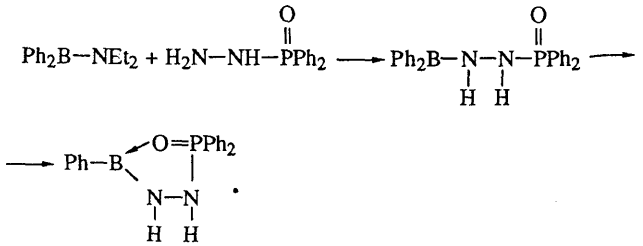
R = Alk, NMe_2; X = Cl, F.

If bromides or iodides of the boranes are used in the reaction with the aminophosphine oxides, it is possible to isolate unusual ions of compounds in which the cation contains an anionic borate fragment.[71]

$$(Me_2N)_3P{=}O + BX_3 \longrightarrow [(Me_2N)_3P{-}O{-}BX_2{-}O{-}P(NMe_2)_3]^+X^-,$$

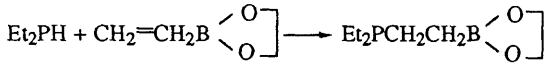
$$(Me_2N)_3P{=}O + R_3NBHI_2 \longrightarrow [((Me_2N)_3P{-}O{-})_2BH{-}NR_3]^{2+}2I^-.$$

Reference should be made to yet another study concerning the formation of aminoboranes but describing the synthesis of a compound with a phosphorus-containing fragment.[73] The spectral data indicated that the boron atom in this compound is in the following state:



VI. Compounds containing fragments P–C–C–B and P–C=C–B

Only a few compounds of this type have been described. Phosphorylation of vinyl derivatives of boron is the most obvious route for the synthesis of these compounds.[74,75]

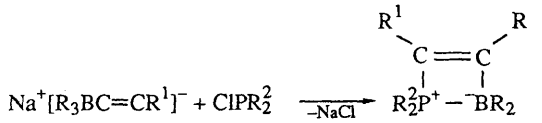


This is a general type of reaction in which silicon, tin, and sulphur hydrides may be added to the ethylene fragment.[74]

There are many reports in the literature describing the synthesis and study of the properties of compounds containing the P–C=C–B fragment. 1,2-Heteroethenes containing P, As, Si, Sn, B, O, N and Al atoms in different combinations are known. Those compounds in which heteroatoms, for example phosphorus and boron atoms, possess different electronic characteristics are of especial interest. Such a combination leads to the appearance of new properties in the compounds.

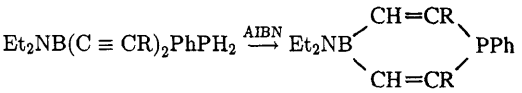
The first member of the borylphosphinoethenes has been described.[76] The principal method used to synthesise compounds containing the P–C=C–B fragment with three-coordinate P and B atoms is the interaction of halogenphosphines or phosphines with alkinyl borates or alkinyl boranes respectively.[76–79] Thus in the reaction of sodium trialkyl(alkinyl)borates with diorganylchlorophosphines, substituted 1-borata-4-phosphoniacyclobutenes-2 were isolated.[76,79]

A four-membered cyclic structure was assigned to these compounds on the basis of ^{11}B- and ^1H-NMR and mass-spectroscopic data and from a cryoscopic determination of the molecular mass and structure of the hydrolysis products. Their structure was subsequently confirmed by an X-ray diffraction analysis,[80] by determination of the dipole moment, and by studying the chemical properties (see below)



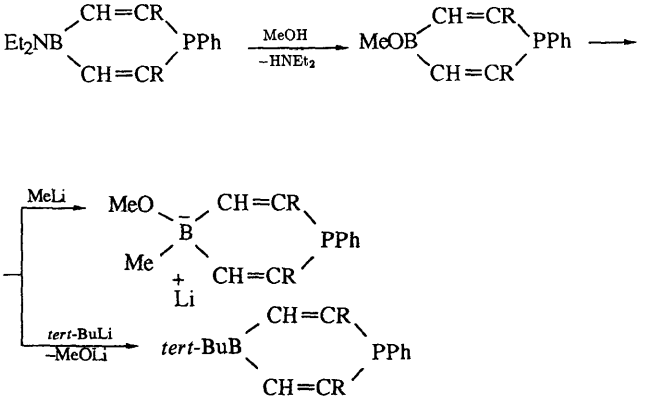
R, R^1, R^2 = Me, Et, Bu, *cyclo*-Hex, Me_3Si.

Addition of phenylphosphine to dialkinyl(diethylamino)boranes is a radical process and leads to the formation of 1,4-boraphosphacyclohexa-2,5-dienes.[77,78]



