Russian Chemical Reviews **74** (9) 781 – 805 (2005) © 2005 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2005v074n09ABEH001182

Organic chemistry of elemental phosphorus

V A Milyukov, Yu H Budnikova, O G Sinyashin

Contents

I. Introduction 781
II. Activation and transformations of a white phosphorus molecule in a metal coordination sphere 782
III. Reactions of white phosphorus with nucleophilic and electrophilic reagents 790
IV. Electrochemical methods for the synthesis of organophosphorus compounds from elemental phosphorus 798

Abstract. The principal achievements and the modern trends in the development of the chemistry of elemental phosphorus are analysed, described systematically and generalised. The possibilities and advantages of the preparation of organophosphorus compounds directly from white phosphorus are demonstrated. Attention is focused on the activation and transformation of elemental phosphorus in the coordination sphere of transition metal complexes. The mechanisms of the reactions of white phosphorus with nucleophilic and electrophilic reagents are discussed. Electrochemical approaches to the synthesis of organic phosphorus derivatives based on white phosphorus are considered. The bibliography includes 251 references.

I. Introduction

The extensive use of organic derivatives of phosphorus in various branches of industry imposes certain requirements on the methods of their preparation. Until recently, phosphorus chlorides and their derivatives (oxy- and thiochlorides) have served as the main starting reagents for the synthesis of compounds containing an organic substituent at a phosphorus atom. Industrial methods for the production of organophosphorus compounds (OPC) by direct chlorination of white phosphorus and by substitution of organic ligands for the chlorine atoms suffer from a number of serious drawbacks. The first one is evolution of large amounts of hazardous and corrosive wastes (hydrogen chloride, alkyl halides, *etc*.), which damage the process equipment and are harmful for the environment. Modern requirements for environmental safety of industrial plants dictate the need to develop OPC production processes free from the chlorination stage. This has attracted attention to the chemistry of elemental phosphorus.

The search for highly efficient methods for the synthesis of OPC from elemental phosphorus, long carried out in scientific centres of the world, has resulted in the discovery of a large number of new reactions. The chemical behaviour of phosphorus with respect to reagents of different nature was investigated.

Elemental phosphorus has two allotropes, white and red phosphorus. The white phosphorus molecule is a P_4 tetrahedron with a P–P bond length of 2.21 Å. The ring strain and the presence of vacant p orbitals and a lone pair at each P atom account for its high reactivity. Red phosphorus has a planar layered polymeric structure; therefore, it is chemically more inert than white phosphorus.

In many cases, reactions involving white and red phosphorus are of the same type, although they differ in their rates and conditions of conduction. For this reason, we consider them in the same review. It should be noted, however, that irregularities in the polymeric structure of red phosphorus hamper investigation of the mechanisms of its reactions and identification of intermediates, whereas the molecular structure of white phosphorus unambiguously indicates that its reactions would require cleavage of the P_4 tetrahedron. This permits one to predict the structures of intermediates and to control the process.

In the last 15 years, phosphorus chemistry has undergone a qualitative change. The line of research dealing with methods for activatiing white phosphorus in the coordination sphere of transition metal complexes has been developed most appreciably. Meanwhile, the existing reviews dealing with the chemistry of elemental phosphorus[1–12] consider only particular aspects and give no general view of the new trends in this field of chemistry. We have attempted to generalise and analyse the information on the chemistry of elemental phosphorus published in recent years from modern standpoint.

This review considers the reactions of elemental phosphorus that take place under relatively mild conditions. In these reactions, intermediates can be detected and, in some cases, even isolated, which provides information on the reaction mechanisms. Attention is concentrated on the chemical behaviour of white phosphorus towards organic transition metal complexes. This is one of the most convenient and promising approaches to investigatiing the transformation routes of the P_4 molecule. Determination of the structures of the intermediates underlies the development of new catalytic processes for the preparation of organophosphorus compounds directly from white phosphorus. This study considers the reactions of white phosphorus with organic and organometallic compounds from a unified standpoint, which clearly demonstrates the relationship between various fields of chemistry. A special section is devoted to reactions of white phosphorus with organic substrates under electrochemical activation, which is a promising method for the preparation of organophosphorus compounds from elemental phosphorus under mild conditions.

V A Milyukov, Yu G Budnikova, O G Sinyashin A E Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre of the Russian Academy of Sciences, ul. Akad. Arbuzova 8, 420088 Kazan, Russian Federation. Fax (7-8432) 75 22 53, tel. (7-8432) 73 23 92, e-mail: miluykov@iopc.knc.ru (V A Miluykov), yulia@iopc.knc.ru (Yu G Budnikova), tel. (7-8432) 73 93 64, e-mail: oleg@iopc.knc.ru (O G Sinyashin)

Received 29 December 2004
Uspekhi Khimii **74** (9) 859 – 885 (2005); translated by Z P Bobkova

II. Activation and transformations of a white phosphorus molecule in a metal coordination sphere

Despite certain progress in the study of the mechanisms of OPC formation from white phosphorus, these reactions have not been fully investigated as yet. The search for and the development of new methods for the preparation of phosphorus-containing derivatives are based on the elucidation of the rules of cleavage of the P_4 molecule and the factors governing the formation of new compounds (including the structures and transformation pathways of the intermediates). This task is complicated by the high reactivity of white phosphorus and the instability of intermediates formed. In addition, the transformations of P_4 into the target products require fairly drastic conditions.

For the correct interpretation of data on the structures and chemical properties of phosphorus intermediates, one can use the isolobal analogy principle,[13] which is the key link [14] and a sort of 'bridge between organic and inorganic chemistry and, hence, supports the continuity of chemistry as a whole'.[15] According to this principle, 'two fragments are isolobal if the number, symmetry properties, approximate energy and shape of the frontier orbitals, and the number of electrons in them are similar — not identical but similar.'[13] Thus, the phosphorus atom is isolobal to the CH fragment, which allows one to draw analogies between the usual organic compounds and the phosphorus fragments formed upon transformation of a white phosphorus molecule.

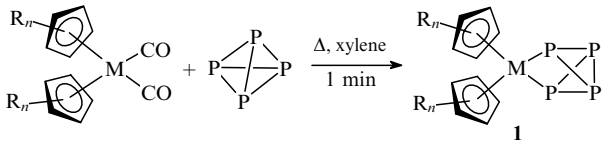
Study of the behaviour of the white phosphorus molecule in the coordination sphere of transition metal complexes is a promising approach that allows one to clarify the complex processes of opening of the initial P_4 molecule and OPC formation. The transition metal atom acts as a sort of stabiliser for all phosphorus intermediates, ranging from the simple phosphide anion to complex phosphorus oligomers P_n containing up to 14 phosphorus atoms. The reactions of these complexes with other transition metal derivatives and with organic compounds may underlie the design of production processes of organic and organoelement phosphorus compounds directly from elemental phosphorus.[7,8]

Researchers who try to classify the reactions of white phosphorus with transition metal complexes are faced with the problem of identification of the diverse products formed in this seemingly simple reaction. Here we try to avoid the classifications used previously. Cleavage of the P_4 tetrahedron is considered from the standpoint of a relationship between the structures of the initial complex (the electronic structure of the metal, the presence of vacant and latent coordination sites, and the ligand nature and stereochemistry) and the phosphorus intermediates stabilised in the metal coordination sphere. In our opinion, by using this approach, one can consider more comprehensively the activation of white phosphorus in the metal coordination sphere and identify the factors that determine the structure of the phosphorus fragment in the metal complex formed.

1. Derivatives of Group IVB metals (Ti, Zr, Hf)

The chemical behaviour of white phosphorus towards Group IVB metal derivatives has been little studied. A probable reason for this is the low stability of the complexes formed, which can be attributed, from the standpoint of the hard and soft acid–base (HSAB) theory,[16] to the low affinity of the phosphorus atom (soft base) for Group IVB metal atoms (soft acids).

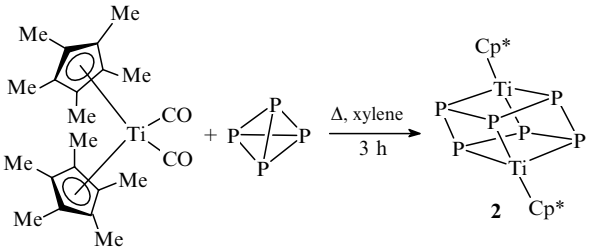
The reaction of white phosphorus with zirconium or hafnium bis(cyclopentadienyl)dicarbonyl complexes occurs *via* elimination of two carbonyl ligands, giving rise to bicyclo[1.1.0]tetraphosphabutane **1** stabilised in the metal coordination sphere.[17] The yields of complexes **1** are nearly quantitative.



1

M = Zr, Hf; R = Bu^t, 1,3-Bu^t_2.

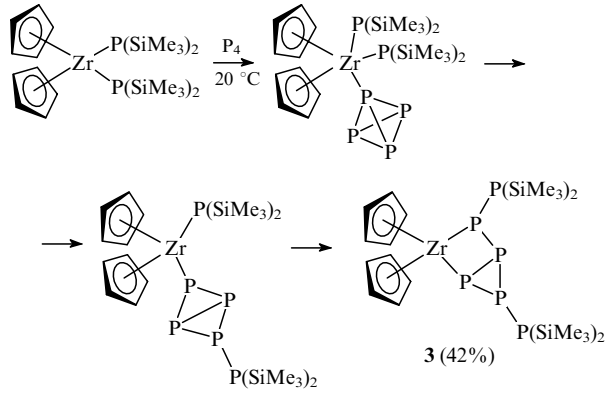
In the case of the bis(pentamethylcyclopentadienyl) titanium derivative, the reaction requires more drastic conditions.[18] Elimination of not only the CO groups but also one pentamethylcyclopentadienyl ring takes place. This gives a triple-decker compound of titanium **2** containing a μ,η^3,η^3-distorted hexaphosphacyclohexane in the chair conformation (yield 19%). Note that the change in the structure of the phosphorus ligand is directly related to the change in the titanium coordination number.



2

Cp* is pentamethylcyclopentadienyl.

The structure of the phosphorus fragment also depends on the coordination environment of the metal. The replacement of the carbonyl groups in the zirconium dicyclopentadienyl complex by phosphide groups switches the route of reactions with white phosphorus, which now give under mild conditions, instead of complexes **1**, metal complexes **3** with basically different phosphorus ligands.[19] The reaction pathway considered by the authors includes the activation of white phosphorus *via* complexation to a coordinatively unsaturated zirconium atom and the subsequent double intramolecular rearrangement.



3 (42%)

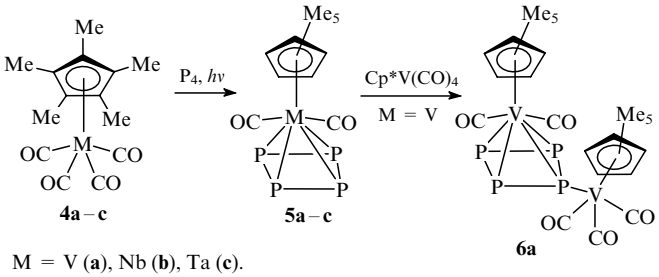
An X-ray diffraction study has shown that the P–P bond length in the cyclo-P_3-fragment of complex **3**, equal to 2.213 Å, differs little from the bond length in the P_4 molecule.

Thus, it can be seen from the above examples that in the reactions of white phosphorus with transition metal complexes, the nature of the ligands has a substantial influence on the structure of the phosphorus fragment formed.

2. Derivatives of Group VB metals (V, Nb, Ta)

The outcome of the reactions of white phosphorus with (cyclopentadienyl)carbonyl derivatives of vanadium group metals is a vivid example demonstrating the dependence of the structure of the polyphosphorus fragments stabilised in the metal coordination sphere on the process conditions.[20–22] For example, photochemical substitution of the carbonyl groups in compounds **4a–c**

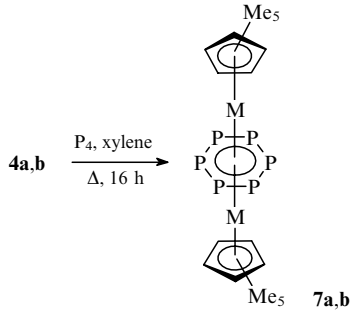
by a white phosphorus molecule yielded a product mixture which was separated by column chromatography to give organometallic tetraphosphacyclobutane derivatives **5a–c**. In the case of vanadium, the reaction did not stop at this stage but proceeded to give binuclear complex **6a**. It is of interest that the reaction of P_4 with tantalum 1,3-di-*tert*-butylcyclopentadienyl complex followed a more complicated route, resulting in a polynuclear complex $[(Cp''Ta)_3(\mu_3\text{-}P_4)(\mu_3\text{-}P_2)]$ (Cp'', 1,3-di-*tert*-butylcyclopentadienyl).[22]



M = V (**a**), Nb (**b**), Ta (**c**).

