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Carborane-containing organophosphorus compounds. Synthesis and properties

N N Godovikov, V P Balema, E G Rys

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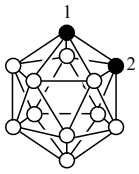
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Abstract. Published data on the synthesis, chemical properties and practical use of carborane-containing organophosphorus compounds are surveyed. Their properties are compared with those of similar organophosphorus derivatives devoid of carboranyl groups. The bibliography includes 89 references.

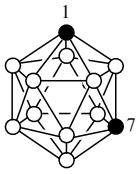
I. Introduction

Carborane-containing organophosphorus derivatives constitute an interesting class of compounds that has been insufficiently investigated.

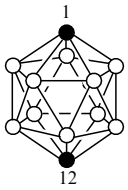
Although a large number of studies devoted to these substances have been published, these publications are not systematic, and this does not make it possible to estimate adequately the influence of carboranyl and phosphorus-containing fragments on the reactivity of these derivatives. In this review, we generalise and describe systematically the published data dealing with carborane-containing organophosphorus derivatives; our consideration has been restricted to dicarba-*closo*-dodecaborane derivatives. The structures and the numbering of atoms in 1,2-, 1,7- and 1,12-dicarba-*closo*-dodecaboranes are presented below.



1,2-Dicarba-*closo*-dodecaborane (*o*-carborane)

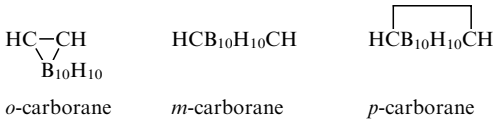


1,7-Dicarba-*closo*-dodecaborane (*m*-carborane)



1,12-Dicarba-*closo*-dodecaborane (*p*-carborane)

These isomers are usually represented using the following brief symbols:



o-carborane *m*-carborane *p*-carborane

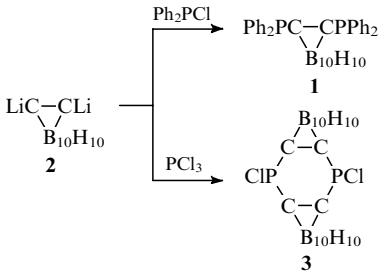
We consider methods for the synthesis of carborane-containing derivatives of trivalent and pentavalent phosphorus and discuss their chemical properties and their potential applications.

II. Carborane-containing derivatives of trivalent phosphorus

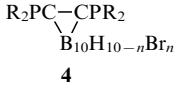
1. Carboranylphosphines

a. Synthesis of carboranylphosphines

The first representative of carboranylphosphines, namely, bis(diphenylphosphino)-*o*-carborane **1** was synthesised in 1963 by the reaction of dilithio-*o*-carborane **2** with chlorodiphenylphosphine.[1–3] Subsequently, reactions of lithiocarboranes with trivalent phosphorus acid chlorides have been widely used to prepare various carborane-containing organophosphorus compounds including those with cyclic structures like compound **3**.[3]



Reactions of the compound **2** and dilithio-derivatives of *B*-bromo-*o*-carborane with chlorodiphenylphosphine[4] and chlorodiethylphosphine[5] gave rise to the corresponding bis-phosphines **4**:



4

R = Et, Ph; n = 0, 1.

Monolithiocarboranes **5** substituted at the 1-position have also been introduced into the reactions with chlorophosphines.[5–7]

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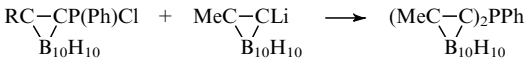
Received 30 October 1996
Uspekhi Khimii **66** (12) 1125 – 1140 (1997); translated by Z P Bobkova



5a–e **6a–e**

R = H (**a**), Me (**b**), Ph (**c**), HC=CH$_2$ (**d**), MeC=CH$_2$ (**e**);
R′ = Me, Et, Ph.

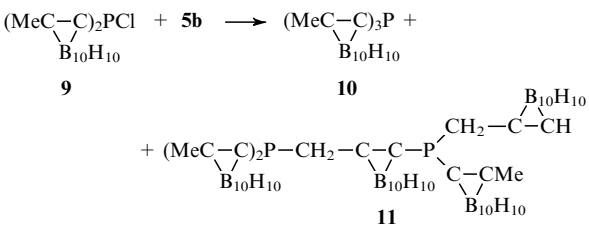
Bis- and tris-carboranylphosphines have been prepared in a similar way; for this purpose, the lithiocarborane **5b** was made to react with carboranylchlorophosphines. Chloro(2-methyl-*o*-carboranyl)phenylphosphine **7** (R = Me) was converted in this way into bis(2-methyl-*o*-carboranyl)phenylphosphine **8**.[7]



7 **5b** **8**

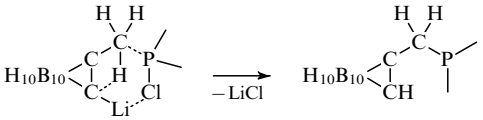
R = Me, Ph.

At the same time, chloro(2-phenyl-*o*-carboranyl)phenylphosphine **7** (R = Ph) does not enter into this reaction. This was attributed [7] to both steric and electronic influences of the substituent at the second carbon atom of the carborane nucleus. It is of interest that the reaction of chlorobis(2-methyl-*o*-carboranyl)-phosphine **9** with the lithio-derivative **5b**, in addition to tris(2-methyl-*o*-carboranyl)phosphine **10**, has given a complex pentacarboranyl compound **11**, the structure of which has been confirmed by X-ray diffraction analysis.[8]

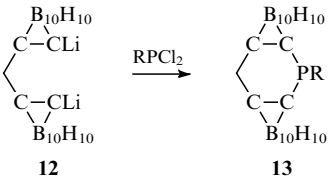


9 **10** **11**

The formation of the abnormal reaction product **11** was explained [8] by the occurrence of a number of processes including either metallation of a methyl group in chlorobis(methyl-*o*-carboranyl)phosphine **9** and disproportionation of the resulting carboranylmethyllithium or transfer of the reaction site in the lithio-derivative **5b** from the carbon atom linked to lithium to the carbon atom of the methyl group *via* a six-centred transition state.[8]



A number of cyclic *o*-carboranylphosphines have been described. For example, phosphines **13** containing a phosphinane ring have been obtained by the reaction of bis(lithiocarboranyl)-methane **12** with MePCl$_2$ or PhPCl$_2$.[9]

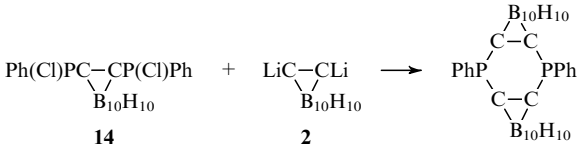


12 **13**

R = Me, Ph.

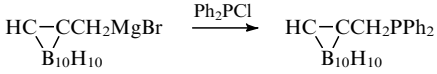
According to X-ray diffraction analysis, the C–P–C angle in the six-membered ring in the methyl derivative **13** (R = Me) differs only slightly from its normal value, whereas the C–CH$_2$–C angle is markedly larger than the tetrahedral angle and is equal to 121.8°.[10]

Phosphine **15** having a similar structure but containing two phosphorus atoms in the ring has been prepared by treatment of 1,2-bis(chlorophenylphosphino)-*o*-carborane **14** with the dilithiocarborane **2**.[3]



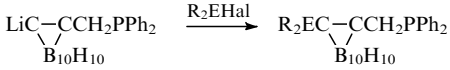
14 **2** **15**

Synthesis of carboranylphosphines in which the phosphorus atom is separated from the carboranyl nucleus by methylene groups has been reported. Thus the reaction of *o*-carboranylmethylmagnesium bromide **16** with chlorodiphenylphosphine has given rise to (*o*-carboranylmethyl)diphenylphosphine **17**.[11]



16 **17**

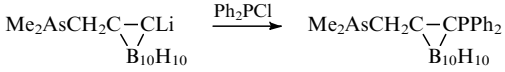
The compound **11** mentioned above belongs to the same type of derivative. 1,2-Disubstituted *o*-carboranes **18** containing a dimethylphosphino, diphenylphosphino or dimethylarsino group, in addition to the diphenylphosphinomethyl group, have been obtained by treatment of the lithio-derivative of the phosphine **17** with chlorodimethylphosphine, chlorodiphenylphosphine or iododimethylarsine, respectively.[12]



18a–c

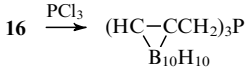
R = Me, E = P (**a**); R = Ph, E = P (**b**); R = Me, E = As (**c**);
Hal = Cl, I.

1-Diphenylphosphino-2-dimethylarsinomethyl-*o*-carborane **19** was prepared by the reaction of chlorodiphenylphosphine with the lithio-derivative of the corresponding carborane.



19

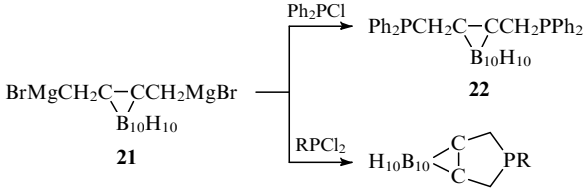
The reaction of *o*-carboranylmethylmagnesium bromide **15** with PCl$_3$ yields tris(*o*-carboranylmethyl)phosphine **20**.[13]



20

Treatment of bis(bromomagnesiomethyl)-*o*-carborane **21** with Ph$_2$PCl has resulted in the synthesis of 1,2-bis(diphenylphosphinomethyl)-*o*-carborane **22**.[12]

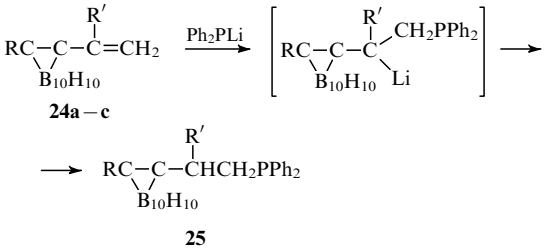
The reaction of **21** with MePCl$_2$ or PhPCl$_2$ affords the corresponding phospholanes **23**.[6]



21 **22** **23**

R = Me, Ph.

Carboranylphosphines **25** in which the phosphorus atom is separated from the carboranyl nucleus by two carbon atoms have been synthesised by nucleophilic addition of Ph$_2$PLi to the double bonds in 1-vinyl- and 1-isopropenyl-2-substituted carboranes **24**, activated by the presence of the *o*-carboranyl substituent, in a boiling ether–benzene mixture.[14]



24a–c **25**

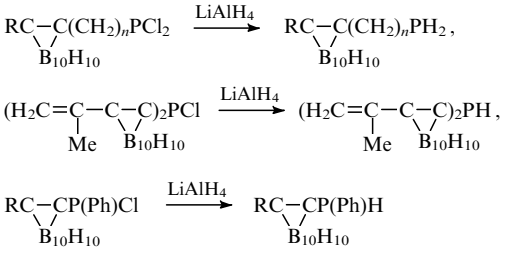
R = Me, R′ = H (**a**); R = R′ = Me (**b**); R = MeC=CH$_2$, R′ = Me (**c**).