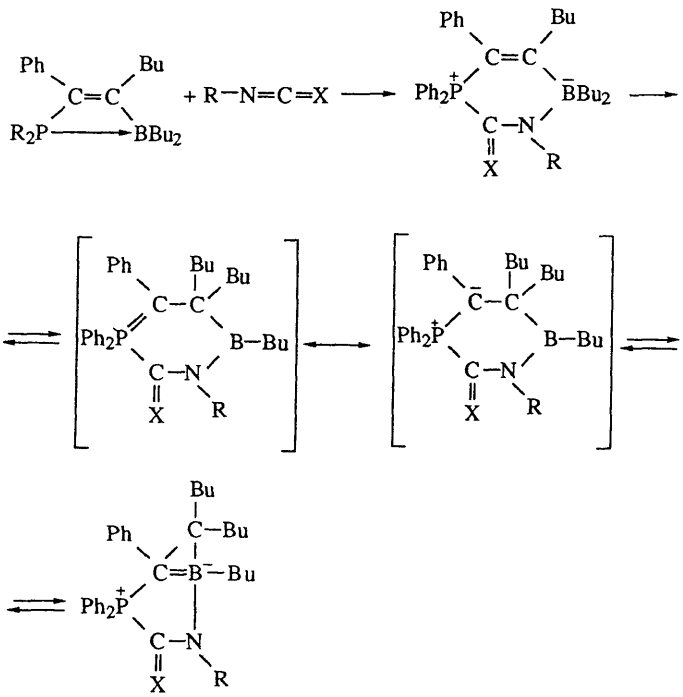
R = H, Me.

These compounds are heat stable but sensitive to oxidation. The reactivity of boron in these compounds is somewhat reduced as a consequence of the coupling of its vacant orbital with that of the unshared electron pair of the N atom, which leads to the absence of intermolecular coordination, although they undergo methanolysis. The resultant methoxy-derivative interacts with alkyllithium compounds, giving rise to borates or B-alkylated derivatives depending on their nature.



The 1-bora-4-phosphacyclohexadienes-2,5 are typically reactive towards tertiary phosphines and together with NMR spectroscopy data there is evidence that the unshared electron pair of the P atom in these rings is not delocalised and the P and B atoms do not have a significant influence on each other. In this regard the heterocycles differ from cyclic compounds containing the P–C–O–B fragment which will be examined below.

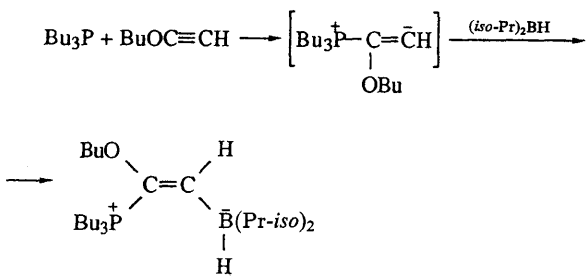
In recent years the authors of the present review have carried out systematic studies of the properties of the 1,2-borylphosphinoethenes,[81–89] and the results obtained have been grouped into one of the sections of a previous review.[4] It has recently been shown that reactions with heterocumulenes are characteristic of the borylphosphinoethenes,[90–93] and these reactions proceed as [4 + 2]-cycloaddition and lead to the formation of 6-oxo(thioxo, imino)-1-aza-5-phosphonia-2-boratacyclohexa-3-enes. These monocyclic betaines undergo anionotropic regrouping leading to the formation of bicyclic betaines, 2-aza-4-phosphonia-1-boratabicyclo[3.1.0]-hexanes. One should particularly note that this is a reversible regrouping and that the reverse process involves the migration of the butyl anion from the sp^3-hybrid C atom to the sp^3-hybrid B atom.



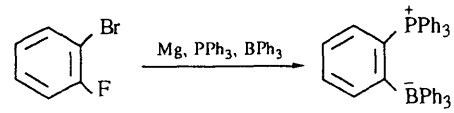
R = Ph; X = NPh, O, S; R = C_6H_{11}, X = NC_6H_{11}.

The structure of the compounds was established by X-ray diffraction studies. The equilibrium processes were studied by NMR and i.r. spectroscopy.

In the studies presented above examples have been described of cyclic betaines containing the P–C=C–B fragment. Such a fragment occurs also in the acyclic molecule 1-borato-2-butoxy-2-phosphonium ethene.[94]

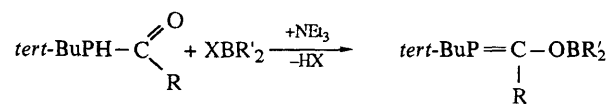


A betaine in which the phosphonium cation and the borate ion are separated by a phenylene fragment was obtained as a secondary product at low yield on interaction of *o*-bromofluorobenzene with Mg, Ph_3P and BPh_3.[95,96]

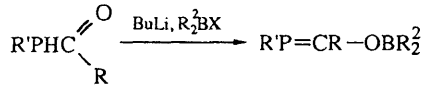


VII. Compounds containing fragment P=C–O–B

This type of compound may be obtained from acylphosphites[97] or from their lithium derivatives[98–100] on interaction with halogenboranes:



X = Cl, Br, R = Alk, R' = Alk, NMe_2;



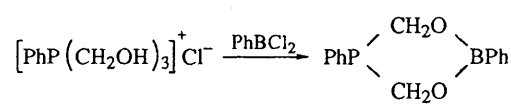
R', R = Alk, Ar; R^2 = Alk, $NAlk_2$.

Germanium, tin and phosphorus halides were used in the reactions, although in these cases not methylenephosphines but hetero-substituted acylphosphines are formed.