According to X-ray diffraction, the phosphorus atom in niobium complex **5b** is slightly disordered; this should be considered as the initial stage of decomposition of the P_4-ring into P_3- and P_1-fragments.

The same reactions carried out under thermolysis conditions (refluxing in xylene, 16 h) result in a different structure of the phosphorus ligands formed. The triple-decker compounds **7a**,**b** containing cyclo-P_6, isolobal to benzene, as the central fragment were formed as the major products in the reaction of complexes **4a**,**b** with white phosphorus.[15, 17, 20, 23]

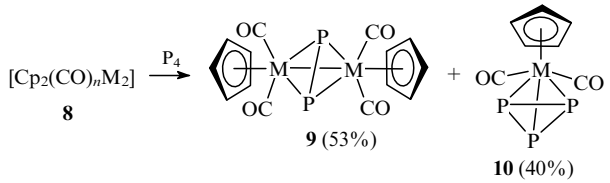


M = V (**a**), Nb (**b**).

The ^{51}V NMR spectrum of vanadium derivative **7a** exhibits a septet with the spin–spin coupling constant $^1J(^{51}V^{31}P) = 56$ Hz, which confirms the structure of the complex.

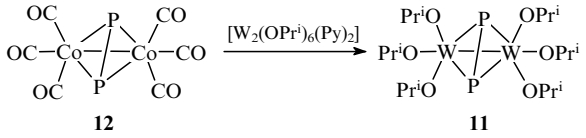
3. Derivatives of Group VIB metals (Cr, Mo, W)

The reactions of cyclopentadienylcarbonyl complexes formed by chromium group metals with white phosphorus are most studied. A number of research groups have detected various phosphorus intermediates stabilised in the metal coordination sphere. For example, the reaction of organometallic compounds **8** with white phosphorus yields a mixture of transition metal complexes **9** and **10**, containing μ,η^2-diphosphorus and μ^3-triphosphacyclopropane ligands, respectively.[23–25]



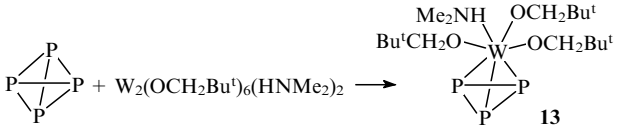
n = 4: M = Mo, W; n = 6: M = Cr, Mo, W.

According to the isolobal analogy theory, both compounds represent a P_4 molecule in which one or two phosphorus atoms have been replaced by a 15-electron organometallic fragment $[P{\leftrightarrow}M(CO)_3]$. The tungsten alkoxide complex **11**, containing a μ,η^2-coordinated diphosphine as an additional ligand, was prepared using diphosphine transfer from cobalt derivative **12**. The reaction takes place under mild conditions to give the target product in a high yield.[26]

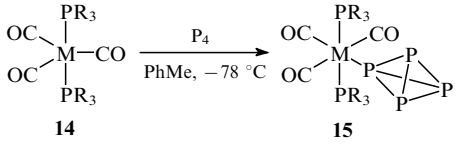


Py is pyridine.

However, the direct introduction of white phosphorus into the reaction with tungsten alkoxide results in metal complex **13**, containing a η^3-triphosphacyclopropane fragment.[27, 28]



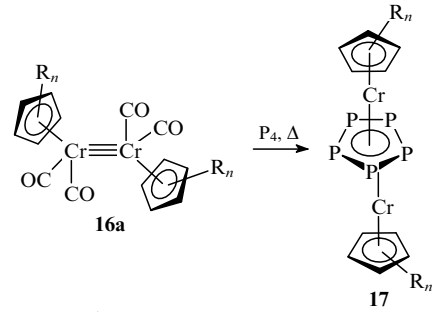
The change in the electronic state of tungsten on passing from cationic to neutral complexes and the appearance of bulky ligands both influence the structure of the phosphorus fragment formed. At low temperatures, coordinatively unsaturated tungsten and molybdenum complexes **14** form derivatives **15** containing an intact molecule of white phosphorus.[29]



M = W: R = cyclo-C_6H_{11} (Cy), Pr^i; M = Mo: R = Cy.

The structure of complexes **15** has only been proved[29] by ^{31}P NMR spectroscopy as these compounds are stable only in toluene at a temperature below -40 °C.

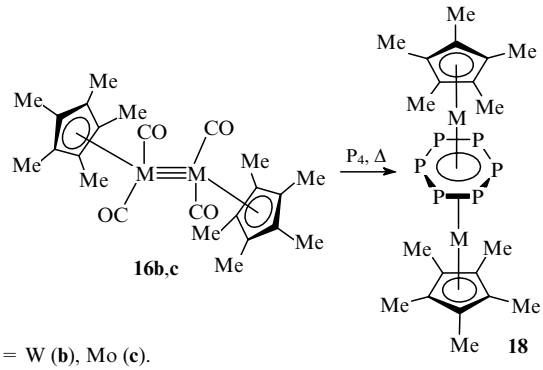
Thermolysis of white phosphorus in the presence of bis(cyclopentadienyl)dicarbonyldichromium **16a** affords a 27-electron triple-decker paramagnetic ($\mu = 2.07\,\mu_B$) chromium complex **17**, containing a μ,η^5-pentaphosphacyclopentadienyl ligand.[30]



R_n = Me_5, Bu^t.

A cyclic voltammetry study of the electrochemical properties of compounds **17** has shown that they can be either reversibly reduced ($E_{red} = -0.97$ V) or reversibly oxidised ($E_{ox} = 0.07$ V). For preparative purposes, ferrocenium derivatives $[Cp_2Fe]^+$ have been proposed as the oxidants.[31]

Thermolysis of white phosphorus in the presence of similar molybdenum and tungsten derivatives **16b**,**c** is also accompanied by the elimination of all carbonyl groups, and gives 28-electron triple-decker complexes **18**, containing hexaphosphabenzene as a ligand.[23, 32–34]

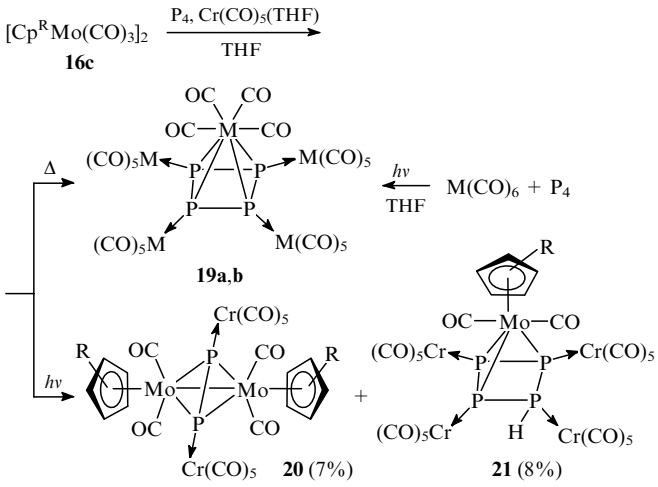


16b,**c** **18**

M = W (**b**), Mo (**c**).

According to quantum-chemical data obtained for the model compound [$CpMoP_6MoCp$],[35] the optimal number of valence electrons for this complex is 28. For this reason, complexes **18** are distinguished by high thermal stability and resistance against oxidation by air oxygen.

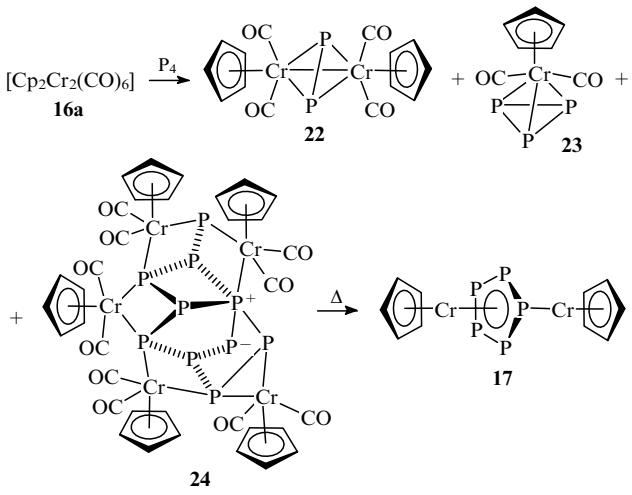
Scheer *et al.*[36] have proposed a method for investigation of the mechanism of P_4 cleavage. The method consists of conducting the reactions with organometallic compounds in the presence of labile metal complexes [as a rule, $Cr(CO)_5(THF)$]. This method was successfully used to study the reactions of white phosphorus with the molybdenum dimer $[Cp^RMo(CO)_3]_2$ (**16c**) (hereinafter Cp^R designates a cyclopentadienyl fragment containing an R substituent).[36] Heating a mixture of reactants in THF affords polynuclear complex **19a**, containing a distorted tetraphosphacyclobutane fragment. It is noteworthy that this complex and similar tungsten derivative **19b** were prepared previously by the photolysis of a mixture of white phosphorus and metal hexacarbonyl (of chromium or tungsten, respectively).[37, 38]



16c **19a**,**b** **20** (7%) **21** (8%)

M = Cr (**a**), W (**b**); R = Bu^t.

The photochemical reaction of dimer **16c** with white phosphorus in the presence of $Cr(CO)_5(THF)$ (UV irradiation) yielded compound **20**, containing a P_2 fragment, and unusual complex **21**. The formation of the P–H bond in the latter compound was interpreted [36] as being due to hydrolysis of the Mo–P bond by traces of water. The modelling of the last-mentioned reaction for a white phosphorus molecule and chromium compound **16a** (R = H) in the absence of other chromium derivatives resulted in the formation of two tetrahedral chromium complexes, **22** (with the composition $[\{CpCr(CO)_2\}_2(\mu,\eta^{2:2}\text{-}P_2)]$ similar to molybdenum derivative **20**) and **23** ($[CpCr(CO)_2(\eta^3\text{-}P_3)]$ with the cyclo-P_3 fragment as the ligand), and polynuclear phosphorus-containing complex **24**.[24, 39]



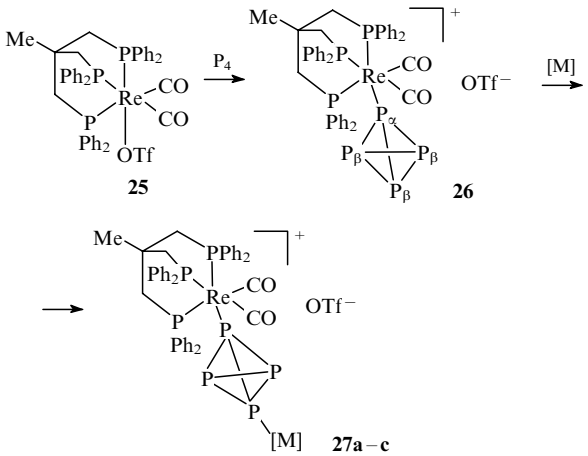
16a **22** **23** **24** **17**

Thermolysis of this mixture furnished a triple-decker chromium complex **17** (R = H), containing a pentaphosphacyclopentadienyl ligand.[30] This reaction clearly demonstrates the ability of the phosphorus atom to form complex oligomers. Also noteworthy are the difficulties that arise in the studies of multicomponent reaction mixtures formed in the reactions of white phosphorus with transition metal derivatives.