The resulting phosphines are difficultly crystallisable viscous substances, which have been isolated after treatment with MeI as the corresponding phosphonium salts.

The activation of the double bond in 1-vinyl- and 1-isopropenyl-2-substituted *o*-carboranes **24a–c** towards nucleophilic addition is due to the high electron-withdrawing ability of the *o*-carborane nucleus. In the case of 1,2-diisopropenyl-*o*-carborane **24c**, Ph_2PLi adds only to one double bond. This is due to the fact that the negative charge arising upon the addition of a Ph_2PLi molecule decreases the electronegativity of the carboranyl fragment and thus prevents the reaction at the second isopropenyl group.

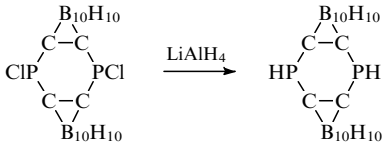
For the same reason, a similar derivative of *m*-carborane does not react with Ph_2PLi at all;[14] in fact, *m*-carboranyl is a weaker electron-withdrawing group than *o*-carboranyl.

Synthesis of *o*-carboranylphosphines containing a PH group has required a totally different approach. These compounds have been obtained in 50%–70% yields by reduction of the corresponding chlorophosphines with $LiAlH_4$ in ether.[7,11] However, the attempt to reduce chlorobis(2-phenyl-*o*-carboranyl)phosphine failed.



R = Me, Ph; *n* = 0, 1.

The reduction of the cyclic dichlorophosphine **3** with $LiAlH_4$ in ether gives diphosphine **26** in 60% yield.[7]



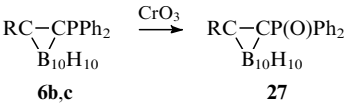
3 **26**

It should be noted that the use of an excess of $LiAlH_4$ in the reduction of carboranylchlorophosphines leads to the cleavage of the C–P bond giving the corresponding carborane and phosphine. However, in the case of carboranyl(chloro)phenylphosphines, this reaction pathway was not observed.[7] This indicates that a Ph group at the phosphorus atom increases the stability of the phosphorus–carboranyl carbon bond with respect to nucleophiles.

b. Properties of carboranylphosphines

All the main properties of phosphines containing no carboranyl groups are also characteristic of carboranylphosphines. At the same time, carboranyl groups have a certain influence on the properties of the phosphine group. This effect depends on the number of carboranyl groups and on their structure and also on the nature of substituents in the carborane nucleus and at the phosphorus atom. In the majority of cases, it is difficult to determine whether electronic or steric factors exert the major influence.

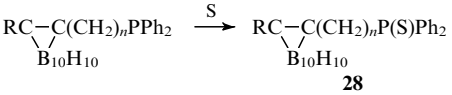
Carboranylphoshines are stable with respect to atmospheric oxygen. They are oxidised under relatively drasrtic conditions. For example, oxidation of methyl- and phenyl-substituted *o*-carboranylphosphines **6b,c** to the corresponding phosphine oxides **27** has been accomplished only by treating them with CrO_3 in acetic acid.[11]



6b,c **27**

R = Me, Ph.

The addition of sulfur to tertiary carboranylphosphines occurs with greater difficulty than its addition to ordinary tertiary phosphines, the reaction conditions being dependent both on the substituents in the carborane nucleus and on the distance between this nucleus and the phosphorus atom.[11]

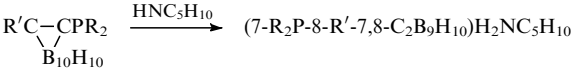


28

n = 1, R = H (**17**); *n* = 0, R = CH=CH$_2$ (**6d**);
n = 0, R = MeC=CH$_2$ (**6e**).

Whereas (*o*-carboranylmethyl)diphenylphosphine **17** enters into this reaction under mild conditions, namely, in benzene at 60 °C, the same reaction involving the carboranylphosphines **6d** and **6e** requires heating to 180 °C.[11]

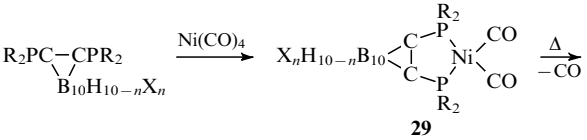
In an alkaline medium, carboranylphosphines are easily cleaved at the P–C(carborane) bond; however, on treatment with pyridine under mild conditions, this bond is retained. In this case, the carborane nucleus is opened to give *nido*-carboranylphosphines.[15]



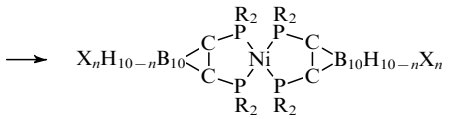
R = Ph, Et, Pr^i, OEt; R′ = Me, PR_2.

c. Transition metal complexes with carboranylphosphines

Soon after the first carboranylphosphines had been obtained, publications dealing with their use as ligands in transition metal complexes appeared. The first carboranylphosphine complexes of nickel, namely, dicarbonyl-1,2-bis(diphenylphosphino)- and -1,2-bis(diethylphosphino)-*o*-carboranylnickel **29** (R = Et, Ph, X = H), were obtained from the corresponding carboranyldiphosphines and $Ni(CO)_4$ in chloroform or in hydrocarbon solvents at 20 °C.[3] Dicarbonyl-1,2-bis(diethylphosphino)-*o*-halocarboranylnickel complexes **29** (R = Ph, X = Cl, Br) are prepared in a similar way under mild conditions.[16]



29



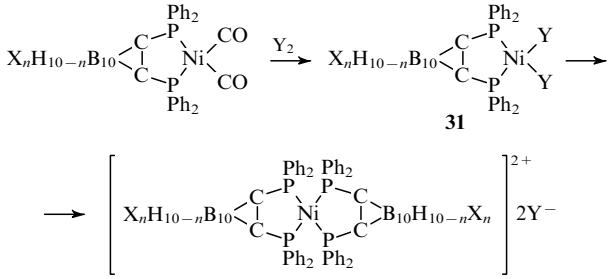
30

$n = 1-3$; R = Et, Ph; X = H, Cl, Br.

Study of the IR spectra of the complexes **29** shows that the characteristic CO frequencies are markedly greater than those for other complexes of the same type [for example, *o*-$(Ph_2P)_2C_6H_4Ni(CO)_2$ or $(Ph_3P)_2Ni(CO)_2$]. The introduction of a halogen atom in the 9-position of the carboranyl nucleus has no substantial influence on the position of the CO band.

These complexes were found to be thermally unstable. On refluxing in high-boiling organic solvents, they lose CO and are thus converted into more stable complexes **30**.[5,16]

Nickel dihalide complexes **31**, which are prepared by treatment of the corresponding nickeldicarbonyl complexes of halogenated *o*-carboranes with halogens, undergo a similar transformation.[16,17]

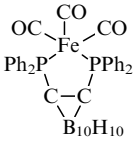


31

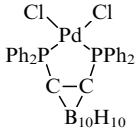
30

$n = 1-3$; X = Cl, Br; Y = Cl, Br, I.

Based on 1,2-bis(diphenylphosphino)-*o*-carborane **1**, irontricarbonyl **32** and palladium **33** complexes have also been obtained.[18]



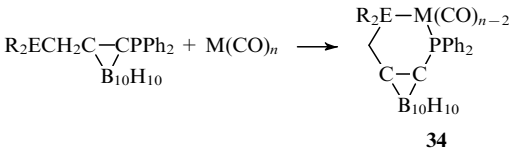
32



33

A large number of complexes with bidentate ligands containing two phosphorus atoms or a phosphorus and an arsenic atom have been synthesised.[12]

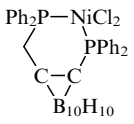
These ligands react with $Ni(CO)_4$ under mild conditions at 20 °C to give the corresponding complexes **34**; however, similar reactions with Mo, W, Cr and Fe carbonyls occur only on exposure to UV radiation.[12]



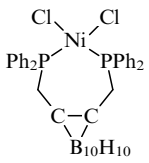
34

R = Me, Ph; E = P, As; M = Ni, Cr, Mo, W, Fe; $n = 4-6$.

The bis-phosphine ligands **18** and **22** readily react with $NiCl_2$ to yield complexes **35** and **36**, which are stable in air but rapidly decompose in alcoholic media.[12]

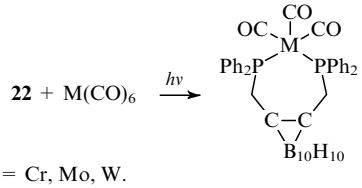


35



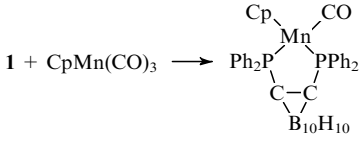
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The reactions of the carboranylphosphine **22** with chromium, molybdenum and tungsten carbonyls occur only on exposure of benzene solutions of the reactants to UV radiation for 5–15 h.[19]

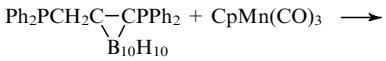


M = Cr, Mo, W.

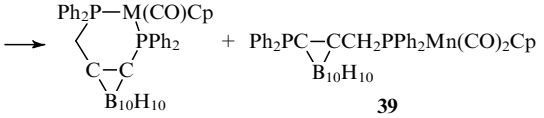
The carboranylphosphines **1** and **18b** react with cyclopentadienylmanganesetricarbonyl in different ways.[19] In the case of **1**, the reaction yields complex **37**. In the latter case, complex **38** with a similar structure is formed together with compound **39** in which the carboranylphosphine **18b** acts as a monodentate ligand.[19]



37



18b

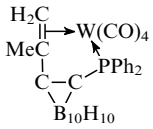


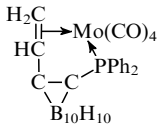
38 **39**

Cp = cyclopentadiene.

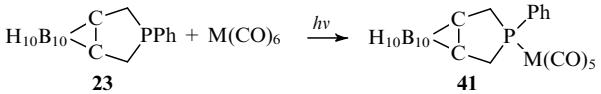
o-Carborane derivatives containing one diphenylphosphine group such as *o*-carboranyldiphenylphosphine **6a** (R′ = Ph), 1-diphenylphosphinomethyl-2-dimethylarsino-*o*-carborane **18c**, 1-diphenylphosphino-2-methylthiomethyl-*o*-carborane **40** and 1-diphenylphosphino-2-isopropenyl-*o*-carborane **6e** (R′ = Ph) react with $CpMn(CO)_3$ (Cp is cyclopentadiene) with replacement of only one CO group.[19]

Diphenylphosphinocarboranes **6d,e** (R′ = Ph) containing a vinyl or isopropenyl substituent in the 2-position react with $W(CO)_4$ and $(COD)_2Mo(CO)_4$ (COD is cyclooctadiene) to give complexes in which the C=C double bond participates in coordination.[12]





When THF solutions containing *o*-carboranylphospholane **23** (R = Ph) and Cr, Mo or W hexacarbonyl are irradiated by UV light, one CO group is displaced to give complexes **41**.[6]

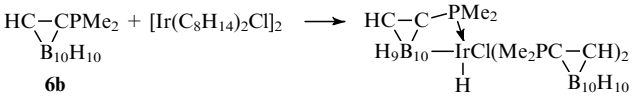


23 **41**

M = Cr, Mo, W.