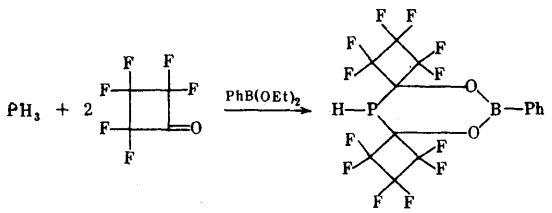
Boryloxymethylenephosphines, i.e. compounds containing a two-coordinate phosphorus atom, constitute an interesting class of hetero-organic derivatives possessing considerable synthetic potential.

VIII. Compounds containing fragment P–C–O–B

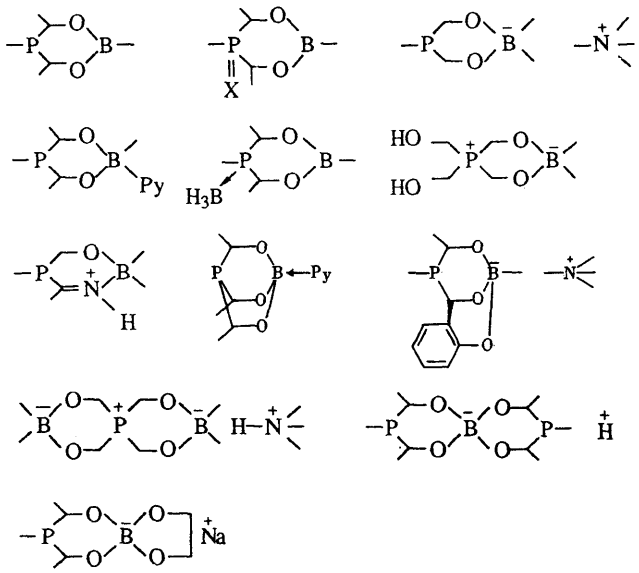
A study of the properties of compounds containing P and B atoms separated by a particular fragment shows that these properties are often determined by the presence of an interaction of heteroatoms, and the nature of the interaction may differ. For chemical compounds containing the P–C–O–B fragment the interaction of the P and B atoms plays a decisive role and is reflected in both the reactivity and the three-dimensional structure of the compounds. The synthesis and properties of the boryloxyalkylphosphines and their analogues are described in a number of articles and reviews.[3,5,90,101] Most of the boroxyalkylphosphines and their derivatives are heterocyclic compounds. The first member in this series was obtained in 1964.[102]



A report was then published which described the synthesis of 1,3,2,5-dioxaboraphosphorinane with hexafluorocyclobutyl substituents in the heterocycle.[103]

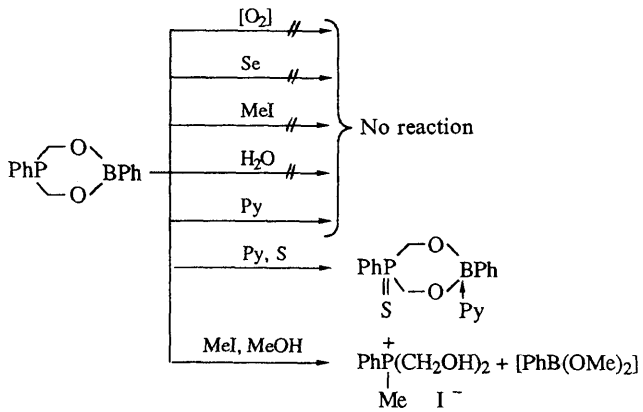


Starting from 1979 a series of studies by B A Arbuzov, O A Erastov, and G N Nikonov was published on the synthesis and properties of boroxyalkyl derivatives of phosphorus. Various heterocyclic compounds containing the P–C–O–B fragment in which the P and B atoms occur in different valence states were synthesised.

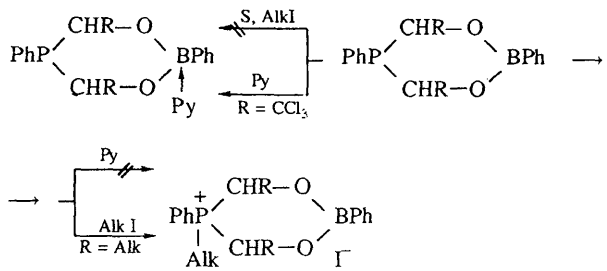


Here we shall emphasise only the properties which illustrate the interaction of the heteroatoms in the P–C–O–B system. They are most clearly apparent in the three-coordinate P and B atoms. Thus the unusually high content of conformer with axial orientation of Ph at the P atom in the conformational equilibrium of 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinone (95%) can be attributed to the n-σ^*-interaction of the unshared electron pair at the P atom and the vacant orbital of the C–O bond. The interaction resulted from the expression of the acceptor properties of the B atom. This type of interaction by the heteroatoms explains satisfactorily the change in content of the stereoisomers or conformers on transition from dioxaboraphosphorinanes to their oxides, sulphides and selenides, which is contrary to the change in ratios of the stereoisomers in the series of dioxaphosphorinanes and their oxides, sulphides and selenides.[101]

The mutual effect of the heteroatoms is even more obviously expressed on examination of the chemical properties of 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane.[3,101] The presence of three-coordination P and B atoms should confer upon this compound properties typical of tertiary phosphines and phenylboric acid esters. However this compound shows anomalous reactivity. Despite the presence of the phosphine fragment it is not oxidised by atmospheric oxygen, it slowly adds sulphur, forms an unstable selenide, and does not interact with methyl iodide. The reactivity of the oxyboryl fragment also fell sharply, which is reflected in the resistance to hydrolysis even by aqueous methanol and in the absence of complex formation with pyridine. However if it operates simultaneously at two reaction centres (the P and B atoms), the reaction proceeds normally, giving rise to the corresponding derivatives with the same reagents.