4. Derivatives of group VIIB metals (Mn, Re)

The chemical transformations of white phosphorus under the action of manganese group metal derivatives have been little studied. Only two examples have been described in the literature.[40, 41] The rhenium carbonyl complex **25** with a bulky 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) ligand reacts with white phosphorus under mild conditions to give charged rhenium compound **26**, containing an intact P_4 molecule as a ligand. The properties of the molecule are typical of trivalent phosphorus derivatives.[40] The P_4 ligand in complex **26** is coordinated by rhenium and ruthenium derivatives under mild conditions, giving rise to homo- and heterobinuclear complexes **27a**–**c**,[41] which also contain a P_4 ligand.

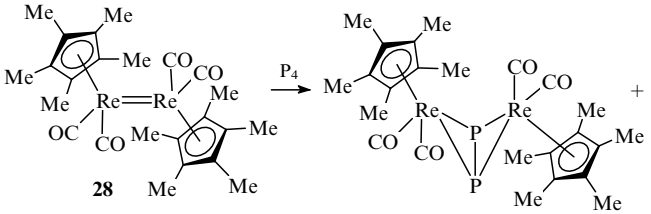
The formation of binuclear complexes **27** was demonstrated by ^{31}P NMR spectroscopy. Indeed, without additional splitting from NMR-active phosphorus or metal nuclei, complexes with a P_4 ligand exhibit a well-resolved AB_3-system. The signal of the P_α atom shifts by 200–250 ppm, whereas the position of the signal from P_β almost coincides with that for the free white phosphorus molecule.



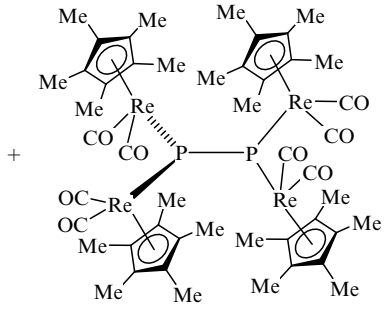
25 **26** **27a**–**c**

[M] = (triphos)$Re(CO)_2(OTf)$ (**a**), $Cp^*Re(CO)_2$ (**b**), $Cp^*Ru(PEt_3)_2(OTf)$ (**c**).

It has been suggested[42] that transition metal complexes containing an intact P_4 molecule as a ligand are stable only when bulky ligands are present near the metal atom. The change in the ligand environment of rhenium changes the structure of the final reaction products. The reaction of white phosphorus with the 16-electron intermediate $Cp^*Re(CO)_2$, generated from the corresponding dimer **28**, gives a mixture of rhenium complexes **29** and **30**, differing in coordination number and, hence, in the type of coordination of the P_2 ligand.[43,44]



28 **29**



30

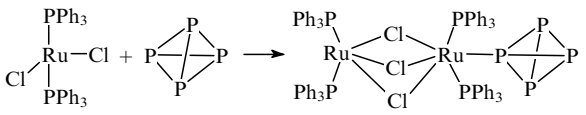
Thus, these examples demonstrate the important role of steric factors for realising of a particular route of transformation of white phosphorus in the presence of transition metal complexes.

5. Derivatives of Group VIIIB metals

Published data on the reactions of white phosphorus with group VIIIB metal derivatives are very abundant. The ready availability of the initial compounds, the ease of processing and the stability of the final products are the factors that lead to success in these studies. Almost all types of phosphorus intermediates resulting from cleavage of the P_4 tetrahedron followed by aggregation of the phosphorus species have been stabilised in the coordination sphere of Group VIIIB metals. These complexes were isolated and characterised by various physicochemical methods. In addition, Group VIIIB metals allowed researchers to demonstrate the relationship between the structure of the starting metal complexes (the presence of vacant coordination sites, steric and electronic characteristics of the ligands) and the structure of the metal-coordinated phosphorus fragments.

a. Iron group metal derivatives

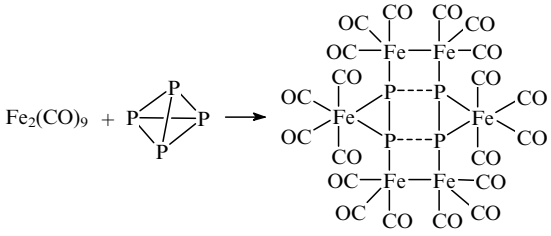
As noted above, the P_4 molecule can act as a η^1-ligand when bulky ligands are present in the metal atom environment.[41] The first binuclear complex **31**, containing a η^1-P_4 ligand, has been prepared[45] in a study of the hydrogenation of white phosphorus in the presence of a homogeneous catalyst, bis(triphenylphosphine)ruthenium(II) chloride.



31

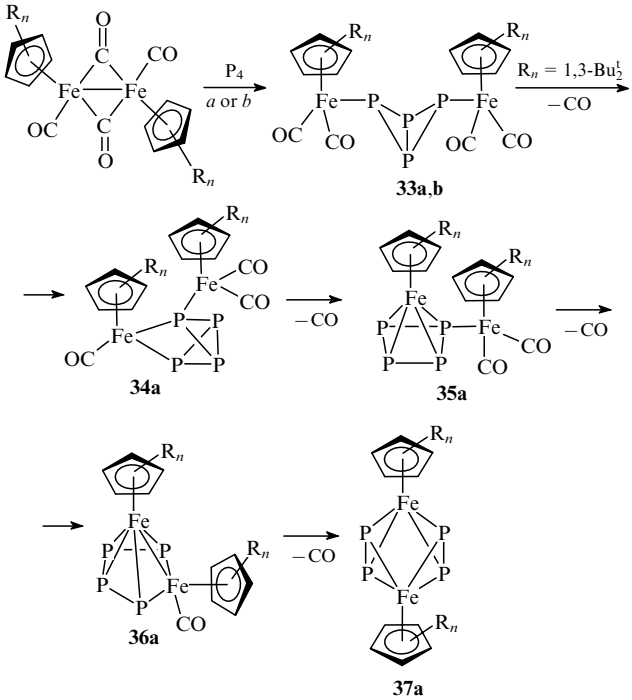
The poor solubility and the low stability of compound **31** precluded[45] its full characterisation; only its ^{31}P NMR spectrum was reported.

Thermolysis of a mixture of white phosphorus and iron carbonyl $Fe_2(CO)_9$ results in partial decarbonylation. Four phosphorus–phosphorus bonds are cleaved during the reaction. This gives cluster **32** containing two separated P_2 fragments.[46]



32

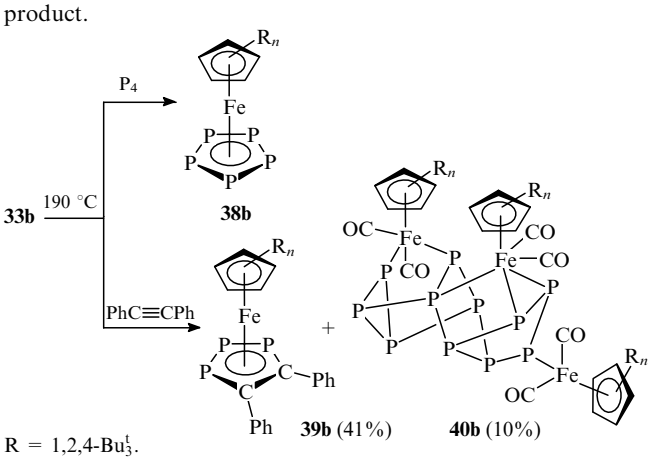
The most important and interesting results were obtained for the reactions of white phosphorus with cyclopentadienylcarbonyl complexes of iron group metals. The study by Scherer *et al.*[47] made a significant contribution to investigations of the activation of white phosphorus in the coordination sphere of transition metals and the mechanism of P_4 cleavage. This study is devoted to the transformations of white phosphorus under the action of binuclear (cyclopentadienyl)carbonyliron complexes $[Cp^RFe(CO)_2]_2$, which contain sterically crowded ligands. It was shown that photolysis of $[Cp''Fe(CO)_2]_2$ (Cp'' is 1,3-di-*tert*-butylcyclopentadienyl) yields two 17-electron $Cp''Fe(CO)_2$ fragments, and one P–P bond in the P_4 molecule is cleaved to give complex **33a** with the composition $[Cp''Fe(CO)_2]_2(\mu,\eta^{4:1}\text{-}P_4)$. This complex loses one carbonyl group under the reaction conditions, being converted into the binuclear adduct **34a**, whose formula is $\{Cp''Fe(CO)_2\}[\{Cp''Fe(CO)\}(\mu,\eta^{1:2}\text{-}P_4)]$ and in which the geometry of the P_4 ligand is essentially preserved. The subsequent photochemical elimination of CO affords a 13-electron iron complex **35a**, in which the metal atom is easily inserted into the phosphorus–phosphorus bond to give a sandwich type complex **36a** with an almost planar five-membered P_4Fe ring. The elimination of a CO ligand from complex **36a** induces an intramolecular rearrangement of the FeP_4 ring into triple-decker complex **37a**, $[\{Cp''Fe\}_2(\mu,\eta^{4:4}\text{-}P_4)]$, in which the tetraphosphabutane fragment is connected to two equivalent $\{Cp''Fe\}$ residues.



33a,**b** **34a** **35a** **36a** **37a**

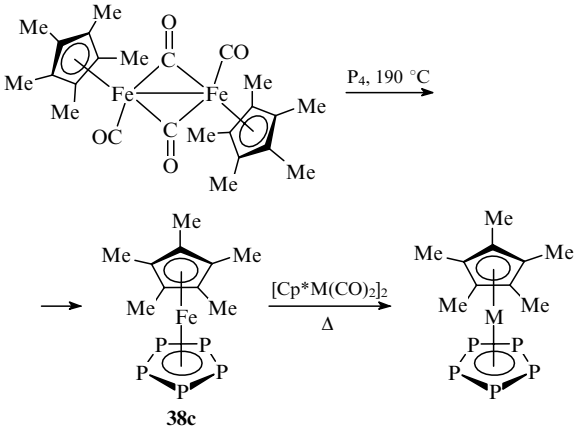
(*a*) *hv*; (*b*) toluene, 110 °C, 2 min; R = 1,3-Bu^t_2 (**a**), 1,2,4-Bu^t_3 (**b**).

The structure of the binuclear complex **33**, containing bicyclo[1.1.0]tetraphosphabutane as the ligand and first proposed on the basis of spectroscopic data,[47–49] was recently proved by the X-ray diffraction of **33b** (R_n = 1,2,4-Bu^t_3). It has been shown[50] that the process considered above can be terminated after the formation of compound **33** by introducing one more *tert*-butyl substituent into the cyclopentadienyl ring of the initial complex. In this case, the reaction with white phosphorus proceeds in toluene on heating to 110 °C over a period of 2 min. The resulting binuclear complex **33b** can react with excess white phosphorus at 190 °C to give 1,2,4-tri-*tert*-butylpentaphosphaferrocene **38b**.[51] Under these conditions, compound **33b** and diplenylacetylene form sandwich iron complex **39**, in which one ligand is 4,5-diphenyl-1,2,3-triphosphacyclopentadiene, an isolobal analogue of the cyclo-P_5 ligand. In the last-mentioned reaction, polynuclear phosphorus-containing complex **40** was also isolated as a side product.



R = 1,2,4-Bu^t_3.

The introduction of five methyl substituents instead of the *tert*-butyl groups into the cyclopentadienyl ring of the initial Fe complex changes crucially the process route. Thermolysis of a mixture of white phosphorus and bis(pentamethylcyclopentadienyl)dicarbonyliron $[Cp^*Fe(CO)_2]_2$ in xylene affords pentamethylpentaphosphaferrocene Cp^*FeP_5 in ~15% yield. This reaction has become an important stage of development of the organometallic chemistry of highly reactive phosphorus intermediates.[52,53]

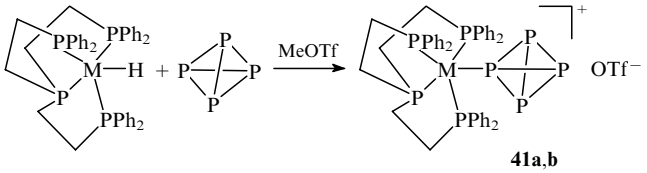


M = Ru, Os.