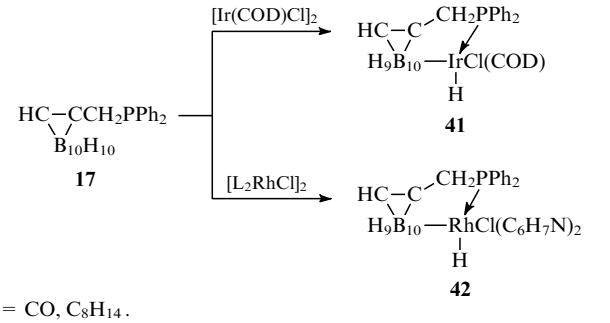
All the complexes described above are solids stable in air; however, most of them decompose in the light. In the structures of these complexes, the metal is coordinated by the lone electron pair of the phosphorus atom.

Transition metal complexes with carboranylphosphines containing B–M bonds that involve the boron atom in the 3(6)-position of the carborane ring, in addition to the P–M bonds, have also been synthesised. A complex of this type is formed, for example, when the carboranylphosphine **6a** (R′ = Me) is made to react with the iridium cyclooctene complex.[20]



6b

Other representatives of this type of complexes, for example **41** and **42**, have been prepared by the reactions of (*o*-carboranylmethyl)diphenylphosphine **17** with iridium and rhodium complexes in the presence of 4-methylpyridine.[21]

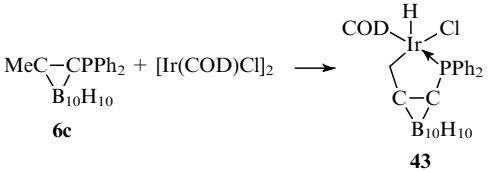


17 **41** **42**

L = CO, C_8H_{14}.

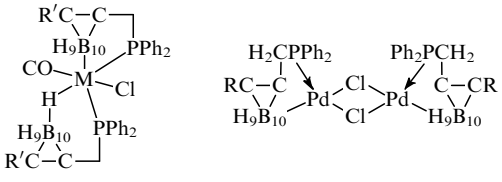
The reaction of **17** with $[Rh(CO)_2Cl]_2$ (in hydrocarbon solvents at 25 °C) yields a square-planar d^8-complex of rhodium, *trans*(*o*-$HCB_{10}H_{10}CCH_2PPh_2)_2Rh(CO)Cl$, which does not give intramolecular metallation products on heating with excess phosphine or 4-methylpyridine.[21]

Further studies of cyclometallation of carborane-containing phosphines with Rh(I) and Ir(I) complexes have shown that both the structure and the nature of the substituent in the 1-position of the carborane nucleus can have a substantial effect on the reaction pathway and on the nature of the final product.[22] It was found that (2-methyl-*o*-carboranyl)diphenylphosphine **6b** (R′ = Ph) does not react with Rh(I) complexes but does react with $[Ir(COD)Cl]_2$ yielding product **43**.

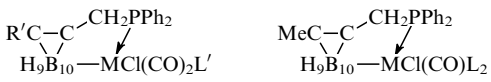


6c **43**

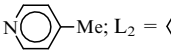
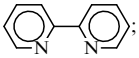
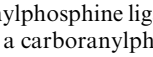
In addition to *B*-metallated Rh and Ir complexes of carboranylphosphines, a series of Pd, Os and Ru complexes of this type have also been prepared by reductive carboranylation.[23–25]



44



M = Ru, Os; R = H, Pr^i; R′ = H, Me;

L = ; L_2 = ; L′ = 

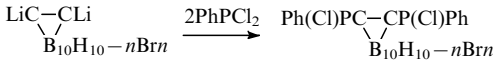
Apart from the *B*-metallated carboranylphosphine ligand, the complexes **44** (M = Ru, Os) also contain a carboranylphosphine coordinated to the metal atom through the phosphorus atom and the hydrogen atom in the 9-position of the carboranyl nucleus.[25]

2. Carborane-containing derivatives of acids of trivalent phosphorus

a. Carborane-containing halophosphines

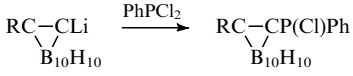
The main method for the synthesis of carborane-containing halophosphines is based on the reaction of lithio-derivatives of carboranes with halophosphines or with PCl_3.

The first carboranylchlorophosphines **46a**,**b** were prepared from 1,2-dilithio-*o*-carborane **2**[3] or its *B*-bromo-substituted analogue **45**[4] and $PhPCl_2$.



n = 0 (**2**), 2 (**45**). *n* = 0 (**46a**), 2 (**46b**).

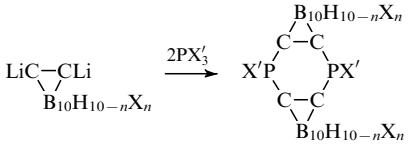
The carborane-containing chloro(phenyl)phosphines **7** were obtained in a similar way from the lithio-derivatives of 1-substituted *o*-carboranes **5** and $PhPCl_2$.[7]



5 **7**

R = Me, Ph.

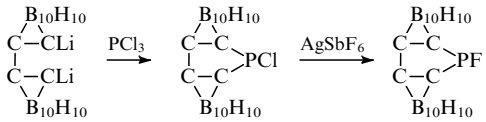
Dilithio-carboranes react with PCl_3, PBr_3 and PI_3 to give dimeric halodicarboranodiphosphinanes **47**.[3,4,26]



47

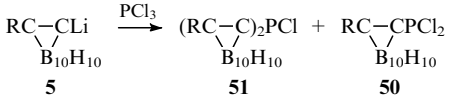
n = 0–10; X, X′ = Cl, Br, I.

The interaction of the dilithio-derivative of bis-*o*-carborane **48** with PCl_3 affords cyclic chlorophospholane **49** in 94% yield. By treatment with $AgSbF_6$, **49** has been converted into the corresponding fluorophospholane.[27]



48 **49**

The reaction of PCl_3 with the lithio-derivatives **5** results in the formation of bis(*o*-carboranyl)chlorophosphines **51** together with *o*-carboranyldichlorophosphines **50** as an impurity.[7,28]



5 **51** **50**

R = HC=CH_2, MeC=CH_2, Me, Ph.

1,7-Dimetallated *m*-carboranes react with PCl_3, $PhPCl_2$ or $AlkPCl_2$ to give bis(dichlorophosphino)-, bis[(chloro)phenylphosphino]- or bis(alkylchlorophosphino)-*m*-carboranes **52** together with oligomeric products. No cyclic phosphines have been detected among the reaction products.[29–31]

$$MCB_{10}H_{10-n}X_nCM \xrightarrow{2RPCl_2} \underset{\mathbf{52}}{Cl(R)PCB_{10}H_{10-n}X_nCP(R)Cl} + Cl(R)P[CB_{10}H_{10-n}X_nCP(R)]_zCl$$

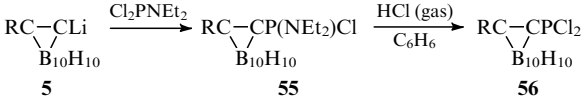
$n = 0-10$; $z = 2-10$; M = Li, Na, K; R = Cl, Ph, Alk; X = F, Cl, Br, I.

A drawback of the above methods is that some difficulties arise in the purification of the carboranylchlorophosphines. Treatment of carborane-containing phosphamidites **53** with dry HCl in benzene permits preparation of the corresponding carboranylchlorophosphines **54** in yields of up to 95% and in a highly pure state.[32–34]

$$\underset{\mathbf{53}}{RCB_{10}H_{10}CP(NR'_2)_2} \xrightarrow[C_6H_6]{HCl\ (gas)} \underset{\mathbf{54}}{RCB_{10}H_{10}CPCl_2}$$

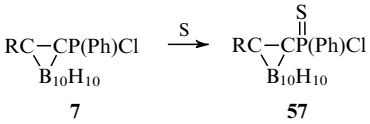
R = *o*-H, *m*-H, *o*-Me, *o*-Ph, *o*-MeC=CH$_2$; R′ = Me, Et.

o-Carboranyl(dialkylamino)chlorophosphines **55**, which can be easily prepared by treatment of lithio-derivatives of the substituted carboranes **5** with (dialkylamino)dichlorophosphines, react with HCl in a similar way.[33]



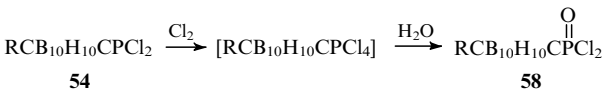
R = Me, Ph.

Carboranyl-containing chlorophosphines are much less reactive than alkyl- or arylchlorophosphines. This may be due both to the steric factors and to the electronic influence of the electron-deficient carboranyl group. They are stable with respect to atmospheric oxygen at room temperature. Carboranyldichlorophosphines and dicarboranylchlorophosphines do not add sulfur under drastic conditions even in the presence of $AlCl_3$ or $FeCl_3$, whereas *o*-carboranyl(chloro)phenylphosphines **7** add sulfur upon heating to 170–180 °C and are thus converted into the corresponding (*o*-carboranyl)phenylphosphinothioic chlorides **57**.[11,32]



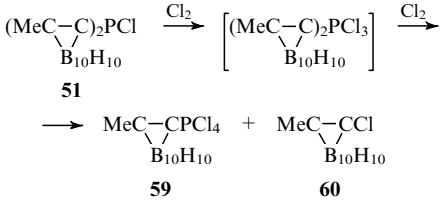
R = Me, Ph.

The addition of chlorine to carborane-containing chlorophosphines occurs readily and is usually accompanied by an exothermal effect. The addition products have not been isolated; however, it has been assumed that the reaction involves intermediate formation of carboranylchlorophosphoranes, which are readily hydrolysed in moist air or in aqueous dioxane to give the corresponding dichlorides **58**.



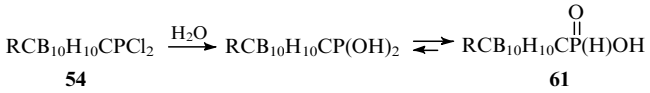
R = *o*-Me, *o*-Ph, *m*-H.

At the same time, it has been reported but not confirmed experimentally [7] that the reaction of chlorobis(2-methyl-*o*-carboranyl)phosphine **51** with excess chlorine affords crystalline methyl-*o*-carboranyltetrachlorophosphorane **59** and 2-chloro-1-methyl-*o*-carborane **60**, *i.e.* it is accompanied by cleavage of one phosphorus–carboranyl carbon bond.