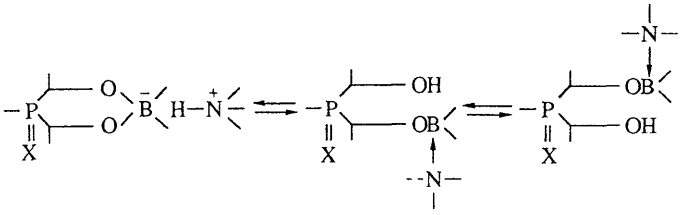


This all indicates the existence of an intramolecular interaction of the heteroatoms (an intermolecular interaction is discounted on the basis of data obtained by using physicochemical techniques). This interaction may be disrupted by varying the nature of the substituent in positions 4 and 6 of the heterocycle. Thus the presence of donor (alkyl) substituents in the 4,6-positions of the 1,3,2,5-dioxaboraphosphinane leads to alkylation by alkyl halides in the absence of methanol. On the contrary 4,6-*bis*-(trichloromethyl)-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane is not alkylated at the P atom and does not add sulphur, but forms a stable complex with pyridine, despite the three-coordinate P atom.



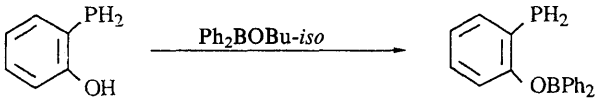
The chemical properties of the boroxialkyl derivatives of phosphorus have been described in a number of reports.[3,101] Reactions with electrophilic reagents leading to an increase in the coordination number of the P atom, the reaction with dipolar reagents (aldehydes) leading to betaines, and reactions with nucleophilic reagents (amines) in which the P–C–O–B fragment is preserved, or disrupted with the formation of aminomethyl derivatives of phosphines, ion-exchange reactions, and thermal transformations, etc. were studied. One of the characteristic features

of the boroxyl derivatives of phosphorus possessing a mobile hydrogen atom is high tautomeric lability, and the tautomeric transformations are caused by the transfer of two particles, a hydrogen atom and a nitrogen atom with the involvement of oxygen and boron atoms, and migration of the boryl grouping also occurs when degenerated tautomerism is taken into account.[3,101]

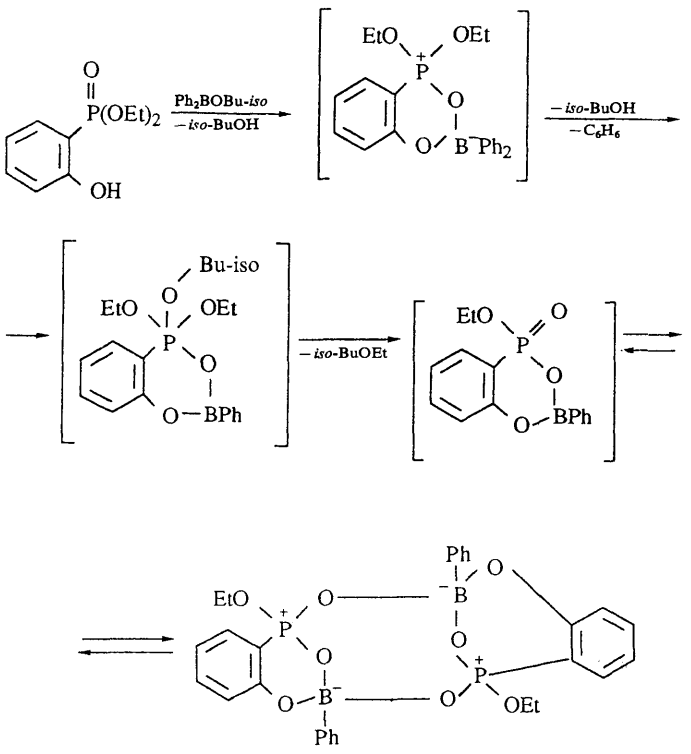


Polymers have been described for this type of tautomerism, ion-complex tautomerism: bicyclo-cyclic ion-complex tautomerism, ion–ion ring-chain, and other.[3,101]

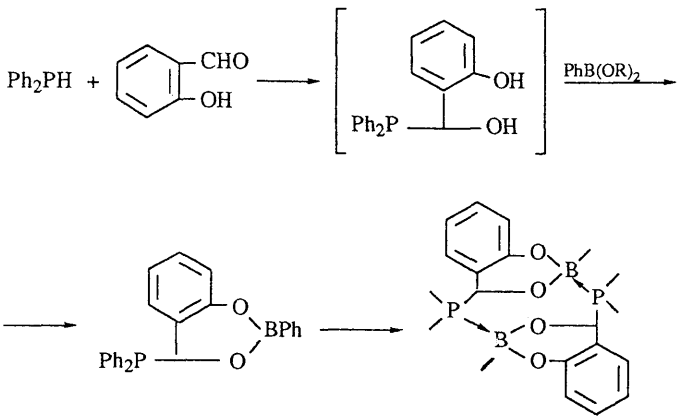
It has been previously shown that borating of *o*-oxyphenylphosphine leads to the formation of *o*-diphenylboryloxyphenylene phosphine and takes place under severe conditions.