Raising the reaction temperature to 190 °C increased the yield of the target product **38c** to 80%.[54] The ruthenium and osmium sandwich compounds containing a pentaphosphacyclopentadienyl fragment were obtained in moderate yields on heating complex **38c** with bis(pentamethylcyclopentadienyl)dicarbonylmetals $[Cp^*M(CO)_2]_2$ (M = Ru, Os) at 220–250 °C.[55]

b. Derivatives of cobalt group metals

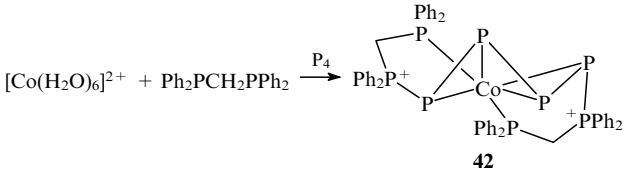
As shown above, transition metal complexes containing an intact P_4 molecule are stable only in the presence of bulky ligands at the metal atom.[42] Derivatives of cobalt and rhodium hydrides with the tris[2-(diphenylphosphino)ethyl]phosphine ligand are convenient starting compounds for the preparation of complexes containing a P_4 molecule. The reductive elimination of the hydride ion on treatment with methyltrifluoromethanesulfonate (MeOTf) affords a coordinatively unsaturated intermediate, which coordinates white phosphorus under mild conditions giving rise to cationic complexes **41a**,**b**, containing an intact P_4 molecule.[56,57]



M = Co (**a**), Rh (**b**).

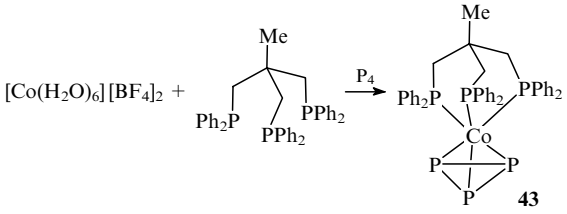
Like W and Mo derivatives, complexes **41a**,**b** are stable only at low temperatures (< −40 °C).

The use of transition metal complexes containing other phosphines as ligands in reactions with white phosphorus results in the generation of diverse phosphorus fragments which can be stabilised in a metal coordination sphere. For example, in the presence of bis(diphenylphosphino)methane, the aqua complexes of $Co(BF_4)_2$ are converted into mononuclear complex **42**, containing an unusual P_6 ligand formed by four phosphorus atoms of the P_4 molecule and two phosphorus atoms of the phosphine.[58]

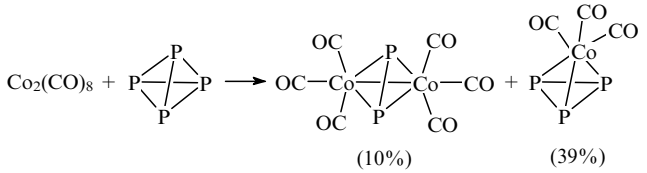


An X-ray diffraction study of complex **42** has shown that all atoms of the P_4 fragment are coordinated to cobalt. The phosphorus–phosphorus bond lengths are 2.17–2.19 Å, *i.e.*, they are shorter than the bond length in P_4 (2.21 Å).

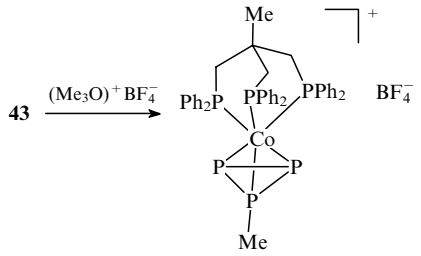
The introduction of 1,1,1-tris(diphenylphosphinomethyl)ethane into this reaction results in cobalt compounds **43**, containing a cyclo-P_3 fragment.[59]



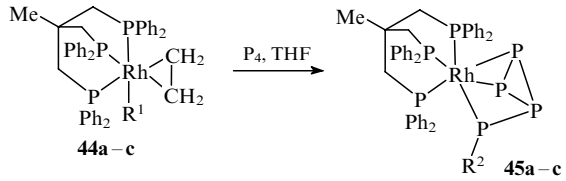
Cobalt complexes containing similar phosphorus ligands are also formed on treatment of white phosphorus with dicobalt octacarbonyl.[60,61]



Using complex **43**, it has been demonstrated that a phosphorus–carbon bond can be formed in these systems by treatment with trimethyloxonium tetrafluoroborate, resulting in the methylation of one phosphorus atom; the structure of the triphosphacyclopropane fragment remains unchanged.[62]



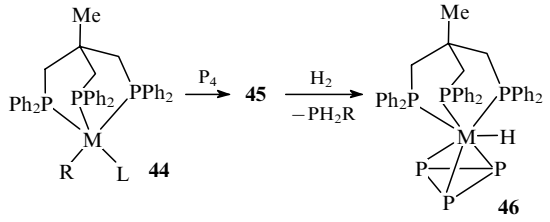
A scheme for the formation of the cyclo-P_3 fragment upon the destruction of P_4 has been proposed after an investigation of the reaction of white phosphorus with rhodium and cobalt compounds.[63, 64] It was shown that on treatment with rhodium complexes **44a**,**b** under mild conditions, the P_4 tetrahedron is converted into an unusual $\eta^{2:1}$-P_4R ligand, which is stabilised in the coordination sphere of the metal. A similar Rh complex **45c** has been obtained from hydride derivative **44c**. The same transformations are known for iridium.



44a–c **45a–c**

$R^1 = R^2 = Me$ (**a**), Ph (**b**); $R^1 = H$, $R^2 = Et$ (**c**).

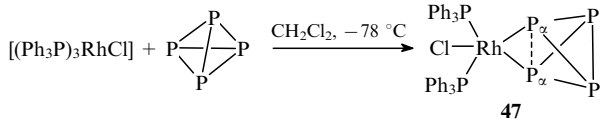
These reactions are among the first examples of the formation of compounds with P–C bonds from white phosphorus by the participation of a metal complex; they also represent the first examples of metal-mediated direct transfer of an organic fragment to phosphorus coordinated as a tetrahedron. Hydrogenation of **45** yields alkylphosphine PH_2R and a stable non-reactive compound **46** containing the cyclo-P_3 ligand.[42]



44 **45** **46**

M = Rh, Ir; L = H_2, R = H; L = C_2H_4: R = H, Me, Et, Ph.

The generation of a highly reactive bicyclo[1.1.0]tetraphosphabutane and its subsequent stabilisation in a metal coordination sphere is observed in the reaction of P_4 with Wilkinson's catalyst or other square planar Rh(I) or Ir(I) complexes.[65, 66] At low temperatures, one triphenylphosphine molecule is eliminated to give rhodium complex **47** containing a η^2-P_4 fragment.

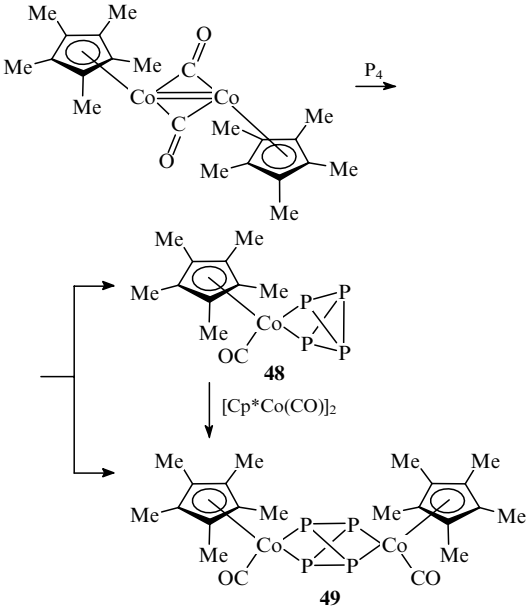


47

This reaction can formally be considered as an oxidative addition of a white phosphorus molecule with a simultaneous increase in the rhodium coordination number.

The structure of (bicyclo[1.1.0]tetraphosphabutane)bis(triphenylphosphine)rhodium **47** was proved by X-ray diffraction. The η^2-coordination of the P_4 fragment results in an increase in the $P_\alpha-P_\alpha$ bond length to 2.4616 Å. This type of coordination was previously predicted theoretically by Albright *et al.*[67] for the model complex $[(PH_3)_2ClRhP_4]$, in which the η^2-coordination of the P_4 fragment proved to be 15 kcal mol^{-1} more favourable than the η^1-coordination.[67] However, the computation data do not provide an unambiguous answer to the question of whether or not the structure of the white phosphorus molecule is retained or whether the oxidative addition takes place due to cleavage of the phosphorus–phosphorus bond.

On the basis of experimental data, one can conclude that the initial formation of bicyclo[1.1.0]tetraphosphabutane fragment is a general step in the opening of the white phosphorus molecule on treatment with transition metal derivatives. The formation of metal complexes is the result of the subsequent transformation of this intermediate and depends on the reaction conditions (first of all, on the reactant ratio). The η^2-coordination of the P_4 fragment, arising from the cleavage of one P–P bond in the P_4 tetrahedron of metal complex **48**, is observed upon reaction of the white phosphorus with (pentamethylcyclopentadienyl)carbonylcobalt $[Cp^*(CO)_2]_2(Co=Co)$.[68] This reaction may also involve the simultaneous cleavage of two P–P bonds, giving rise to complex **49** with a bridging $\mu,\eta^{2:2}$-tetraphosphacyclobutane ligand. Note that complex **49** was obtained in 30% yield on treatment of compound **48** with an excess of the initial metal complex.[68]



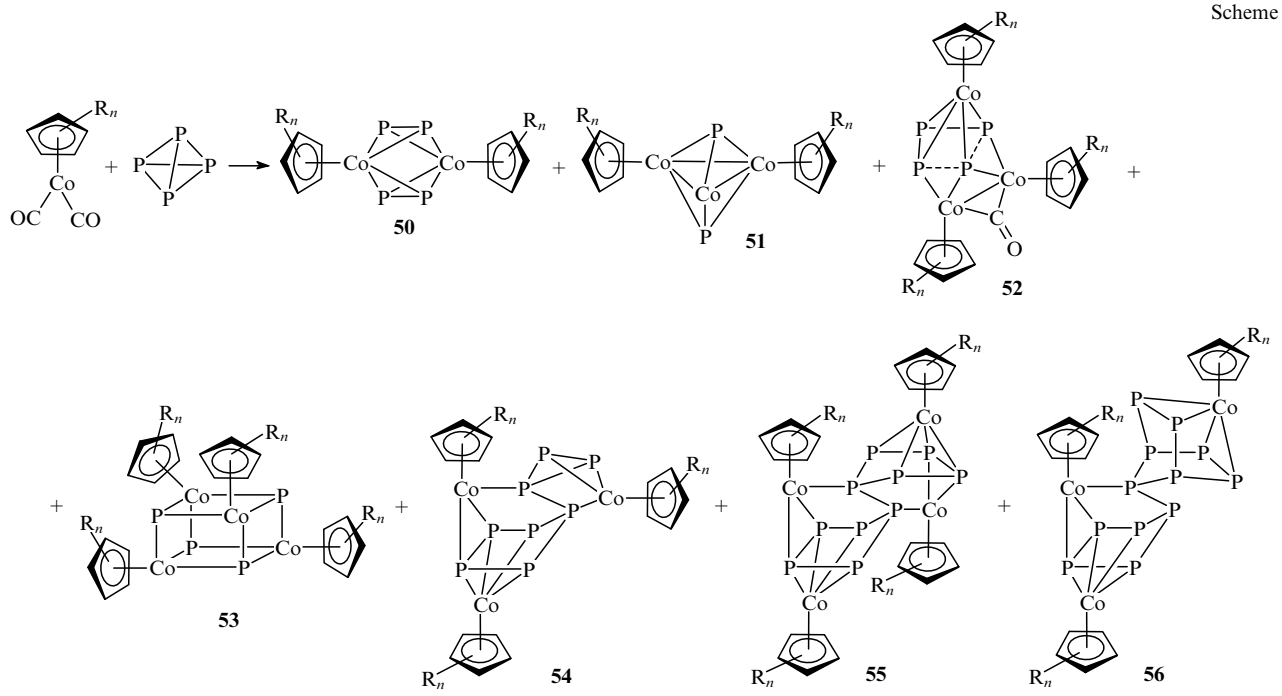
48 **49**

On introduction of a similar mononuclear cobalt complex into the reaction with P_4, complete decarbonylation of the metal atom takes place, ultimately giving a series of compounds. The reaction affords both the complexes **50**–**53**, with highly reactive phosphorus ligands, and products of their further transformations containing P_8, P_{10} and P_{12} type polyphosphorus fragments as ligands, compounds **54**, **55** and **56**, respectively (Scheme 1).[69, 70] The latter were isolated from the reaction mixture in low yields (< 5%).