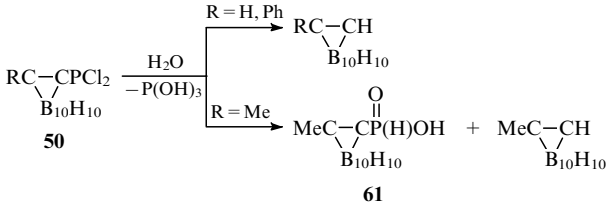
Chlorobis(2-phenyl-*o*-carboranyl)phosphine **51** (R = Ph) does not react with chlorine;[7] this can be explained by steric hindrance caused by the presence of two 2-phenyl-*o*-carboranyl groups at the phosphorus atom.

Carborane-containing chlorophosphines readily react with various nucleophiles, for example, water, alcohols, amines, azides and others. However, these reactions are often accompanied by cleavage of the P–C bond, the reaction pathway depending both on the nature of the attacking nucleophile and on the structure of carboranylchlorophosphine. It was shown that *o*- and *m*-carboranyldichlorophosphines **54** are smoothly hydrolysed at room temperature by atmospheric moisture to give the corresponding carboranylphosphonous acids. According to IR spectral data, these compounds contain pentavalent phosphorus, despite the electron-withdrawing effect of the carboranyl groups.[33,34]

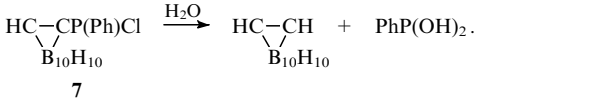


R = *m*-H, *o*-H, *o*-Me, *o*-Ph.

Hydrolysis of *o*-carboranyldichlorophosphines **50** (R = H, Ph) in aqueous dioxane in the presence of hydrochloric acid gives only the products of rupture of the P–C(carborane) bond, whereas dichloro(2-methyl-*o*-carboranyl)phosphine **50** (R = Me) is mostly converted under the same conditions into (2-methyl-*o*-carboranyl)phosphinic acid **61** (R = Me) (yield 75%) and also into the products of rupture of the C–P bond.[32] Probably, this reaction pathway is due to the influence of the methyl substituent, which decreases the electron-withdrawing ability of the carboranyl group and increases the strength of the C–P bond.

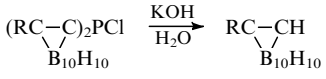


o-Carboranylchlorophenylphosphine is fairly unstable with respect to hydrolysis, apparently owing to the presence of three electron-withdrawing substituents at the phosphorus atom; it is cleaved into carborane and phenylphosphonous acid even by the atmospheric moisture.[7]



The easy rupture of the C–P bond in the carborane-containing chlorophosphines may be due to the fact that a carboranyl group attached to a phosphorus atom can act as a pseudo-halogen under certain conditions. Similar behaviour has been observed for carboranylphosphinous acids in which the phosphorus–C(carborane) bond is cleaved on heating of their aqueous solutions.[32]

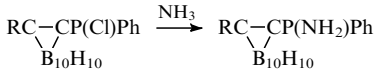
Bis(*o*-carboranyl)chlorophosphines are resistant to the action of water; their alkaline hydrolysis gives only products resulting from cleavage of the C–P bond.[32]



50

R = Me, Ph.

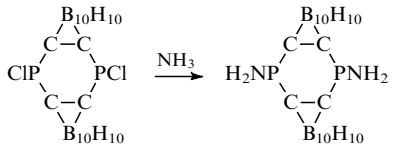
The reactions of carboranyl-containing chlorophosphines with ammonia, unlike their reactions with water, occur with replacement of the chlorine atom to give the corresponding amides **62**, the C–P bond remaining intact.[7]



7 **62**

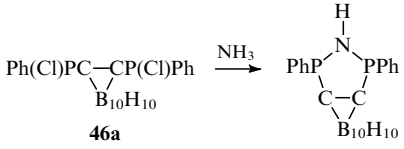
R = Me, Ph.

The dimeric dichlorophosphine **3** reacts with ammonia in a similar way yielding cyclic diamide **63**.[3]



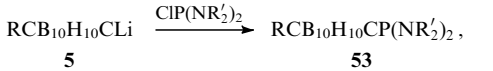
3 **63**

The interaction of dry ammonia with 1,2-bis(chlorophenylphosphino)carborane **46a** involves both chlorine atoms and gives rise to cyclic imide **64**.

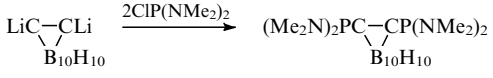


46a **64**

Dialkylamido-derivatives of carborane-containing acids of trivalent phosphorus have been described. These compounds were obtained as intermediates in the synthesis of carboranylchlorophosphines; the methods for their preparation were based on the reactions of monolithiocarboranes[11, 32, 34] or dilithiocarborane[35] with chlorobis(dialkylamino)phosphines.



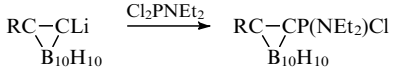
5 **53**



2 **65**

R = *m*-H, *o*-H, *o*-Me, *o*-Ph; R′ = Me, Et.

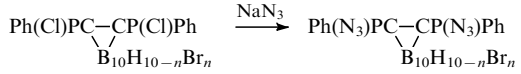
The attempts to prepare bis(carboranyl)dialkylaminophosphines by treating aminodichlorophosphines with the lithioderivatives of *o*-carboranes **5** were unsuccessful. In this case, only one chlorine atom was substituted resulting in the formation of dialkylamino(*o*-carboranyl)chlorophosphines **66**. The second chlorine atom was not replaced, apparently, due to steric hindrance.[11, 33]



5 **66**

R = Me, Ph.

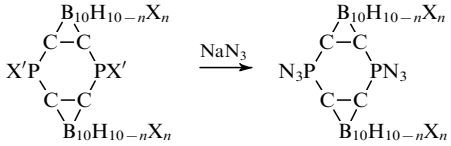
Carborane-containing chlorophosphines readily react with sodium azide. For example, bromo-substituted 1,2-bis(azidophenylphosphino)-*o*-carboranes **67** have been obtained in this way.[3, 4, 26]



46 **67**

$n = 0-2$.

The bis-azide **67** is unstable and polymerises at 60 °C. Similarly, cyclic bis-halophosphines **47** have been converted into cyclic bis-phosphine azides **68**.[3, 4, 26]



47 **68**

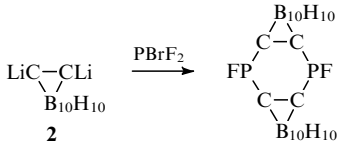
$n = 0-10$; X = Cl, Br; X′ = Cl, Br, I.

These compounds readily react with tertiary phosphines to give the corresponding phosphazo-derivatives. Polymers based on these derivatives possess valuable properties.[4, 26]

Carborane-containing fluorophosphines and their platinum complexes were synthesised for the first time in the late 70s and early 80s. Various methods have been used for this purpose. Thus treatment of 2-lithio-1-diphenylphosphino-*o*-carborane **69** with $PBrF_2$ yielded 2-difluorophosphino-1-diphenylphosphino-*o*-carborane **70**.[36] A similar reaction involving dilithio-*o*-carborane **2** resulted in the formation of cyclic difluorophosphine **71**.[35]

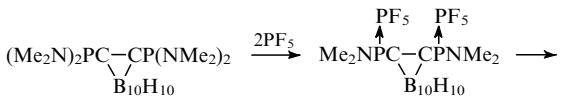


69 **70**

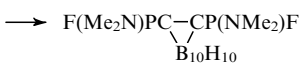


2 **71**

Fluoroamides were synthesised by the reaction of PF_5 with 1,2-bis[bis(dimethylamino)phosphino]-*o*-carborane **67** ($n = 0$).[35] It was found that this reaction yields initially adduct **72** containing two PF_5 molecules; upon prolonged heating, it is converted into the corresponding fluorophosphine **73**, only one fluorine atom being introduced to each phosphorus atom.



67 **72**

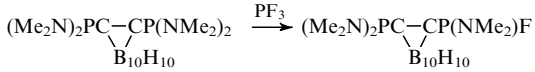


73

The adduct **72** is a complex containing a P(III)–P(V) bond. It has been assumed[38] that in acetonitrile solutions, this compound is ionic. This reaction has also been studied in relation to other compounds.[35–38]

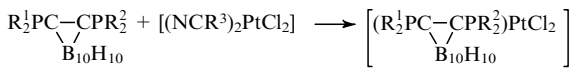
Attempts to replace the NMe_2 group in the carborane-containing aminophosphine **67** by a fluorine atom by treating this compound with PF_3 were undertaken.[35, 36] This reaction

occurred slowly: only one fluorine atom was introduced into the molecule upon heating the reaction mixture for several days.[36]



67

Carborane-containing fluorophosphines are stable in air but are slowly hydrolysed in solution. On treatment with Pt(II) cyanide complexes, they are readily converted into the corresponding *cis*-complexes **74**, their yields ranging from 42% to 85%.[39]



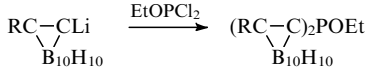
74

R^1 = Ph, NMe_2; R^2 = F, C_6F_6, Ph, NMe_2; R^3 = Me, Ph.

b. Carborane-containing esters of trivalent phosphorus acids

Carborane-containing esters of acids containing trivalent phosphorus have been studied in detail. Esters in which the phosphorus atom is either directly linked to the carborane carbon atom or separated from it by other atoms as well as sulfur- and selenium-containing esters in which the phosphorus atom is connected to the boron atom of the carboranyl group *via* sulfur or selenium have been synthesised.

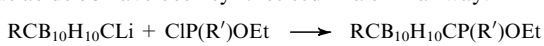
Carborane-containing esters of trivalent phosphorus acids in which the phosphorus atom is directly attached to the carbon atom of the carborane nucleus have been prepared by several methods. The most reliable procedure is based on the reaction of lithiocarboranes with the corresponding phospho- or phosphonochloridites. For example, ethyl bis-(*o*-carboranyl)phosphinites **75** have been prepared in yields of up to 70% by the reaction of the corresponding 2-substituted 1-lithio-*o*-carboranes **5** with $EtOPCl_2$.[40]



5 **75**

R = Me, Ph, $MeC{=}CH_2$.

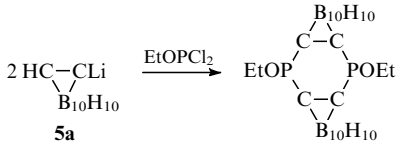
Esters of carborane-containing phosphinous and phosphonous acids **76** have been synthesised in a similar way.[41–43]



76

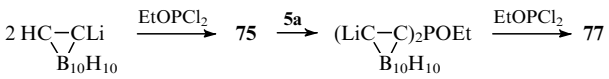
R = *o*-H, *m*-H, *p*-H, *o*-Me, *o*-Ph, *o*-$MeC{=}CH_2$; R′ = Me, OEt.