The reaction with *o*-oxophenylphosphonate also occurs at high temperatures but in this case the dimer of the corresponding 1,3,2,4-dioxaborophosphinone is formed, which has been shown by X-ray diffraction. The reaction probably takes place with the involvement of isobutyl alcohol formed in the first stage.



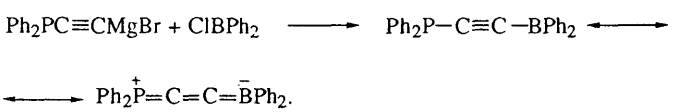
The synthesis of a compound in which the phosphine fragment is the exocyclic substituent relative to the oxyboryl ring has been described. The nature of the interaction of the heteroatoms changed despite the fact that the P–C–O–B fragment was preserved. By combining the data obtained (chemical behaviour, spectral characteristics, RMM, etc.) it was concluded that the P and B atoms undergo intermolecular interaction.[105]



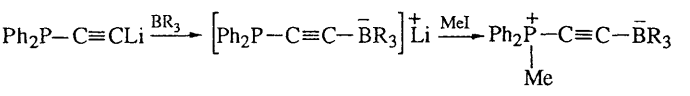
The specific characteristics and the diversity of properties of the boroxyalkyl derivatives of phosphorus can be attribtued to the presence of heteroatoms with opposite electronic behaviour (donor and acceptor) and to the ability of the atoms to change reversibly their coordination and to the presence of an interaction of the heteroatoms transferring in the P–C–O–B system. These features may form the basis of the construction of new structures containing fragments with interacting groups or type A–X–Y–B heteroatoms where A is the donor, B is the acceptor, and X–Y is the fragment with the ability to conduct the interaction of the heteroatoms (C–O, C–N, C–P, C=C, etc.).

IX. Compounds containing fragment P–C≡C–B

Among a large number of acetylene phosphines the synthesis of 1,2-borylphosphinoacetylene with a yield of 64% is presented. Taking into account the ability of the P and B atoms to form betaine structures, the end product structure should be presented as a canonical equation:[106]

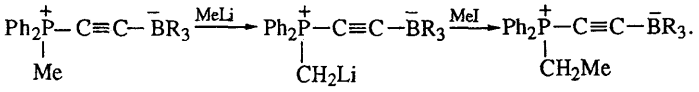


Diphenylphosphinoacetylene may serve as the original compound for the synthesis of phosphinoboratoacetylene[107]



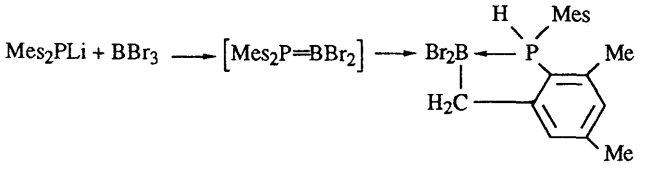
R = CH_2Ph, Ph.

Sequential treatment of this betaine with lithium using MeLi and treatment with MeI leads to the extension of the hydrocarbon chain at the phosphorus atom:

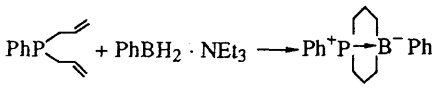


X. Compounds containing fragment P—(C)$_n$—B and others

There are several studies describing P,B-containing compounds in which the P and B atoms are separated by a chain of three carbon atoms and in which these atoms are even more remote from each other. In this case the nature of the interaction of the P and B atoms is different and is manifested as a transannular interaction of the donor and acceptor centres, which leads to the formation of a P→B intramolecular bond. One report is noteworthy in this regard.[108] An attempt was made to obtain dimesitylphosphenylborane from lithium dimesitylphosphide and tribromoborane. However instead a new heterocycle was isolated. The reaction is accompanied by a 1,3-migration of the hydride ion.

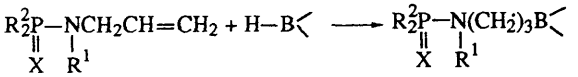


The formation of a strong intramolecular P→B cordinated bond during the hydroboration of dialkylphenylphosphine by triethylaminephenylborane leads to the formation of the bicyclic product, 1-borata-5-phosphoniabicyclo[3.3.0]octane.[109]



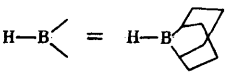
The presence of a coordinate bond in this compound is confirmed by NMR spectra and also by its resistance to oxidation and hydrolysis.

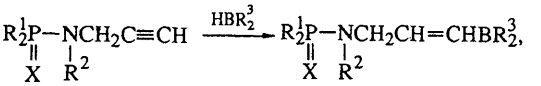
A series of studies has been described of the hydroborination of allyl and propionyl derivatives of N-phosphorylated amines.[110–113]





R^1, R^2 = OAlk, Alk, Ar, X = O, S,

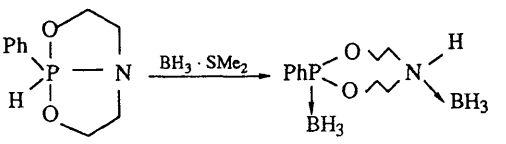




R^1 = OEt, NMe_2; R^2 = Me, CH_2Ph; R^3 = C_5H_{11}, C_6H_{11}, C_8H_{14}; X = O,S.