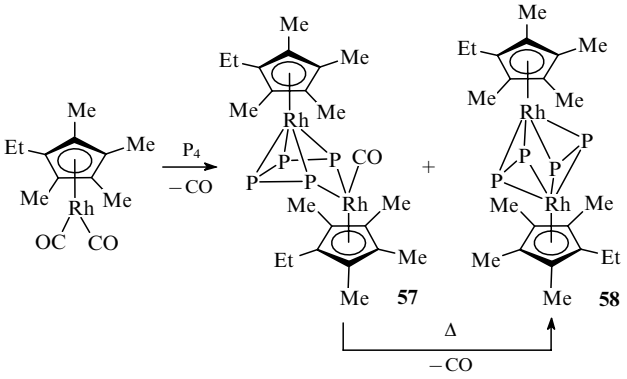
A similar chemical behaviour for white phosphorus was found in its joint thermolysis with rhodium and iridium complexes $[\{Cp^*M(CO)_n\}_m]$ ($m + n = 3$; M = Rh, Ir).[17, 68, 71–76]

A study of the reaction of P_4 with rhodium derivatives has provided one more step towards understanding the cleavage of P–P bonds in metal coordination spheres and elucidating the relationship between the structures of the resulting phosphorus ligands and the initial metal complexes.[17] The thermolysis of white phosphorus in the presence of (tetramethylethylcyclopentadienyl)dicarbonylrhodium was found to give complex **57**, containing two non-equivalent rhodium atoms. The long-term heating of compound **57** induces the loss of CO, resulting in binuclear complex **58**, in which the P_4 fragment splits into two P_2 fragments stabilised by two rhodium atoms.

Scheme 1



R_n = 1,3-Bu^t_2, 1,2,4-Bu^t_3, Me_3Si.

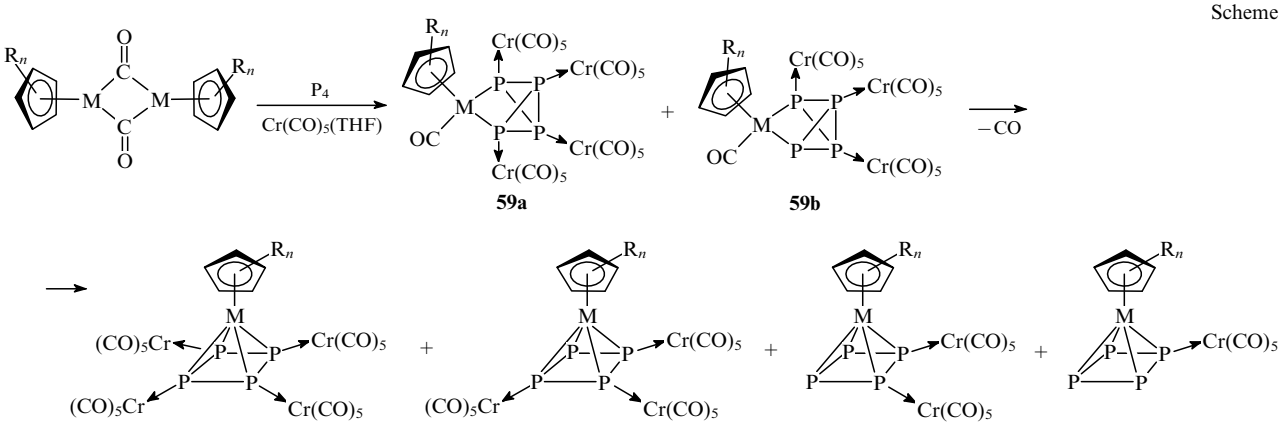


Fuller information on the pathways of cleavage of the P_4 molecule, resulting in one or another phosphorus ligand, has been gained from a study of the reaction of the cyclopentadienylcarbonyl complexes of cobalt group metals with white phosphorus in the presence of $Cr(CO)_5$(THF). It has been found [74, 77, 78] that the process starts with the generation of bicyclo[1.1.0]tetraphosphabutane, which forms heteropolynuclear complexes of type **59a**,**b** with transition metal compounds. Analogous cobalt complexes have also been isolated in the absence of $Cr(CO)_5$(THF).[68]

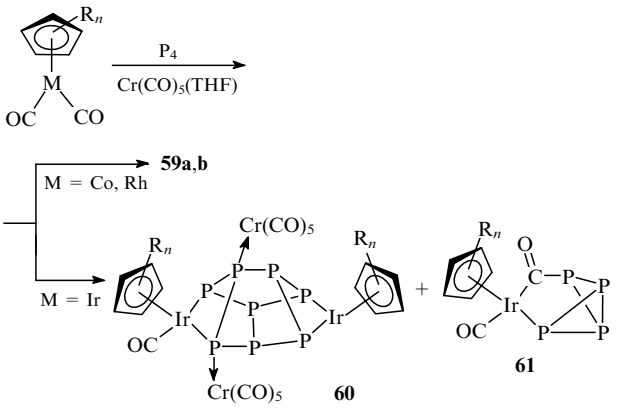
The decarbonylation of polynuclear complexes **59a**,**b** gives four types of coordination compound with a planar tetraphosphacyclobutane fragment, which has not been observed previously for cobalt group metals (Scheme 2). The product of the coordination of four $Cr(CO)_5$ molecules is the predominant product.

In complex **59a**, the bicyclo[1.1.0]tetraphosphabutane fragment is a 10-electron-donor ligand, which is its maximum value. In the case of iridium derivatives, in addition to complex **60**, the product of inserting the carbonyl group into the metal–phosphorus bond, compound **61**, was isolated quite unexpectedly (yield 58%).[79]

Scheme 2



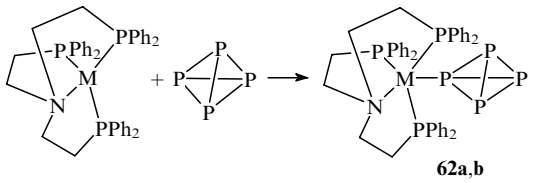
R_n = Me_5, Bu^t, 1,3-Bu^t_2; M = Co, Rh, Ir.



R_n = Me_5, Bu^t, 1,3-Bu^t_2.

c. Derivatives of nickel group metals (Ni, Pd, Pt)

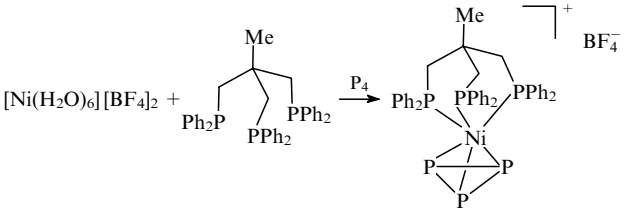
Derivatives of nickel group metals containing a white phosphorus molecule as a ligand were the first representatives of metal complexes of this class.[6,7,15,80–85] The $[(NR_3)M(\eta^1\text{-}P_4)]$ complexes, where NR_3 is tris(2-diphenylphosphinoethyl)amine, M = Ni (**62a**)[86] or Pd (**62b**),[87] were obtained in the late 1970s by Sacconi and co-workers, who studied the reactions of white phosphorus with nickel and palladium derivatives, $[(NR_3)M]$, which are strong Lewis acids.



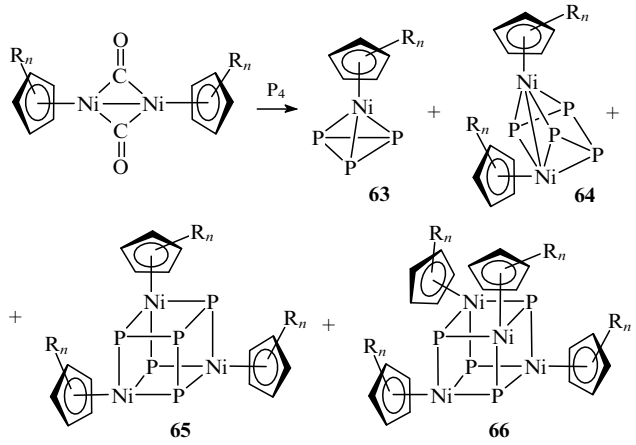
M = Ni (**a**), Pd (**b**).

The structure of nickel complex **62a**, relatively insensitive to oxidation in the solid state, was proved by X-ray diffraction,[86] which confirmed the presence of η^1-coordination of a phosphorus molecule to the metal. Due to coordination of only one phosphorus atom, the P_4 tetrahedron is converted into a trigonal pyramid, which shows itself as a change in the $P_\alpha-P_\beta$ and $P_\beta-P_\beta$ bond lengths (see below).

Changes in the steric and electronic parameters of ligands surrounding the nickel atom influence the route of the reaction between nickel complexes and white phosphorus. The reaction of P_4 with nickel tetrafluoroborate in the presence of 1,1,1-tris(diphenylphosphinomethyl)ethane results in a cationic complex containing a cyclo-P_3 ligand.[59]



The transformation of a P_4 molecule in the coordination sphere of a metal with a 15-electron configuration has been studied in relation to nickel (cyclopentadienyl)carbonyl complexes. Thermal activation of white phosphorus under the action of (cyclopentadienyl)carbonylnickel dimer results in the formation of a mixture of products containing sandwich-type 18-electron complex **63**, binuclear complex **64** with an open-chain P_4 fragment, and two organometallic 'cubanes': **65** with separated P_4 and P_1 fragments and **66** with four P_1 fragments.[88,89] Complex **65** is the major product of this reaction (yield 58%).

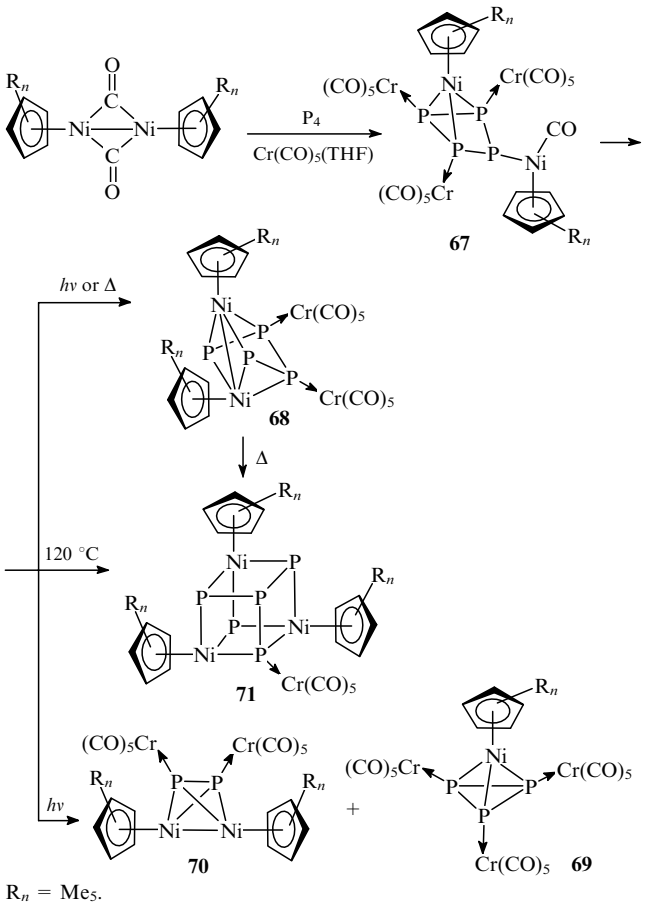


R_n = Me, Pr^n, Me_5.