The lithio-derivative of the unsubstituted carborane reacts with ethyl phosphodichloridite to give only cyclic diphosphinite **77**.[40]



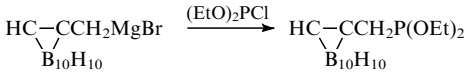
5a **77**

This may be due to the fact that 1-lithio-*o*-carborane **5a** disproportionates[44,45] to give 1,2-dilithio-*o*-carborane **2** and carborane, and the dilithio-derivative **2** reacts with ethyl phosphodichloridite. However, it cannot be ruled out that the compound **77** results from metallation of the intermediate bis(*o*-carboranyl)phosphinite **75** by 1-lithio-*o*-carborane **5a** and subsequent interaction of the lithio-derivative with ethyl phosphodichloridite.



5a

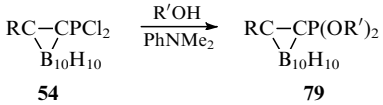
Diethyl (*o*-carboranylmethyl)phosphonite **78** has been synthesised by the reaction of diethyl phosphodichloridite with (1-bromomagnesiomethyl)carborane **16**.[46]



16 **78**

Esters of carborane-containing acids of trivalent phosphorus can be obtained by the interaction of alcohols with the corresponding carboranylchlorophosphines. However, this method is inconvenient, because it is difficult to purify the reaction products. It has been reported[31] that the treatment of 1,7-bis(dichlorophosphino)- or 1,7-bis(chlorophenylphosphino)-*m*-carboranes **52** with methanol gives rise to the corresponding tetramethyl or dimethyl esters of carborane-containing acids of trivalent phosphorus. However, no evidence confirming the structures of the reaction products was presented in the study cited.

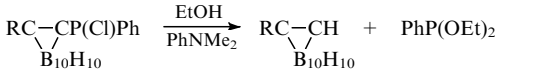
Reactions of carborane-containing chlorophosphines with alcohols in the presence of dimethylaniline or sodium ethoxide have been studied. The reaction pathway was found to depend both on the structure of the corresponding chlorophosphine and on the reaction conditions. When 2-substituted *o*-carboranyldichlorophosphines **54** are made to react with methanol or ethanol in the presence of dimethylaniline, the corresponding dialkyl phosphonites **79** are formed in yields of up to 80%.[7]



54 **79**

R = H, Me; R′ = Me, Et.

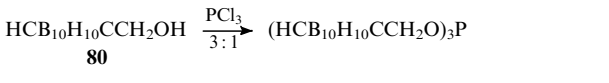
The attempt to carry out the reaction between *o*-carboranyldichlorophosphines **16** and sodium ethoxide has led only to products resulting from the cleavage of the C–P bond.[7] The reaction involving 2-substituted *o*-carboranylphenylchlorophosphines **6** occurs in a similar way. These substrates are cleaved even by alcohols under mild conditions in the presence of dimethylaniline. This was explained[7] by the fact that phosphorus carries a phenyl group and a chlorine atom, in addition to the carboranyl group, and this decreases the strength of the C–P bond.[7]



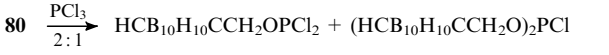
7

R = Me, Ph.

To synthesise carborane-containing esters of trivalent phosphorus acids and thioacids, carborane-containing alcohols and dithiols have also been used. For example, the reaction of 1-hydroxymethyl-*m*-carborane **80** with PCl_3 leads to the products of replacement of one, two or three chlorine atoms, depending on the ratio of the reactants.[47] Despite the absence of bases, no hydrogen phosphite was formed in the reaction.

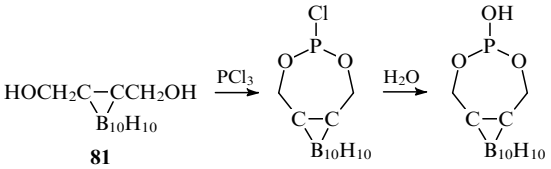


80



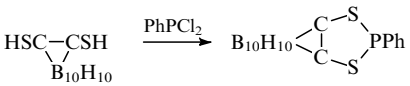
1,2-Bis(hydroxymethyl)-*o*-carborane **81** has also been introduced in the reaction with PCl_3. This gave the corresponding

cyclic phosphochloridite **82**, which was converted into hydrogen phosphite **83** by controlled hydrolysis.[48]



81 **82** **83**

Cyclic carborane-containing phenylphosphonodithioite **85** has been prepared by the reaction of carborane-1,2-dithiol **84** with $PhPCl_2$.[49]



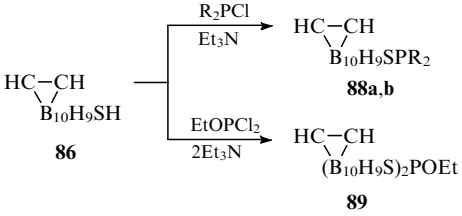
84 **85**

The reactivity of carboranyl or carboranylmethyl esters of trivalent phosphorus acids is markedly lower than that of similar esters containing no carboranyl groups. It depends both on the number of carboranyl groups attached to the phosphorus atom and on the character of the substituents in the carborane nucleus.

Carboranyl phosphonites are stable with respect to atmospheric oxygen and are not oxidised even upon heating to 100 °C; however, they are readily oxidised by N_2O_4.[50] The addition of sulfur, CuCl and azides to these derivatives as well as the Arbuzov and Perkow reactions occur less readily than those for phosphonites devoid of the carboranyl group.[41–43]

Bis(carboranyl)phosphinites do not add sulfur, do not form complexes with CuCl, do not react with azides and do not enter into the Arbuzov reaction.[40] The inertness of these compounds can be due both to the steric hindrance caused by the two carboranyl groups and to the large overall electron-withdrawing effect of these groups.[40]

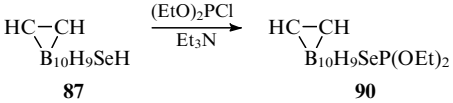
B-substituted carborane-containing esters of trivalent phosphorus thioacids [51–53] and selenoacids [54] have been synthesised from *o*-carborane-9-thiol **86** or *o*-carborane-9-selenol **87**. The reactions were carried out in the presence of triethylamine under an inert atmosphere at −30 °C. When the compound **86** was made to react with $EtOPCl_2$, $(EtO)_2PCl$ and Ph_2PCl, the corresponding thioesters **88** and **89** were obtained in high yields.[51–53]



86 **88a,b** **89**

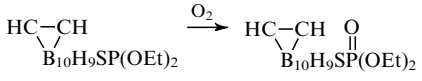
R = EtO (**a**), Ph (**b**).

When $(EtO)_2PCl$ reacts with *o*-carborane-9-selenol **87**, the corresponding selenoester **90** is formed but the researchers have not been able to isolate it in a pure state.[54]



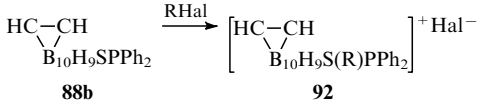
87 **90**

o-Carboran-9-yl esters of trivalent phosphorus thioacids of type **88a,b** add sulfur and selenium; they form complexes with metal carbonyls and enter into the Arbuzov and Perkow reactions. As a rule, these thioesters are quite stable in air; however, the phosphorothioite **88a** is oxidised by atmospheric oxygen to phosphothioate **91** even during chromatography on silica gel.[52]



88a **91**

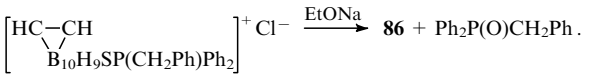
On treatment with alkylating reagents, phosphinothioite **88b** is converted into stable quasi-phosphonium salts **92**.[55]



88b **92**

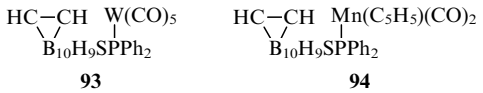
92	R	Hal	Yield (%)
a	Me	I	98
b	$PhCH_2$	Cl	50
c	$H_2C=CHCH_2$	Br	62

It was shown that treatment of the salt **92b** with sodium ethoxide in ethanol results in the rupture of the P–S bond and gives the thiol **86** in an almost quantitative yield, together with benzyldiphenylphosphine oxide.[55]



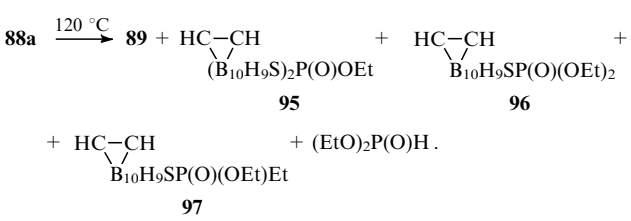
92b

The phosphinothioite **88b** forms complexes **93** and **94** with pentacarbonyl tetrahydrofuranotungsten and with dicarbonyl cyclopentadienyltetrahydrofuranomanganese, respectively.[53]



93 **94**

The phosphinothioite **88b** is fairly stable when heated to 200 °C under an argon atmosphere, whereas the phosphorothioite **88a** decomposes even at 120 °C to give a mixture of products containing the compound **89** (29.9%), *O*-ethyl *S*,*S*-bis(*o*-carboran-9-yl) phosphodithioate **95** (4.8%), *O*,*O*-diethyl *S*-*o*-carboran-9-yl phosphothioate **96** (10.6%), *O*-ethyl *S*-*o*-carboran-9-yl ethylphosphonothioate **97** (17.6%), $(EtO)_2PHO$ (30.5%) and non-identified products (6%).[55]



95 **96** **97**

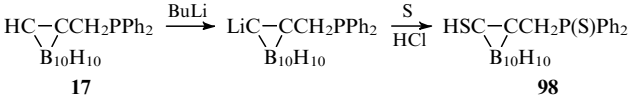
III. Carborane-containing derivatives of pentavalent phosphorus

Derivatives of pentavalent phosphorus constitute a large portion of all known phosphorus-containing carboranes. These compounds are synthesised by reactions typical of derivatives of both trivalent and pentavalent phosphorus.

1. Carboranylphosphine oxides and sulfides, derivatives of carborane-containing phosphinic and phosphonic acids

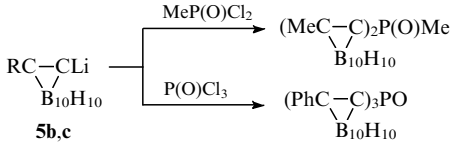
Syntheses of some carborane-containing phosphine oxides and sulfides have been mentioned in Section II.1.b. These derivatives were synthesised by addition of oxygen or sulfur to the corresponding carborane-containing phosphines. 2-Diphenylphosphinothioylmethyl-*o*-carboranethiol **98** has been prepared using a

different approach consisting in metallation of *o*-carboranylmethyldiphenylphosphine **17** and treatment of the resulting lithio-derivative with sulfur. The reaction product was isolated after acidification by hydrochloric acid.[12]



17 **98**

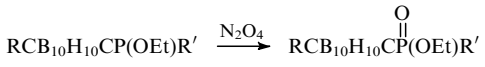
Bis- and tris-carboranylphosphine oxides have been synthesised by treatment of the lithio-derivatives of 2-substituted carboranes **5b**,**c** with methylphosphonoyl dichloride or with phosphorus oxychloride.[33]



5b,**c**

R = Me (**b**), Ph (**c**).