The hydroborination reactions are regioselective and stereoselective. Compounds in which the boron atom is situated in the δ-position relative to the P atom are formed with a yield of 90–100%. No data are presented on the interaction of the phosphoryl and boryl groups.

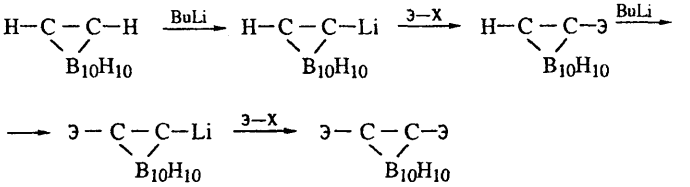
The following is yet another example of a compound containing a δ-atom of boron.[114]



There are also groups of compounds with a different combination of P and B atoms. There are the phosphaborohydrides and coordination compounds in which ligands contain P and B atoms separated by a particular fragment. Compounds of different structure are grouped into one section because the heteroatoms in these compounds are involved in the formation of coordinated or multiple-centre bonds. In line with the general layout of this review only compounds with a fragment between the P and B atoms will be examined.

XI. Phosphaborohydrides

These types of compounds have been known for a long time and have been described in the monograph by B M Mikhailov.[6] However, as before, they continue to attract the attention of research workers. This is because the carborane framework structure imposes certain steric requirements and possesses strong acceptor properties, while on account of the high mobility of the hydrogen atoms at the carbon atoms or in the framework structure different heteroatomic fragments may be introduced via the lithium derivatives.[115,116]



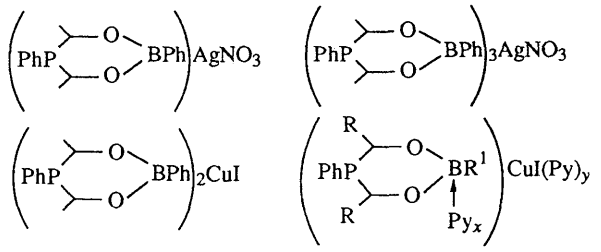
Э = H, As, Si, P.

The opportunity of introducing alkyl or vinyl groups to the C atoms in the *o*-carboranes increases the number of possible compounds. The compounds formed may contain one or two phospha groups separated by one or several carbon atoms from the carborane fragment.

XII. Coordination compounds

On account of the presence of an acceptor or an *o*-carborane group as a functional group in the organophosphorus compound, especially when the P and B atoms interact, these compounds are found to be an interesting type of ligand, and in complexes of these compounds new unusual interactions and bonds may be realised. On the whole all types of PBC compounds may be regarded as potential ligands. The coordination derivatives of PBC may be synthesised by different methods. This is the use of PBC as ligands, the introduction of the phospha group into the coordination compound already containing a boryl fragment in the ligand, or introduction of the boryl group into the complex with a phosphorus-containing ligand.

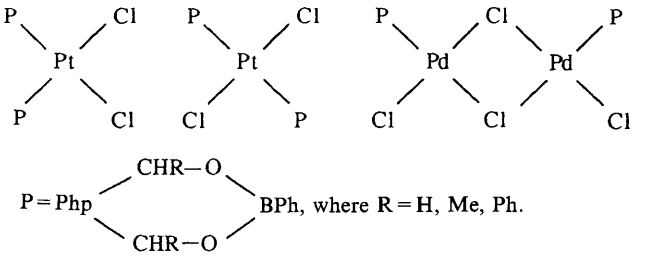
Thus the 1,3,2,5-dioxaboraphosphorinanes have been used as ligands during the synthesis of compounds coordinated to metal salts.[117–119] It was found that Cu(I) and Ag(I) are coordinated at the oxyboryl fragment and depending on the ratio of the reagents complexes of different composition may be obtained.



R = Me, R^1 = Ph, $x = 0, y = 1$
R = Me, R^1 = CBu_3, $x = 0, y = 1$
R = Ph, R^1 = Ph, $x = 1, y = 2$
R = Ph, R^1 = CBu_3, $x = 0, y = 1$

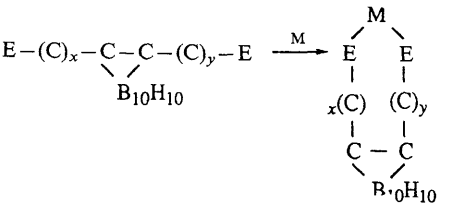
Attempts have been made to determine the three-dimensional structure of the heterocyclic ligands in solutions of the complexes and to correlate the composition and structure of the complexes with the nature of the substituents in the ring.[118]

1,3,2,5-Dioxaboraphosphorinones form complexes with platinum(II) chloride (composition 2:1). Conclusions on the structure of complexes in the solutions have been made from ^{1}H- and ^{31}P-NMR and i.r. spectra in the longwave range and they have been compared with data on the free ligands. The configuration of the central ion differs depending on the substituent in the 4,6-position of the heterocycle.[119]



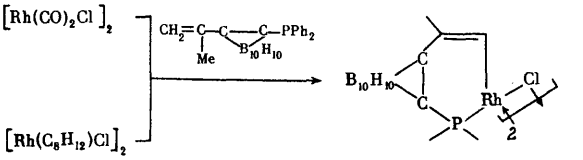
These heterocycles form 1:1 complexes with palladium(II) chloride even in excess of ligand.