In order to elucidate the mechanism of complexation of $[Cp^RNi(CO)]_2$, this reaction was investigated in the presence of a pentacarbonyl chromium complex. Exposure of the reaction mixture to the UV light afforded complex **67**, containing the tetraphosphacyclobutane ligand in an unusual distorted square conformation (Scheme 3).[90,91] Owing to the additional stabilisation by bulky $Cr(CO)_5$ fragments, intermediate **67** was isolated and studied.[90]

It was found that further photolysis of complex **67** was accompanied by elimination of chromium hexacarbonyl and the simultaneous rupture of one P–P bond of the tetraphosphacyclobutane fragment, giving rise to complex **68** with an open-chain P_4 substituent. Heteropolynuclear nickel complexes **69** and **70**, containing cyclo-P_3 and P_2 ligands, respectively, were isolated as

Scheme 3



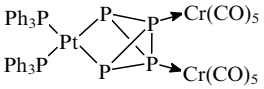
R_n = Me_5.

the minor products. The formation of complex **70** was attributed[90] to the dimerisation of the highly reactive intermediate [Cp*Ni≡P→Cr(CO)$_5$].

Thermolysis of complex **67** can also yield compound **68**. This rearranges at high temperature to cubane **71** with separated μ_3-P and tridentate P_4 ligands.[90]

It has been noted above that the stabilisation of P_3 or P_4 fragments in the coordination sphere of transition metals is possible only in the presence of bulky ligands (*e.g.*, triphos) at the metal atom. The stabilising role of the Cr(CO)$_5$ group has also been found for platinum derivatives containing a P_4 ligand in the coordination sphere.

The oxidative addition of white phosphorus to platinum(0) complexes in the presence of Cr(CO)$_5$(THF) allowed the preparation of compound **72**, in which the bicyclo[1.1.0]tetraphosphabutane fragment acts as a P_4^{2-} ligand, stabilised *via* coordination to two [Cr(CO)$_5$] groups.[92]



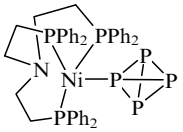
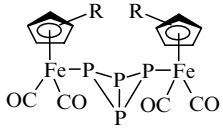
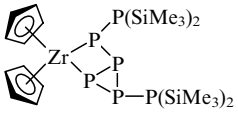
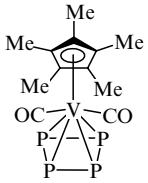
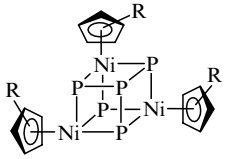
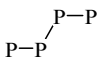
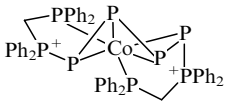
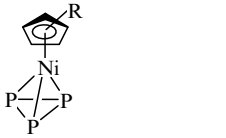
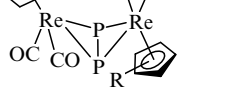
72

Thus, the route of cleavage of the P_4 tetrahedron has been elucidated as a result of studies into the transformations of a white phosphorus molecule under the action of transition metal complexes, and into the structures of phosphorus intermediates thus generated and stabilised in metal coordination spheres (Table 1). In addition, factors responsible for the formation of particular types of phosphorus species were revealed.

In summary, one can represent the general scheme of cleavage and subsequent transformation of the white phosphorus molecule in the coordination sphere of a transition metal. The presence of four lone electron pairs (LEP) in the initial molecule accounts for the formation of complexes containing a P_4 fragment at the metal atom. When additional bulky ligands (for example, triphos) are present, these complexes can be isolated in a pure state. A small steric bulk of ligands and additional vacant coordination sites at the metal atom dictate the pathway of P–P bond cleavage in P_4 during its coordination to transition metal complexes, accompanied by the formation of bicyclo[1.1.0]tetraphosphabutane stabilised in the metal coordination sphere. The cleavage of the P–P bond in this product furnishes two types of phosphorus species, tetraphosphacyclobutadiene and triphosphacyclopropane. The rupture of P–P bonds in these intermediates yield a series of highly reactive phosphorus-containing fragments, many of which have also been stabilised in a metal coordination sphere. This pathway is simplified, as it does not include the aggregation processes of phosphorus intermediates. These processes afford complex polyphosphorus ligands P_n ($n < 14$), which can also be isolated as complexes with transition metals.

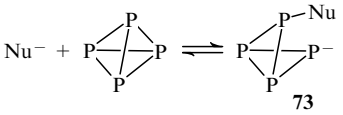
The reactions of organic compounds with transition metal complexes containing P_n species ($n \leqslant 4$) with unsubstituted phosphorus atoms as ligands have been barely studied as yet. These reactions result in P–C and P–E bonds (where E = O, S, N, *etc.*). This is undoubtedly a topical problem. The fact is that all complexes described in this Section are relatively stable. The use of these compounds as efficient catalysts of the reactions of white phosphorus with organic substrates implies the presence of coordinative or electronic unsaturation of the metal atom. Hence, less stable transition metal complexes with phosphorus intermediates should become objects of investigation. These complexes are expected to be highly reactive towards organic and organoelement substrates used for the synthesis of organophosphorus compounds directly from white phosphorus.

Table 1. Types of phosphorus species formed from the P_4 tetrahedron and stabilised in a metal coordination sphere.

Type of species	Examples of metal complexes
	
	
	
	
	
	
	
	

III. Reactions of white phosphorus with nucleophilic and electrophilic reagents

The reactions of elemental phosphorus with nucleophilic reagents have been studied in the most detail. Relying on abundant experimental data, Brown and Hudson[93–97] considered some theoretical aspects and rules for these processes. The phosphorus atoms in the P_4 tetrahedron are known to exhibit weak nucleophilic properties, as was confirmed by quantum-chemical calculations.[98] This is attributable to the fact that the electron pair of each phosphorus atom is localised, in the first approximation, in the 3s orbital, *i.e.*, it is arranged as a sphere around the nucleus. In the partially opened P_4 structure, the phosphorus atoms become more nucleophilic. However, due to ring strain and the instability of the P–P bond, the atoms possess strong electrophilic properties. Attack at the P_4 molecule by a nucleophilic reagent (Nu^-) yields the phosphide anion **73**, which is both a strong nucleophile and strong base:[93]



73

In the absence of electrophilic reagents, the equilibrium of this reaction is shifted towards the starting compounds for almost all types of nucleophiles, except for the very strong ones, such as carbanions. Due to its basic properties (pK_a of the corresponding acid is about 29), the phosphide anion **73** is rapidly protonated in a proton-donating medium, giving rise to an unstable intermediate. For example, if a hydroxide or alkoxide anion is used as the nucleophile, this intermediate spontaneously decomposes with evolution of hydrogen, phosphine, hypophosphite anions and phosphite anions.[99] In order to eliminate this undesirable process, it is necessary to use an electophilic reagent capable of competing with the proton. This was attained in the reactions of P_4 with organometallic compounds in the presence of alkyl halides;[100] with the hydroxide ion in the presence of aldehydes,[101] with acrylonitrile and other α,β-unsaturated compounds;[102] with disulfides;[103] and with alkoxide ions in a mixture of an alcohol and tetrachloromethane.[93–96, 104] Repeated nucleophilic attack followed by the capture of the phosphide anion by an electrophilic reagent allows one to obtain diverse products under mild conditions.

It is noteworthy that in the vast majority of cases, the rupture of the P—P bonds in P_4 proceeds by a pattern much more complicated than merely the successive addition of nucleophilic and electrophilic reagents (the latter may be represented by the white phosphorus itself). It was shown [105, 106] that the formation of oligomeric phosphides is a general process accompanying the cleavage of the P_4 molecule. The negative charge on the phosphorus atom, which results from rupture of the first P—P bond on treatment with a nucleophilic reagent, can be stabilised due to fast interaction with the second P_4 molecule, *etc*. The formation of dark solid precipitates with a high content of phosphorus has been observed in the reaction of P_4 with disulfides,[103] phenyllithium and other reagents.[102, 107]

The earliest attempts [100] to determine the structure of the intermediate phosphorus oligomers resulting from the attack by carbanions on P_4 suggest that these polyphosphides have a cross-linked structure. More recent studies attest to even more complex reaction pathways, involving opening of the P_4 molecule under the action of nucleophilic reagents [108] followed by disproportionation and elimination of polyphosphide residues.

$$\frac{m}{4}P_4 + Nu^- \longrightarrow P_mNu^-,$$

$$\frac{n}{4}P_4 + 3\,Nu^- \longrightarrow P_{n-1}^{2-} + PNu_2^-,$$

$$\frac{p}{4}P_4 + 4\,Nu^- \longrightarrow P_{p-1}^{3-} + PNu_3^-,$$

where $m > n > p$.

These transformations have been studied, taking reactions of P_4 with the CN^- and Ph_2P^- anions and other nucleophiles as examples, in order to elucidate the factors that would suppress disproportionation.[108] The selection of the optimal conditions ensures, in some cases, the selective formation of the target products from the intermediate phosphorus oligomers.

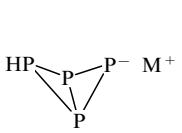
1. Reactions of white phosphorus with alkali metals and magnesium

Studies of the reactions between white phosphorus and alkali metals and magnesium clearly demonstrated the difficulties faced when conducting these seemingly simple reactions. As in the case of transition metal complexes, the product structure is determined by a number of factors, first of all, reactant ratio.

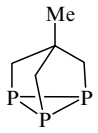
Thus heating a mixture of white phosphorus and sodium (atomic ratio 3 : 1) in THF or dimethoxyethane in the presence of a phase transfer catalyst, 18-crown-6 ether, resulted in a mixture of compounds, from which disodium hexadecaphosphide Na_2P_{16} was isolated by partial crystallisation.[105] A detailed investigation of the reaction mixture showed the formation of an isolobal analogue of sodium cyclopentadienide (NaCp), namely, sodium pentaphosphacyclopentadienide NaP_5,[109] stable only in solution. An alternative method for the preparation of alkali metal pentaphosphacyclopentadienides MP_5 consists of the reaction of white or red phosphorus with alkali metal dihydrophosphides MPH_2 (in 5 : 1 molar ratio).[110, 111] The reaction of white phosphorus with sodium in the presence of catalytic amounts of dibenzo-18-crown-6 ether is a convenient method for the synthesis of NaP_5.[112] Note that the pentaphosphacyclopentadienide anion P_5^- is a new and promising ligand in organometallic chemistry,[109, 113] as has been mentioned in a previous subsection.

The formation of a series of polyphosphides in the reactions of white phosphorus with alkali metals is a general process and depends on many factors, in particular, the boiling point of the solvent. The use of solvents with boiling points lower than the melting point of the alkali metal facilitates the formation of polyphosphides.[114] In particular, the fraction of polyphosphides can be reduced and, hence, the yields of the target products increased by using a Na – K alloy, the melting point of which is lower than the melting points of the pure metals.

For example, white phosphorus reacts with the Na – K alloy (1 : 3) or with Li metal in the presence of naphthalene to give bicyclo[1.1.0]tetraphosphine salts **74**.[106]



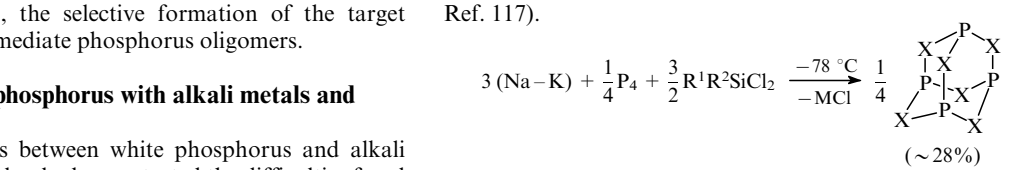
74



75

Phosphine **75**, having a nortricyclane structure, has been isolated [115] in a study of the reaction of P_4 with a Na – K alloy in the presence of 1,3-dibromo-2-bromomethyl-2-methylpropane $MeC(CH_2Br)_3$. Note that phosphine **75** reacts with metal carbonyls $M(CO)_5(THF)$ (M = Cr, W) under mild conditions to form metal complexes in which the metal is coordinated to one, two, or three phosphorus atoms $MeC(CH_2P)_3[M(CO)_5]_n$ (n = 1, 2, 3).