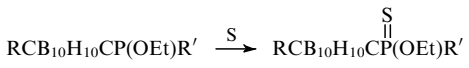
As noted above, carborane-containing esters of acids of trivalent phosphorus are stable against oxidation with atmospheric oxygen; however, they are readily oxidised by N_2O_4 to give the corresponding esters containing pentavalent phosphorus in high yields.[50] For example, this procedure was used to synthesise compounds **99**.



76 **99**

R = *p*-H, *m*-H, *o*-Me, *o*-Ph, *o*-MeC=CH$_2$; R′ = Me, OEt.

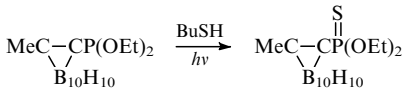
Carborane-containing phosphonothioates and phosphinothioates **100** can be prepared by addition of sulfur, which occurs only on heating to 100–120 °C. The relatively low reactivity of the compounds studied with respect to sulfur is apparently due to the electron-withdrawing effect of the carboranyl group.[42]



76 **100**

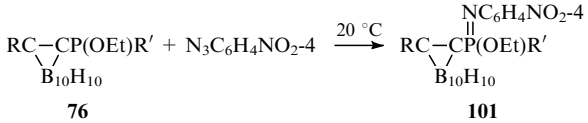
R = *o*-H, *m*-H, *o*-Me, *o*-MeC=CH$_2$; R′ = Me, OEt.

O,*O*-Diethyl (2-methyl-*o*-carboranyl)phosphonothioate **100** (R = Me, R′ = OEt) was also obtained by the reaction of the corresponding carboranylphosphonite **76** with butanethiol under UV radiation.[42]



76 **100**

On treatment with 4-nitrophenyl azide, carborane-containing esters of acids of trivalent phosphorus **76** are converted relatively easily into imino-derivatives **101**.[42, 43]



76 **101**

R = H, Me, Ph, MeC=CH$_2$; R′ = Me, OEt.

However, this reaction occurs more slowly than that involving similar esters of acids of trivalent phosphorus devoid of the carboranyl group. It was also found that substituents at the phosphorus atom as well as those in the *o*-carborane nucleus have a substantial influence on the reactivity.[43]

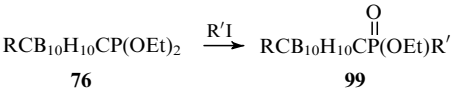
Based on the dissociation constants of imidophosphinates **101**, the σ^{Φ} constants for substituted *o*-carboranyl groups were calculated (Table 1).[43] The results obtained confirm the electron-withdrawing properties of the carboranyl group.

Table 1. Dissociation constants and σ^{Φ} values for imidophosphinates **101** (R′ = Me).[43]

R	pK_a	σ^{Φ}
H	5.48	2.10
Me	6.10	1.79
MeC=CH$_2$	5.83	1.92
Ph	5.68	2.00

The Arbuzov reaction can also be used to prepare carborane-containing derivatives of pentavalent phosphorus; however, it also occurs under more drastic conditions than the same reaction for esters of trivalent phosphorus acids devoid of the carboranyl group.

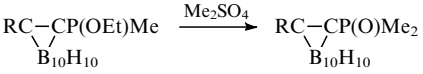
The reaction of diethyl carboranylphosphonite with MeI in acetonitrile carried out by heating the reactants in a tube (100–140 °C) affords the corresponding derivatives of pentavalent phosphorus **99**, their yields ranging from 50% to 73% depending on the character of the substituent at the phosphorus atom. The reaction occurs most readily for the carborane-containing methyl phosphinites **76** (R′ = Me).[42, 43, 50] Ethyl iodide reacts in a similar way.[42]



76 **99**

R = *m*-H, *p*-H, *o*-Me, *o*-Ph; R′ = Me, Et.

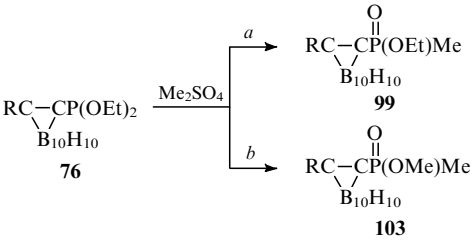
The reaction with dimethyl sulfate occurs under substantially milder conditions (at 20 °C) giving rise to compounds **102** in yields of up to 81%.[43]



76 **102**

R = H, Me.

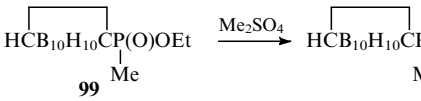
To carry out a similar reaction with diethyl (*o*-carboranyl)-phosphonites, heating to 110–120 °C is required. Whereas the transformation of diethyl (2-methyl-*o*-carboranyl)phos-phonite **76** (R = Me) gave ethyl (2-methyl-*o*-carboranyl)methyl-phosphinate **99** in 78% yield, in the case of *o*-carboranylphosphonites **76** (R = H, MeC=CH$_2$), the reaction is accompanied by transesterification giving the corresponding methyl (*o*-car-boranyl)methyl-phosphinates **103** in yields of up to 56%.[56]



76 **99** **103**

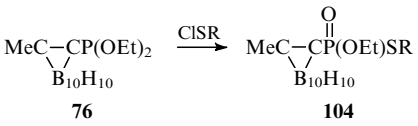
(*a*) R = Me; (*b*) R = H, MeC=CH$_2$.

Transesterification also occurs when ethyl (*p*-carboranyl)-methylphosphinate is heated with excess Me_2SO_4.[56]



99

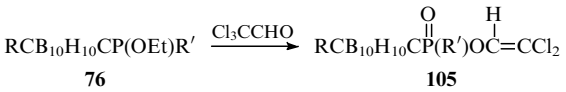
When diethyl *o*-carboranylphosphonites are treated with sulfenyl chlorides, the Arbuzov reaction smoothly occurs.[41,42] For example, the reactions with butylsulfenyl chloride and 2,4-dinitrophenylsulfenyl chloride in tetrachloromethane gave the corresponding thioesters **104** in yields of up to 90%.



76 **104**

R = Bu, 2,4-$(NO_2)_2C_6H_3$.

Several examples of the Perkow reaction have been reported. When the compounds **76** have been made to react with a large excess of chloral without a solvent, the corresponding dichlorovinyl carboranylphosphonates and carboranylphosphinates **105** have been obtained in 44% to 90% yields.[43,50]

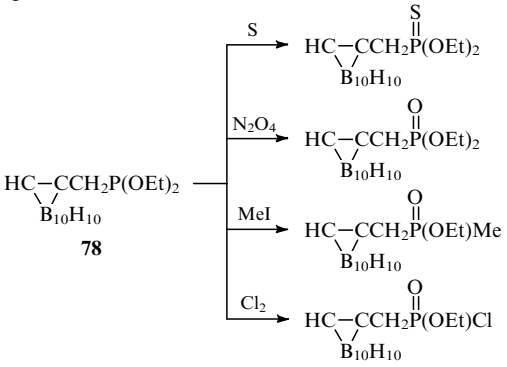


76 **105**

R = *p*-H, *m*-H, *o*-H, *o*-Me, *o*-Ph, *o*-MeC=CH_2; R′ = Me, OEt.

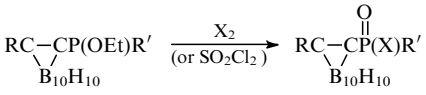
(Carboranyl)methylphosphinites enter into this reaction much more readily than carboranylphosphonites. In addition, the ease of this reaction depends on the electron-withdrawing properties of the carboranyl groups, which are determined in this particular case by the nature of the carboranyl nucleus. The substituents present in these nuclei make only a minor contribution to the overall electronic effect of the carboranyl groups but cause substantial steric effects.[43,50]

Carborane-containing esters of acids of pentavalent phosphorus in which the carboranyl group is separated from the phosphorus atom by a methylene bridge are also known. These compounds have been prepared by means of standard reactions typical of esters of trivalent phosphorus acids devoid of the carborane group.[46]



78

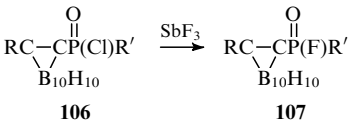
Chlorides and bromides of *o*-carborane-containing acids of pentavalent phosphorus **106** have been synthesised by treating the esters derived from carborane-containing acids of trivalent phosphorus **76** with sulfuryl chloride, chlorine or bromine.[40,42,50]



76 **106**

R = Ph, MeC=CH_2; R′ = Me, OEt, —C(B$_{10}$H$_{10}$)CH; X = Cl, Br.

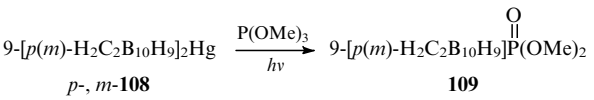
Fluorides **107** were prepared by treatment of the corresponding chlorides **106** with antimony trifluoride.[50]



106 **107**

R = Ph, MeC=CH_2; R′ = Me, OEt.

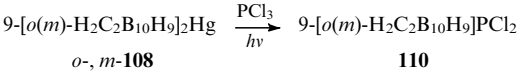
The first representatives of carborane-containing acids of pentavalent phosphorus in which the phosphorus atom is linked directly to the boron atom in the 9-position of the carboranyl group were obtained by the reaction of bis(*p*- or *m*-carboran-9-yl)mercury **108** with trimethyl phosphite under UV irradiation. Dimethyl (*p*-carboran-9-yl)phosphonate **109** was synthesised in this way in 60% yield. However, dimethyl (*m*-carboran-9-yl)phosphonate *m*-**109** was obtained by this procedure only in 5% yield, and in the case of bis(*o*-carboran-9-yl)mercury, the reaction did not occur at all.[57]



p-, *m*-**108** **109**

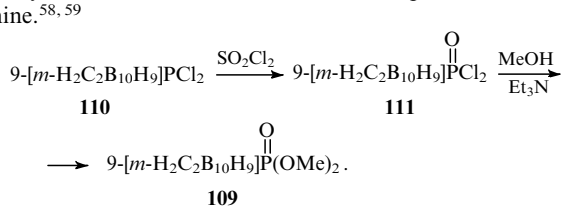
The σ^{Φ} constants for 9-*p*- and 9-*m*-carboranyl groups were found to be equal to −1.68 and −1.81, respectively, which points to electron-donating properties of these groups.[57]

Bis(*o*-carboran-9-yl)mercury **108** reacts with PCl_3 on exposure to UV radiation to give the corresponding dichlorophosphine **110** in 5% yield. The *m*-carboranylmercury derivative reacts in a similar way (yield 10%).



o-, *m*-**108** **110**

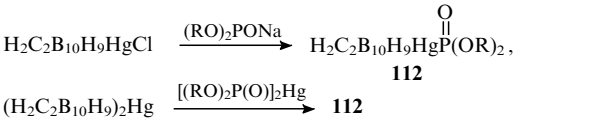
m-Carboran-9-yldichlorophosphine **110** has been oxidised by SO_2Cl_2 to the corresponding phosphonoyl dichloride **111**; the latter was converted into dimethyl (*m*-carboran-9-yl)phosphonate **109** by the reaction with methanol in the presence of triethylamine.[58,59]



110 **111** **109**

The results of X-ray diffraction and IR spectroscopy studies of dimethyl (*p*- and *m*-carboran-9-yl)phosphonates **109** have shown that their crystals contain hydrogen bonds; *p*-carborane-derivatives were found to form dimers.[57,60]

Carborane-containing derivatives of acids of pentavalent phosphorus **112** in which the 9-position of an *o*-, *m*- or *p*-carboranyl group is linked to the phosphorus atom *via* a mercury atom have been synthesised.[61,62]



112

R = Me, Et, Pr^i.