Hetero-substituted carboranes are very interesting types of ligands or chelates.[120] The phosphorylated carboranes and their analogues are systematically used as ligands, and phosphorus-containing or such functional groups as for example isopropenyl may be the donor centres involved in the formation of coordination bonds.[115,116,121]



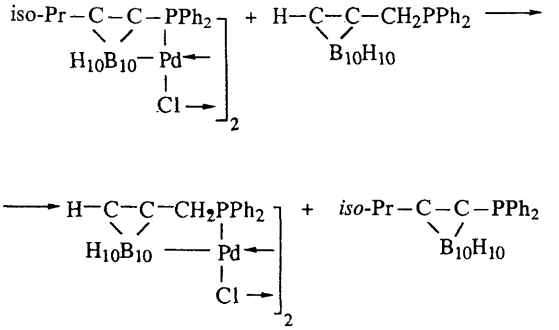
(C) = CH_2, CH_2CH_2, CH=CH etc.
|
Me

x, *y* = 0, 1, 2; E = PR_2, AsR_2, SH; M = Metal

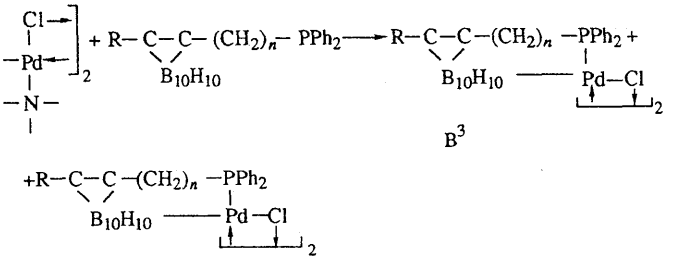


C_8H_{12} = 1.5-cylooctadiene

The metal complexes of phosphorylated carboranes possess the ability to exchange ligands with the involvement of only P-donor molecules. In this case a boron–metal bond is disrupted and formed.[122]



This transition may be attributed to the high stability of the 5-membered ring in comparison with the 4-membered metallo ring. On metallisation of the phorphorylated *o*-carboranes two isomeric products may be formed owing to the formation of the B–Pd bond in a different position of the *o*-carborane.[123]

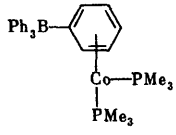


By using coordination compounds of phosphorus and boron for the synthesis of PBS it is possible to obtain most unusual and unexpected structures in which these atoms are linked by bonds of atypical valency or via metal atoms. For example a unique structure has been obtained on interaction of the triethylphosphine complex of cobalt with sodium tetraphenylborate.[124]

$$Co(PMe_3)_3Br + NaBPh_4 \longrightarrow Co(PMe_3)_4BPh_4 +$$

$$+ \quad Co(PMe_3)_2BPh_4 + NaBr.$$

An X-ray diffraction study of the cobalt complex with two phosphine ligands showed the unusual structure of this compound.



Methods have been systematically developed to obtain and study the properties of the $P_x-M-(B_yH_z)$ type of metallo boron hydride complexes where P is the phosphorus-containing ligand, and M = Pt, Os, and Rh, and (B_yH_z) are the boron hydrides, B_6H_9, B_8H_{11}, $B_{10}H_{11}$, $B_{16}H_{15}$ and B_9H_{10}, etc.[125–131] These coordination compounds are formed on interaction of the metal complexes with the anions of the corresponding boron hydrides, for example:[129]

$$[RuCl_2(PPh_3)_3] + [B_{10}H_{10}]^{2-} + 2EtOH \longrightarrow$$

$$\rightarrow [(PPh_3)_2RuB_{10}H_8(EtOH)_2] + PPh_3 + 2Cl^- + 2H_2.$$

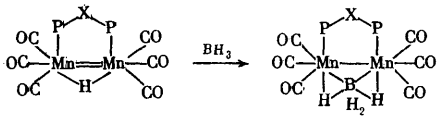
In this type of compound the P atom is linked with the borohydride fragment via a metal atom.

Complexes with a more complicated structure may be obtained in which the substituents are bound in the phosphorus-containing ligand with the borohydride fragment.[129–131]

$$[OsCl_2(PPh_3)_3] + [B_{10}H_{10}]^{2-} + 2EtOH \longrightarrow$$

$$\rightarrow [(PPh_3)(Ph_2PC_6H_4)OsB_{10}H_7(OEt)_2].$$

The interaction of unsaturated manganese dihydrides containing phosphine ligands with B, Si and Sn hydrides has been studied.[132] When a borane was used, a complex in which the hydride anion enters the inner coordination sphere was obtained.