The reaction of white phosphorus with a Na – K alloy has been successfully used to prepare silylphosphines, which are basic reagents for the preparation of diverse derivatives of trivalent phosphorus. Thus treatment of the reaction mixture with chlorotrimethylsilane resulted in the isolation of tris(trimethylsilyl)phosphine, which is widely used in the chemistry of low-coordinate phosphorus compounds.[116] The replacement of chlorotrimethylsilane in this reaction by dichlorodimethylsilane allowed the preparation of silylphosphine $(Me_2Si)_3P_4$ (yield ~1%) with a nortricycyclane structure. Optimisation of the reaction conditions, first of all, changing the reactant ratio, markedly increased the yield of the target silylphosphine. The introduction of a Na – K alloy into the reaction with white phosphorus in a 1 : 3 atomic ratio and subsequent treatment of the reaction mixture with $R^1R^2SiCl_2$ at −78 °C opened up the way to the synthesis of silylphosphines having the adamantane structure $(R^1R^2Si)_6P_4$ (see Ref. 117).



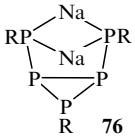
(~28%)

X = R^1R^2Si (R^1, R^2 = Me, Et, Ph).

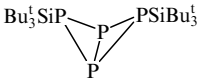
This method was successfully used for the preparation of both the silicon analogues of adamantane, such as $[R(Me)Si]_6P_4$, containing diverse functional groups (for example, R = CH_2=CH), mixed silylphosphines $(MeHSi)(Et_2Si)_5P_4$.[118]

However, due to steric and electronic factors, this approach cannot be applied to the synthesis of silaphosphaadamantanes containing *tert*-butyl and phenyl groups at the silicon atom.[118]

The reactions of white phosphorus with sodium tris(*tert*-butyl)silicide (Bu^t_3SiNa) and hexakis(*tert*-butyl)disilane have been proposed [119] as an alternative pathway to silylphosphines containing a bulky *tert*-butyl group. These reactions furnish a number of silylphosphines containing a tris(*tert*-butyl)silyl group: $Na_2P_4(SiBu^t_3)_2$, $NaP_3(SiBu^t_3)_2$, $Na_2P_5(SiBu^t_3)_2$ (compound **76**, R = Bu^t) and $Na_2P_7SiBu^t_3$.

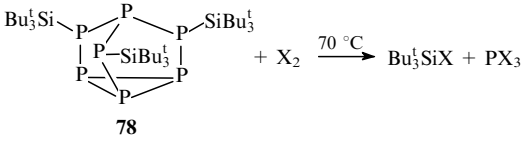


76



77

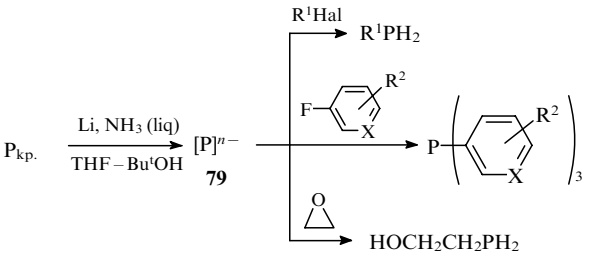
The reaction of P_4 with hexakis(*tert*-butyl)disilane presumably proceeds by a free-radical mechanism. The Bu^t_3Si radical is generated on thermal decomposition of $(Bu^t_3Si)_2$ ($T > 100$ °C) and reacts with white phosphorus, giving rise to silylphosphines $(Bu^t_3Si)_2P_4$ and $(Bu^t_3Si)_3P_7$ (compounds **77** and **78**, respectively).[119] Heptaphosphine **78** has a nortricyclane structure and is distinguished by a high thermal stability. The steric crowding of the Bu^t_3Si groups results in an increase in the exocyclic angles at the equatorial phosphorus atoms but scarcely influences the structure of the phosphorus P_7-skeleton of the molecule. On treatment with chlorine or bromine at 70 °C, heptaphosphine **78** decomposes to give phosphorus trihalides and halosilanes.[119]



78

X = Cl, Br.

Yet another method for decreasing the fraction of polyphosphides in the reaction products and increasing the yield of the target compounds in the reaction of white phosphorus with alkali metals is to conduct the process in liquid ammonia.[120] A good solubility of both reactants in liquid ammonia is favourable for high product yields. It was shown [121] that the reaction of white phosphorus with sodium metal in liquid ammonia yields the previously unknown 1,3-diaminotriphosphine $H_2NPH.PHPHNH_2$, which is stable only in solution. Of the three possible diastereomers, only the *erythro*,*erythro*-isomer, with the transoid arrangement of the NH_2 groups, was isolated. The reduction of white phosphorus with lithium metal in liquid ammonia results in a complex mixture of polyphosphides. On treatment of red phosphorus with lithium under these conditions, phosphide anion **79** is generated *in situ*. This anion is a convenient reagent for the synthesis of diverse compounds of trivalent phosphorus.[122]



R^1 = n-C_9H_{19}, $PhCH_2$, cyclo-C_5H_9; X = CH, N.

When the phosphide anion **79** reacts with alkyl halides, primary phosphines are formed in high yields,[123] while the reaction with alkyl fluorides gives symmetric triarylphosphines (yields 36%–60%).[124] Note that the latter can contain functional substituents, including phosphonodiimide, sulfonamide, 2-oxazole and nitrile groups.

Phosphine $HOCH_2CH_2PH_2$ was isolated in 27% yield from the reaction of the phosphide anion **79** with oxirane at −33 °C.[125] With a sterically crowded oxirane, 7-oxabicyclo[4.1.0]heptane, a good yield of the target phosphinoethanol (60%) was attained when the reaction was carried out at high temperature (40 °C).[126]

An interesting version of the activation of elemental phosphorus has been reported by Bornancini *et al.*[127] They proposed using radiation for initiating the reactions of sodium phosphides and aryl halides. A series of symmetrical and asymmetrical triarylphosphines were prepared in good yields using this approach.

The development of methods for the synthesis of polycyclic organophosphines [128, 129] has resulted in the synthesis of the first representative of this class of compound, tetraisopropyltetradecaphosphine $P_{14}Pr^i_4$. It is formed in the reaction of white phosphorus with magnesium metal in the presence of Pr^iPCl_2.[130] The first stage of the process affords a mixture of polyphosphines $P_9Pr^i_5$ and $P_7Pr^i_5$, and isopropylphosphines with high phosphorus contents. Further thermolysis of the reaction mixture gives, in addition to $P_9Pr^i_3$ and $P_7Pr^i_3$, a substantial amount of less alkylated phosphorus derivatives containing more than 9 phosphorus atoms in each molecule (including $P_{14}Pr^i_4$). As a result of systematic research, both stages were optimised. This unusual synthetic approach has been successfully used for the synthesis of a number of polycyclic organophosphines such as $P_{11}Pr^i_3$ (see Ref. 131), $P_{11}Pr^i_5$, (see Refs 132, 133), $P_{12}Pr^i_4$ (see Refs 134, 135), $P_{13}Pr^i_5$ (see Ref. 136), $P_{18}Pr^i_6$ (see Ref. 137), $P_{18}Pr^i_4$ (see Ref. 138), $P_{20}Pr^i_6$ (see Ref. 139) and $P_{14}Pr^i_4$ (see Ref. 131). The reaction of PEt_5 with PCl_3 in the presence of magnesium metal can be used as an alternative method for the preparation of compounds of this class.[140]

Thus, the reaction of white phosphorus with alkali metals, magnesium and C-electrophiles can be used to prepare OPCs with different oxidation states of phosphorus. However, the scope of this method is limited due to oxidative elimination processes. Metal phosphides formed upon interaction of white or red phosphorus with alkali metals react with alkyl (or aryl) halides to give not only compounds with the P–C bonds, but also polyphosphines, which reduces the yield of the target product.

The oxidative elimination and formation of polyphosphines can be suppressed by using organic derivatives of alkali and alkaline earth metals as nucleophilic agents.

2. The reactions of white phosphorus with organolithium and organomagnesium compounds

The use of organolithium compounds ensured the first synthesis of organophosphorus derivatives with P–C bonds directly from white phosphorus.[100] It was suggested that the reaction yields a mixture of alkali metal phosphides and triphenylphosphine:

$$PhLi + P_4 \longrightarrow Li_3P + Li_2PPh + LiPPh_2 + PPh_3.$$

However, only traces of triphenylphosphine Ph_3P and diphenylphosphine were isolated after hydrolysis of the reaction mixture, unsubstituted phosphine was not even detected, while phenylphosphine was formed as the major product. The yields of primary phosphines in the reaction of P_4 with Bu^nLi and PhLi were 9% and 40%, respectively, while those for reactions with Bu^nMgBr and PhMgBr were 5%–7%.[100]

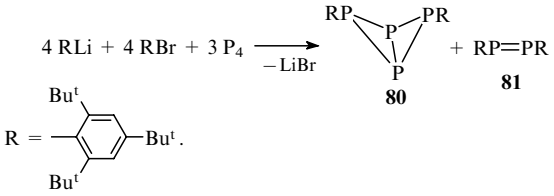
The use of a combination of reactants — carbanions generated from organometallic compounds and electrophiles (for example, alkyl halides) — increased the overall yield of organophosphorus compounds to 70%–80%.[100] The reaction of white phosphorus with phenyllithium in the presence of alkyl halides affords, after hydrolysis, a mixture of tertiary phosphines and their oxides.

$$PhLi + P_4 + Bu^nX \xrightarrow[-LiX]{H_2O} PhPBu^n_2 + Ph_2PBu^n + Ph_2\overset{O}{\overset{\|}{P}}Bu^n$$

X = Cl, Br.

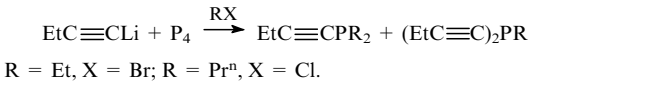
This reaction gives organopolyphosphines as intermediates; most likely, these are cross-linked polymeric phosphorus fragments. Their composition is determined by the reactant ratio. Hydrolysis of these polyphosphines proceeds much more readily than the decomposition of lithium phenyl polyphosphide; therefore, the total yield of OPCs does not depend on the nature of the alkali metal. On changing the reactant ratio (increasing in the proportion of phosphorus), the reaction gives tetrabutylcyclotetraphosphine, resulting from the rupture of two P—P bonds in the P_4 tetrahedron[100]

The introduction of sterically hindered 2,4,6-tri-*tert*-butylphenyllithium and 2-bromo-1,3,5-tri-*tert*-butylbenzene into the reaction with phosphorus affords a mixture of bis(2,4,6-tri-*tert*-butylphenyl)bicyclotetraphosphine (**80**) and bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (**81**) in moderate yields.[107]



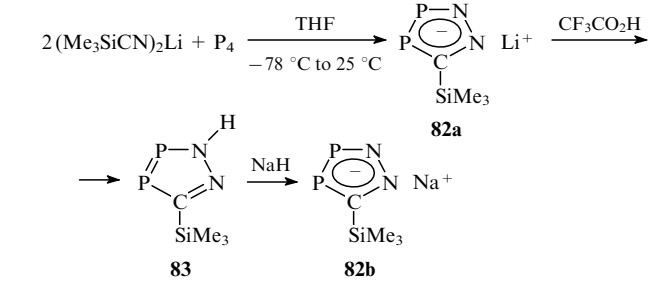
Compound **80** is unstable in air and decomposes in chlorinated hydrocarbons. Attempts to convert it into stable compounds of four-coordinate phosphorus by treatment with elemental sulfur or trimethylsilyl azide failed.

It was found[141, 142] that the but-1-ynylphosphide and di(but-1-ynyl)phosphide anions were generated in the reaction of white phosphorus with but-1-ynyllithium in liquid ammonia; these anions reacted with alkyl halides RHal (R = Et, Pr^n) to give mixtures of approximately equal amounts of but-1-ynyldialkylphosphines $EtC{\equiv}CPR_2$ and alkyldi(but-1-ynyl)phosphines $(EtC{\equiv}C)_2PR$.[141, 142] The overall yield of phosphines was 15%–20%.



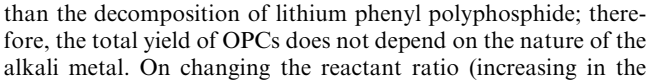
R = Et, X = Br; R = Pr^n, X = Cl.