Synthesis of (*m*-carboran-9-yl)triphenylphosphonium tetrafluoroborate **113** has been reported.[63] The researchers did not succeed in preparing a similar salt derived from *o*-carborane.

$$(m\text{-}H_2C_2B_{10}H_9)_2Br^+BF_4^- \xrightarrow{PPh_3} [m\text{-}H_2C_2B_{10}H_9PPh_3]^+BF_4^- + m\text{-}H_2C_2B_{10}H_9Br.$$

113

2. Derivatives of acids of pentavalent phosphorus containing a carboranyl group in the ester moiety of the molecule

Numerous examples of phosphorus acid esters containing a carboranyl group in the ester moiety of the molecule have been described. In these molecules, the carbon or boron atoms of the carboranyl moiety are linked to the phosphorus atom *via* sulfur or selenium atoms or *via* hydroxyalkyl or thioalkyl groups.

Carboranylalkyl esters of phosphorus-containing acids have been synthesised starting from various hydroxyalkylcarboranes.

The first *o*-carboranyl phosphates **115** were prepared by the reaction of monoacylated 1,2-bis(hydroxymethyl)-*o*-carboranes **114** with H_3PO_4 at 100–120 °C.[64]

$$RCOCH_2C(B_{10}H_{10})CCH_2OH \xrightarrow{H_3PO_4} RCOCH_2C(B_{10}H_{10})CCH_2OP(O)(OH)_2$$

114 **115**

R = Alk.

When hydroxymethyl-*o*-carboranes or -*m*-carboranes **80** are treated with PCl_5, tris(carboranylmethyl) phosphates **116** are formed. The yield of the *m*-carborane derivative is 90%, whereas that of the *o*-carborane derivative does not exceed 26%. This reaction also yields the corresponding chloromethyl derivative **117**.[65, 66]

$$o(m)\text{-}HCB_{10}H_{10}CCH_2OH \xrightarrow{PCl_5} [o(m)\text{-}HCB_{10}H_{10}CCH_2O]_3P(O) + o(m)\text{-}HCB_{10}H_{10}CCH_2Cl.$$

80 **116** **117**

The reaction of PCl_5 with the diol **81** gives rise to a mixture of cyclic phosphochloridite **118** and 3,4-(1,2-*o*-carborano)oxolane **119** (yields 22% and 24%, respectively).[66]

$$HOCH_2C(B_{10}H_{10})CCH_2OH \xrightarrow{PCl_5} H_{10}B_{10}C_2O_2PCl + H_{10}B_{10}C_2O$$

81 **118** **119**

The diol **81** can also be used to synthesise cyclic esters of carborane-containing acids of pentavalent phosphorus. For example, the Todd–Atherton reaction involving the phosphite **83** has given carborane-containing amidophosphate **120**. Cyclic heptylphosphonate **121** was synthesised by the addition of the same phosphite to hept-1-ene.[48]

$$H_{10}B_{10}C_2O_2POH \xrightarrow[CCl_4]{Et_2NH} H_{10}B_{10}C_2O_2P(O)NEt_2$$

83 **120**

$$H_{10}B_{10}C_2O_2POH \xrightarrow{C_7H_{14}} H_{10}B_{10}C_2O_2P(O)C_7H_{15}$$

83 **121**

o-Carboranylmethyl phosphates **122** have been described. These compounds are formed in the reaction of hydroxymethyl-*o*-carborane **80** with $POCl_3$ or with monochlorophosphates in the presence of Mg as a catalyst.[67]

$$HC(B_{10}H_{10})CCH_2OH + ClP(O)RR' \xrightarrow{Mg} HC(B_{10}H_{10})CCH_2OP(O)RR'$$

80 **122**

R, R′ = Cl, OPh, OCH_2CF_3.

The reaction of hydroxymethyl-*o*-carborane **80** with diethoxyphosphoryl isocyanate affords carbamate **123**.[68]

$$\mathbf{80} + (EtO)_2P(O)NCO \longrightarrow HC(B_{10}H_{10})CCH_2OC(O)NHP(O)(OEt)_2$$

123

A series of *o*-carboranylmethyl esters of acids of pentavalent phosphorus have been synthesised by treatment of propynyl esters of the corresponding acids and thioacids with decaborane in the presence of dimethylaniline.[69, 70] The yields of the products vary from 50% to 77%.

$$B_{10}H_{14} + HC{\equiv}CCH_2YP(X)RR' \longrightarrow HC(B_{10}H_{10})CCH_2YP(X)RR'$$

$$2B_{10}H_{14} + (HC{\equiv}CCH_2O)_2P(X)R \longrightarrow (HC(B_{10}H_{10})CCH_2O)_2P(X)R$$

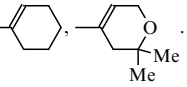
$$3B_{10}H_{14} + (HC{\equiv}CCH_2O)_3PO \longrightarrow (HC(B_{10}H_{10})CCH_2O)_3PO$$

X, Y = O, S; R, R′ = Me, OEt, Ph.

Several methods have been developed for the preparation of *S*-carboranyl esters of dithio-acids of pentavalent phosphorus in which the sulfur atom is directly linked to the carbon atom of the carboranyl ring. According to one of these methods, lithiocarboranes **5** are made to react with bis(dialkoxythiophosphoryl) disulfides in benzene or in an ether–benzene mixture.[71]

$$[(RO)_2P(S)S]_2 + LiCB_{10}H_{10}CR' \longrightarrow (RO)_2P(S)SCB_{10}H_{10}CR'$$

5

R = Me, Et, Pr^i; R′ = *o*-H, *m*-H, *o*-Me, *o*-Ph, , .

Unexpectedly, the reaction of equimolar amounts of bis(dialkoxythiophosphoryl) disulfides with lithio-*m*-carborane in an ether–benzene solvent mixture resulted in the formation of 1,7-bis(thiophosphorylthio)-*m*-carboranes. Similar transformations in benzene yielded only monosubstituted *m*-carboranyl phosphodithioates.

O-Ethyl *S*-(2-phenyl-*o*-carboranyl) methylphosphonodithioate **124** has been prepared by the reaction of lithium 2-phenyl-*o*-carboranethiolate with *O*-ethyl chlorophosphonothioate.[71]

$$PhC(B_{10}H_{10})CSLi \xrightarrow{MeP(OEt)Cl} PhC(B_{10}H_{10})CSP(S)(OEt)Me.$$

124 (72%)

To synthesise esters of thiophosphoric acid containing a 1-methyl-*m*-carboran-7-yl group, 1-methyl-*m*-carboran-7-ylsulfenyl chloride **125** has been introduced into the reaction with triethyl phosphite; this has given *O*,*O*-diethyl *S*-(1-methyl-*m*-carboran-7-yl) phosphothioate **126**. 7-Ethylthio-1-methyl-*m*-carborane **127** was isolated as a side product.[72]

$$MeCB_{10}H_{10}CSCl \xrightarrow{(EtO)_3P} MeCB_{10}H_{10}CSP(O)(OEt)_2 + MeCB_{10}H_{10}CSEt.$$

125 **126** **127**

A series of *S*-*β*-carboranylthio(seleno)ethyl esters of thioacids of pentavalent phosphorus **128** have been synthesised by the reaction of *O*-ethyl *S*-*β*-bromoethyl methylphosphonothioates or *O*,*O*-diethyl *S*-*β*-bromoethyl phosphothioates with lithium or ammonium derivatives of carboranethiols or carboraneselenols.[54, 71, 73]

$$RCB_{10}H_{10}CXM + Br(CH_2)_2SP(O)(OEt)R' \longrightarrow RCB_{10}H_{10}CX(CH_2)_2SP(O)(OEt)R'$$

128

R = *m*-H, *o*-H, *o*-Me, *o*-Ph; R′ = Me, OEt; X = S, Se; M = Li, Et_3NH.

Among carborane-containing acids of pentavalent phosphorus, some *B*-substituted thio- and selenoesters have also been synthesised and studied. Compounds of this type have been prepared from *o*-carborane-9-thiol **86** or selenol **87** using ordinary reactions typical of derivatives of phosphorus-containing acids. For example, treatment of the thiol **86** or the selenol **87** with pentavalent phosphorus acid chlorides in the presence of Et_3N has resulted in the synthesis of thio- or selenoesters containing one (**129**) or two (**130**) carboranyl groups.[54, 73]

$$HC(B_{10}H_9YH) \xrightarrow[Et_3N]{RR'P(X)Cl} HC(B_{10}H_9YP(X)RR')$$

86,**87** **129**

Y = S (**86**), Se (**87**).

R	R′	X	Y	Yield of **129** (%)
Me	OEt	O	S	69
Me	$OC_6H_4NO_2$-4	O	S	74
Ph	Ph	S	S	67
Me	OEt	O	Se	40
Me	OEt	S	Se	71

$$2\,HC(B_{10}H_9SH) \xrightarrow[2Et_3N]{MeP(O)Cl_2} HC(B_{10}H_9S)_2P(O)Me$$

86 **130** (72%)

Other procedures for the synthesis of *B*-substituted derivatives of carborane-containing acids of pentavalent phosphorus are based on reactions of *o*-carboran-9-yl phosphorothioites or phosphoroselenoites (see Section II).

O,*O*-Diethyl *S*-(*o*-carboran-9-yl) phosphinothioite **88a** is readily oxidised even during chromatography on silica gel to give phosphothioate **91** in 70% yield.[52] The attempt to oxidise the corresponding selenium derivative with atmospheric oxygen gave only decomposition products; however, when furfural has been used as the oxidising agent, the corresponding phosphoselenoate **131** has been obtained in 50% yield.[54]

$$HC(B_{10}H_9XP(OEt)_2) \xrightarrow{[O]} HC(B_{10}H_9XP(O)(OEt)_2)$$

88a, **91** **90**, **131**

X = S (**88a**, **91**), Se (**90**, **131**).

B-Substituted *o*-carborane-containing esters of thio- and seleno-acids of pentavalent phosphorus **132** can also be obtained in 60% – 80% yields by the addition of sulfur or selenium to the corresponding thio- or seleno-derivatives of acids of trivalent phosphorus like **88** and **90**.[51 – 54]

$$HC(B_{10}H_9YPRR') \xrightarrow{X} HC(B_{10}H_9YP(X)RR')$$

132

Y = S (**88**), Se (**90**).