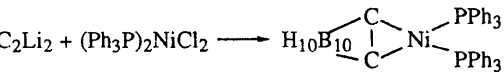


P—X—P = $Ph_2PCH_2PPh_2$, $(EtO)_2PCH_2P(OEt)_2$

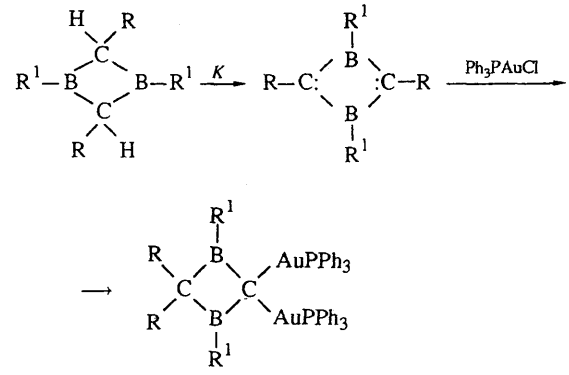
Closo-complexes of the carboranes have been obtained by the interaction of rhodium triphenylphosphine complexes with C-substituted nido-carborane-anions ($C_2B_9H_{12}$).[133,134]

The dilithium derivative of *o*-carborane reacts with the *bis*-(triphenylphosphine)complex of nickel dichloride, expressing the properties of a chelate ligand.[135]

$$o\text{-}B_{10}H_{10}C_2Li_2 + (Ph_3P)_2NiCl_2 \longrightarrow$$

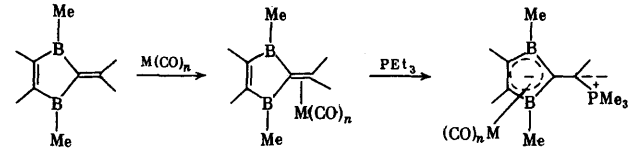


On treatment with metallic potassium 1,2-dihydro-1,3-diboretane gives rise to a dianion, which forms a binuclear complex with the gold triphenylphosphinechloride complex. During complex formation migration of the *tert*-butyl or silyl group in the dianion occurs.[136]



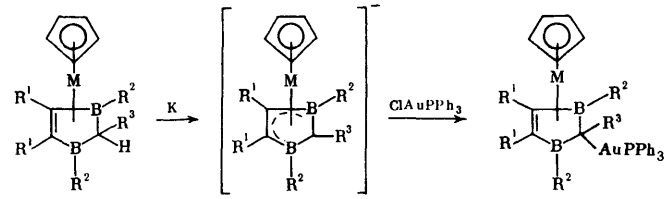
$R^1 = NMe_2$, $N(Pr\text{-}iso)_2$; R = *tert*-Bu, $SiMe_3$.

Coordination compounds containing the phospha- and bora-groups may be obtained also by phosphorylation of organoboron compound complexes with metals.[137,138]



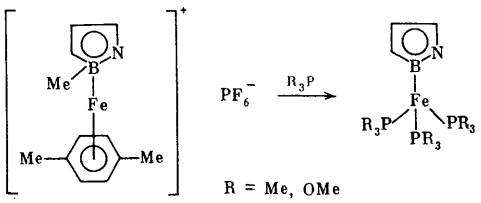
M = Cr, Mo

One example may be given in which on interaction of two complexes, one containing the phosphine ligand and the other with a boron-containing ligand, a third binuclear complex is formed which contains P and B atoms and two different metals.[138]



M = Co, $R^1 = R^2 = Me$, $R^3 = H$; M = Rh, $R^1 = R^2 = Et$, $R^3 = Me$.

The exchange of ligands in the following complex is yet another method used to obtain coordination compounds of PBC.[139]



Most of the above-mentioned coordination compounds containing phosphorylated carborane structures in the ligand have been obtained essentially by an exchange reaction of the ligands at the central ion.

Thus the information presented shows that a large number of quite accessible methods are available to obtain phosphorus-boron-containing compounds leading to the formation of the most diverse cyclic and acyclic structures in which the heteroatoms are bound in different ways and with varied properties which are often dependent on the interaction of the phosphorus-boron-containing functional groups. The nature of these interactions is dependent mainly on the coordination of the heteroatoms and the nature of the fragment, which separates the heteroatoms. When this fragment is a hydrocarbon, for compounds with three-coordinate phosphorus and boron atoms stabilising donor-acceptor interactions through space are most often found, i.e. intermolecular when the heteroatoms are in an α-arrangement and intramolecular when they are in the β- or γ-position, provided that this is not hindered by the rigidity of the binding fragment or the strong *p*-donor substituents at the boron atom. Such interactions reduce the activity of the unshared electron pair of the phosphorus and the vacant orbital of boron, but nevertheless these compounds have a tendency to form very stable betaines. The oxygen atom separating the phosphorus and boron atoms does not hinder the formation of betaine structures, whereas as a result of the partial π-binding with the boron atom the nitrogen atom hinders the donor-acceptor interactions with phosphorus. Even for the betaines the structures with a positive charge on the nitrogen atom and not on the phosphorus atom make a large contribution. Strong donor-acceptor interactions transferring through the system of bonds and stabilising the compounds are also found for the cyclic compounds containing the C–O polar fragment between the heteroatoms. The mutual effect of phosphorus- and boron-containing groups not only changes their reactivity in normal reactions of organophosphorus compounds or organoboron compounds but also in a number of cases leads to a change in their direction. Furthermore processes may occur in which both heteroatoms are involved and in which coordination compounds with unusual bonds are formed, etc. This suggests that this class of compounds has specific characteristics and may be regarded as an independent section of hetero-organic chemistry.

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