R	R′	X	Y	Yield of **132** (%)
Ph	Ph	S	S	60
Ph	Ph	Se	S	79
OEt	OEt	O	S	70
OEt	OEt	S	S	82
OEt	OEt	Se	S	62
OEt	OEt	S	Se	76
OBu	OBu	S	Se	70
OEt	OEt	Se	Se	69
OBu	OBu	Se	Se	68
OEt	9-*o*-$H_2C_2B_{10}H_9S$	S	Se	93

The reaction conditions depend on the character of substituents at the phosphorus atom. When there are two ethoxy-groups, the addition of sulfur and selenium occurs at room temperature over a period of 36 – 40 h. Compounds in which two phenyl groups or two *o*-carboranyl groups are attached to the phosphorus atom react only on heating in benzene. In the case of *O*-ethyl *S*,*S*-bis(*o*-carboran-9-yl) phosphorodithioite **89**, the addition of selenium yields a product mixture that is difficult to separate.[51, 55]

Several *B*-substituted esters of thioacids of pentavalent phosphorus **132** have been prepared by the Arbuzov reaction from the corresponding *S*-(*o*-carboran-9-yl) phosphorothioites and MeI or EtI.[51, 52] The reactions involve only the phosphorus atom. No products resulting from the reaction at the sulfur atom were detected. When *Se*-(*o*-carboran-9-yl) phosphoroselenoite was made to react with MeI, no Arbuzov products were isolated.[54] The reaction gave only non-identified phosphorus-containing compounds and bis(*o*-carboran-9-yl) diselenide. When Me_2SO_4 was used as the alkylating agent in the reaction with *O*,*O*-diethyl *Se*-(*o*-carboran-9-yl) phosphoroselenoite **90**, the Arbuzov reaction product was isolated in 45% yield (see Scheme 1).[54]

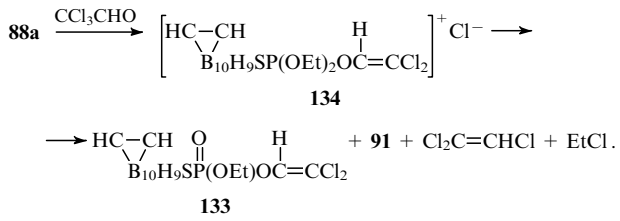
Scheme 1

$$HC(B_{10}H_9YP(OEt)R) \xrightarrow{R'X} HC(B_{10}H_9YP(O)RR')$$

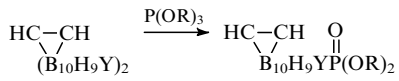
132

R	R′	Y	X	Yield of **132** (%)
OEt	Me	S	I	62
OEt	Et	S	I	65
OEt	Me	Se	SO_4Me	40
9-*o*-$H_2C_2B_{10}H_9S$	Me	S	I	75

Attempts were made to introduce *S*- and *O*-carboran-9-yl esters of acids of trivalent phosphorus into the Perkow reaction.[51 – 53, 55] It was found that *O*-ethyl *S*,*S*-bis(*o*-carboran-9-yl) phosphorodithioite **89** and *S*-(carboran-9-yl) diphenylphosphinothioite **88b** do not react with chloral, whereas *O*,*O*-diethyl *S*-(*o*-carboran-9-yl) phosphorodithioite reacts with chloral according to Perkow to give *O*-ethyl *O*-(2,2-dichloroethenyl) *S*-(*o*-carboran-9-yl) phosphothioate **133** in a yield of 65%.[52, 55] *O*,*O*-Diethyl *S*-(*o*-carboran-9-yl) phosphothioate **91** was also isolated from the reaction mixture. According to GLC analysis, the mixture also contained trichloroethylene and EtCl. This permitted the researchers to suggest that the process involves intermediate formation of quasi-phosphonium compound **134**.[52, 55]

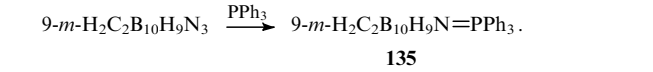


The reaction of bis(*o*-carboran-9-yl) diselenide or bis(*m*-carboran-9-yl) disulfide with trimethyl or triethyl phosphite is a convenient method for the preparation of *B*-substituted carboranyl esters of phosphothioic and phosphoselenoic acids like **132**.[74, 75]

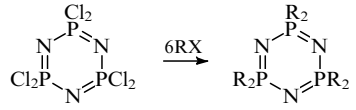


R	Y	Yield of **132** (%)
Me	Se	68
Et	Se	72
Et	S	71

In the series of *B*-substituted phosphorus-containing carboranes, synthesis of carborane-containing phosphinimine **135** is noteworthy. This synthesis has been accomplished by the reaction of *m*-carboran-9-yl azide with PPh_3.[76]

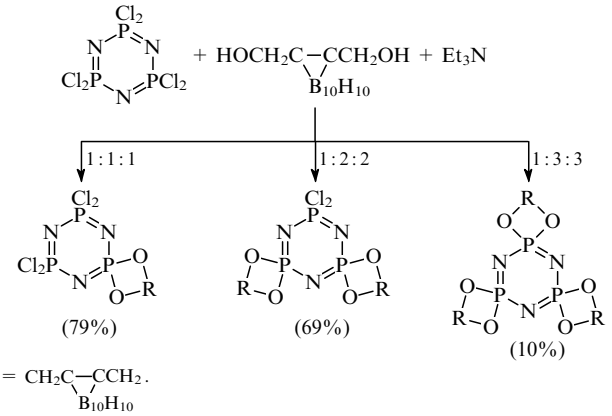


In the series of *C*-substituted derivatives, carborane-containing phosphazenes and polyphosphazenes have been synthesised.[77–82] The reactions of hexachlorocyclotriphosphazene (HCP) with lithio-*m*-carborane and with *m*-carboranethiol in the presence of Et_3N have been described.[77]



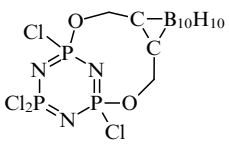
R = $CB_{10}H_{10}CH$, X = Li; R = $SCB_{10}H_{10}CH$, X = H.

The reaction of 1,2-bis(hydroxymethyl)-*o*-carborane **81** with HCP in the presence of Et_3N has resulted in the formation of spiro-compounds. The number of substituted chlorine atoms depended on the ratio of the reactants.[81]



R = $CH_2C(B_{10}H_{10})CH_2$.

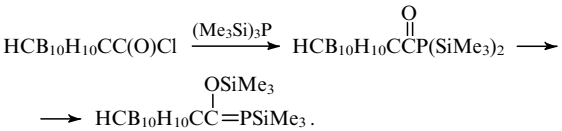
The formation of *ansa*-*o*-carboranylenecyclotriphosphazene has also been observed.[82]



Synthesis of carborane-containing polyphosphazenes by the substitution of carborane-containing groups for the chlorine atoms in polychlorophosphazenes (PCP) has been reported. The reaction was accomplished by treating PCP with lithio-derivatives of *o*- and *m*-carboranes or with *m*-carboranethiol.[77, 79] When 2 or 2.5 moles of *m*-carboranethiol, lithium *o*-carboranylmethoxide or lithium *o*-carboranylmethylphenoxide per mole of PCP was introduced into this reaction, products of replacement of up to 50% of the chlorine were obtained.[77]

The preparation of polymeric carborane-containing phosphazenes by polymerisation of carboranylpentahalodicyclophosphazene has been patented.[80]

In addition to all the carborane-containing organophosphorus compounds listed above, the first, and still the only, derivative of two-coordinate phosphorus **136** has been described. This compound was synthesised by treatment of *m*-carborane-l-carbonyl chloride with tris(trimethylsilyl)phosphine.[83]



IV. Potential fields of application of carborane-containing organophosphorus compounds

The potential practical use of carborane derivatives is substantially restricted by their high cost. This is completely true for the carborane-containing organophosphorus compounds. Nevertheless, there are several patents dealing with practical use of these substances. First of all, this refers to carborane-containing phosphazenes and polyphosphazenes, which have been proposed as thermally stable and flame resistant materials and also as additives decreasing inflammability of polymers and paper.[26, 29, 79, 80]

It has been reported that it is possible to use carborane-containing organophosphorus derivatives as biologically active compounds. In this respect, prospects for using these compounds in the neutron-capture therapy of cancer should be mentioned first.[84–86]

The pesticide, gametocide and bactericide activities of these derivatives have been assayed.[50, 55, 87–89]

Anticholine esterase activities of various esters, thioesters and selenoesters of phosphorus acids have been studied. In the case of compounds in which the carboranyl group is directly attached to the phosphorus atom, this activity is weak and is much lower than that of similar phosphorus derivatives devoid of the carboranyl groups.[50, 87]

For derivatives of thioacids of pentavalent phosphorus in which the carboranyl group is incorporated in the ester moiety, the anticholine esterase activity has been found to be higher than that of the corresponding thioesters without carboranyl group.[55, 88]

The pesticide properties have been tested most extensively for the 2,2-dichlorovinyl carboranylphosphonates. Weak insectoacaricide and relatively low herbicide and fungicide activities have been found.[50] These derivatives were also found to exhibit high gametocide activities. Good prospects for using them in the production of hybrid wheat seed were shown.[50]

Some *o*-carboran-9-yl esters of phosphorus thioacids have been found to exhibit bactericide activities.[89]

V. Conclusion

The most interesting aspect of the information given above is the properties of carborane-containing organophosphorus compounds and their comparison with the properties of similar compounds devoid of the carboranyl group.

closo-Dicarbadodecaboranes are known to be electron-deficient systems with respect to substituents at the carbon atom, the strongest electron-withdrawing effect being observed in the case of the *ortho*-isomer, whereas the weakest effect being typical of the *para*-isomer. The reactivities of these compounds can also be markedly influenced by steric factors caused by the large size of the carboranyl groups.

The above factors influence most crucially reactions of those carborane-compounds in which the carboranyl group is linked directly to a trivalent phosphorus atom. The nucleophilicity of the phosphorus atom in these compounds is substantially decreased; hence, oxidation, addition of sulfur and azides, the Arbuzov and Perkow reactions, *etc*., occur under more drastic conditions than those for conventional derivatives of trivalent phosphorus. The influence of steric factors also cannot be neglected; however, it is often difficult to distinguish it from the electronic influence. In some cases, a carboranyl group attached to a phosphorus atom can act as a pseudo-halogen atom in reactions with nucleophilic reagents, which occur with rupture of the phosphorus – carborane carbon bond.

B-Substituted carborane-containing organophosphorus compounds in which the phosphorus atom is connected to the carboranyl group *via* a sulfur or selenium bridge are more reactive than similar *C*-substituted derivatives. This is apparently due to the fact that carboranylthio- or carboranylselenio-groups exert an electron-donating effect, and the nucleophilicity of the phosphorus atom thus increases. In this case, steric factors are less significant than for *C*-substituted compounds.

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