The discovery of pentaphosphaferrocenes[83] and the development of methods for the preparation of the pentaphosphacyclopentadienide ion[109, 111] have stimulated research into the transformation processes of white phosphorus aimed at the construction of new ligands containing several phosphorus atoms in the molecule. It was suggested that the carbene anion RC^- can be inserted into a P_4 molecule, yielding directly the $[RCP_4]^-$ ion, owing to stabilisation of the aromatic phosphorus-containing heterocycle.[143] This was confirmed in a study of the reaction of white phosphorus with lithium (trimethylsilyl)diazomethanide. The salt with the previously unknown 1,2,3,4-diazaphospholide anion **82a**, formed during the formal [3+2]-cycloaddition of the P≡P fragment to the diazomethyl anion, was isolated as the only reaction product.



The protonation of lithium salt **82a** with trifluoroacetic acid at low temperature produces stable 2*H*-1,2,3,4-diazadiphosphole **83**, which was converted into Na salt **82b**.[143]

The use of dialkylamines as nucleophilic reagents in the reaction of white phosphorus with Bu^nLi results in a mixture of equimolar amounts of lithium dialkylaminphosphide and dilithioalkylaminophosphide.[144]



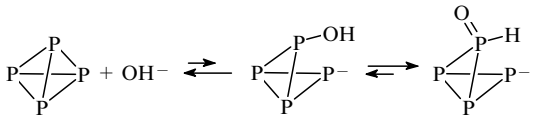
R^1, R^2 = Alk.

In this case, amine is probably first deprotonated to the amide anion, which then attacks the white phosphorus molecule. The formation of a mixture of two products is attributable to different extents of nucleophilic attack.

3. The reactions of white phosphorus with electrophilic reagents in the presence of hydroxide ions

The reactions of elemental phosphorus with electrophiles in the presence of the hydroxide anion are well studied processes. The simple procedures, mild conditions, ready availability of the initial reactants and the easy isolation and identification of products are the reasons for the fast progress in this field of chemistry of elemental phosphorus.

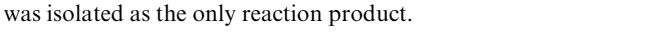
As shown above, the first stage in the cleavage of the P_4 molecule under the action of nucleophilic reagents gives bicyclo[1.1.0]tetraphosphabutane derivatives; in the absence of electrophiles, the equilibrium is shifted towards the starting compounds. In the presence of the hydroxide ion, this equilibrium can be represented as follows:



In our opinion, the prototropic tautomerism inherent in the P(III) intermediates generated *in situ* predetermines the formation of four-coordinate phosphorus compounds in this process. Simultaneously, the tautomeric equilibrium is favourable for the stabilisation of bicyclo[1.1.0]tetraphosphabutane derivatives, which makes it possible to accomplish the reactions of white phosphorus with nucleophilic reagents in the presence of electrophiles under relatively mild conditions.

The combined action of nucleophilic and electrophilic reagents on white phosphorus often allows one to accomplish the consecutive rupture of all P—P bonds and to obtain the target product. However, nucleophilic cleavage of the P_4 tetrahedron in the absence of electrophiles specially added to the reaction mixture is also of interest in itself, and deserves special consideration. These reactions may underlie the synthesis of unknown polyphosphorus structures thus providing new information on the reactivity of white phosphorus.

The nucleophilic cleavage of white phosphorus on treatment with NaOH in water (or in a high-molecular-weight alcohol with surfactant additives) results in the formation of high-purity phosphine PH_3.[145–147]



The reaction of white phosphorus with H_2O in the presence of HI proceeds with PH_3 evolution to give phosphorous acid H_3PO_3.[148] Recall that disproportionation of phosphorous acid to phosphine PH_3 and phosphoric acid is a well-known reaction.[149]

The reaction of elemental phosphorus with electrophilic agents in the presence of strong alkalis (so-called superbasic media) is a convenient way for the preparation of OPCs.[1, 150–160] The most important work on the arylation and alkylation of elemental phosphorus was carried out by Trofimov and co-workers.[150–159] As a rule, these reactions are carried out in the presence of alkali metal hydroxides in aprotic solvents (HMPTA, DMSO) or under phase transfer catalysis conditions. Tertiary phosphines

and phosphine oxides are formed as major products in total yields of 40%. Note that trialkylphosphines cannot be isolated, even when the process is conducted under conditions that absolutely rule out contact with atmospheric oxygen.

$$RX + P_{red} \xrightarrow[2)\ H_2O]{1)\ KOH} R_3P{=}O + R_2P(O)H$$

R = Et, Pr^n, Bu^n, n-C_5H_{11}, n-C_8H_{17}; X = Cl, Br, I.

On heating a suspension of red phosphorus in the KOH–DMSO (or HMPTA) system in the presence of benzyl chloride to 70–80 °C, tribenzylphosphine oxide is formed as the major product (yield 65%). Small amounts of tribenzylphosphine and tetrabenzylphosphonium chloride were also isolated.[151] Since the phosphonium salt and toluene were detected in the reaction mixture, the known decomposition of phosphonium hydroxide could from an alternative route to phosphine oxide.[151]

$$P_{red} + PhCH_2Cl \longrightarrow (PhCH_2)_3P \xrightarrow{PhCH_2Cl} [(PhCH_2)_4P^+]Cl^- \xrightarrow[-KCl,\ -PhMe]{KOH} (PhCH_2)_3P{=}O$$

Allyl halides react with red phosphorus at elevated temperatures in a similar way, resulting in tris(prop-1-enyl)phosphine oxide and tris(prop-2-enyl)phosphine oxide in 35% and 30% yields, respectively.[152, 153]

$$P_{red} + CH_2{=}CHCH_2Br \xrightarrow[2)\ H_2O]{1)\ KOH} (MeCH{=}CH)_3P{=}O + (CH_2{=}CHCH_2)_3P{=}O$$

The simultaneous phosphorylation of alkyl bromides and benzyl chloride with red phosphorus was carried out in the development of a one-step method for the synthesis of asymmetrical tertiary phosphine oxides, which are difficult to obtain by other methods. The yield of these products was found to depend, first of all, on the ratio of the initial organyl halides.[161]

$$P_{red} + RBr + PhCH_2Cl \xrightarrow[2)\ H_2O]{1)\ KOH} R_3P{=}O + R_2P(O)CH_2Ph + (PhCH_2)_2P(O)R + (PhCH_2)_3P{=}O$$

R = Alk.

Since alkyl bromides are subject to side dehydrobromination and hydrolysis under these conditions, and are less reactive than benzyl chloride, the use of a two- to three-fold excess of RBr has been proposed for increasing the yield of asymmetric tertiary phosphine oxides.

In superbasic media KOH–HMPTA(DMSO), unsaturated compounds, namely acrylonitrile, acrylamide, ethyl acrylate, vinylphosphonate, styrene, 4-vinylpyridine and acetylene derivatives, can be used as electrophilic reagents (Refs 125, 141, 144, 155–159, 162–164). For example, the reaction of phosphorus with styrene gave tris(2-phenylethyl)phosphine oxide (yield 60%) with bis(2-phenylethyl)phosphinous acid as the minor product.[155]

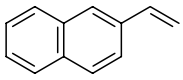
$$P_{red}\ (or\ P_4) + PhCH{=}CH_2 \xrightarrow[2)\ H_2O]{1)\ KOH} (PhCH_2CH_2)_3P{=}O + (PhCH_2CH_2)_2P(O)H$$

In the case of phenylacetylene, in conformity with the rule for addition of nucleophiles to alkynes,[165] tris[(*Z*)-styryl]phosphine is formed stereoselectively in 55% yield.[156–158] Tris[(*Z*)-styryl]phosphine oxide was obtained as a by-product.

$$P_{red}\ (or\ P_4) + PhC{\equiv}CH \xrightarrow[2)\ H_2O]{1)\ KOH} (PhCH{=}CH)_3P + (PhCH{=}CH)_3P{=}O$$

To increase the yield of the target products, it has been proposed to carry out additional activation of elemental phosphorus by using ionising radiation (X-ray or γ electromagnetic radiation); the degree of conversion of red phosphorus reached 97%.[166, 167] The researchers believe that on irradiation, non-paramagnetic cationic and anionic defects appear in the P_{red} layered polymeric structure; these are converted into radical paramagnetic defects,[168] which are responsible for the high activity of elemental phosphorus.

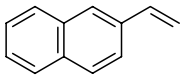
The introduction of 2-vinylnaphthalene into the reaction with elemental phosphorus allows one to synthesise previously unknown phosphines and phosphine oxides with bulky radicals that are promising ligands for metal complex catalysts. In the case of red phosphorus, the reaction takes place on heating of the reactants to 90–96 °C in a superbasic medium, KOH–DMSO. The reaction yields a mixture of compounds: primary and secondary phosphines, phosphinic acid and phosphine oxide, in a total yield of up to 40%.[169]



$$+ P_{red} \xrightarrow[90-96\ ^\circ C]{1)\ KOH-DMSO,\ 2)\ H_2O} NaphCH_2CH_2PH_2 + (NaphCH_2CH_2)_2PH + NaphCH_2CH_2P(O)(H)OH + (NaphCH_2CH_2)_2P(O)H + (NaphCH_2CH_2)_3P{=}O$$

Naph is 2-naphthyl.

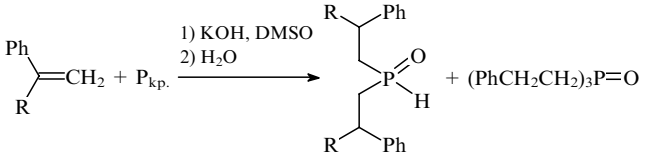
The degree of conversion of white phosphorus in this reaction is twice as high as the degree of conversion of $P_{red.}$. In addition, an increase in the content of 2-vinylnaphthalene in the initial mixture results in a higher reaction selectivity, and in the formation of tertiary phosphine **84** and phosphine oxide **85** in a 1 : 5 ratio as the major products (total yield 63%). After treatment of the reaction mixture with atmospheric oxygen, phosphine oxide **85** was isolated in 58% yield.[169]



$$+ P_4 \xrightarrow[2)\ H_2O]{1)\ KOH} \xrightarrow{O_2} (NaphCH_2CH_2)_3P + (NaphCH_2CH_2)_3P{=}O$$

84 **85**

A convenient method for the preparation of phosphinous acids has been developed on the basis of reactions of red phosphorus with arylalkenes in aprotic solvents in the presence of strong bases.[162] This reaction with styrenes affords tris- and bis(2-phenylethyl)phosphine oxides in yields of up to 20%.

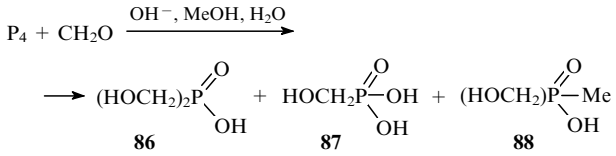


$$Ph(R)C{=}CH_2 + P_{kp.} \xrightarrow[2)\ H_2O]{1)\ KOH,\ DMSO} \text{(Ph, R, O, H)}P + (PhCH_2CH_2)_3P{=}O$$

R = H, Me.

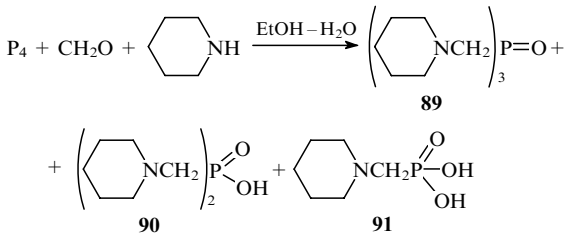
Under similar conditions, tris(2,2-dialkoxyethyl)phosphine oxides $[(RO)_2CHCH_2]_3PO$ were obtained from red phosphorus and 1,1-dialkoxy-2-bromoethanes $(RO)_2CHCH_2Br$ (R = Et, Bu^n), the product yields being moderate (15% and 8%, respectively).[163]

The use of formaldehyde as an electrophilic reagent in the reaction with white phosphorus results in a mixture of bis(hydroxymethyl)phosphinic (**86**), hydroxymethylphosphonic (**87**) and methyl(hydroxymethyl)phosphinic (**88**) acids.[101,144]



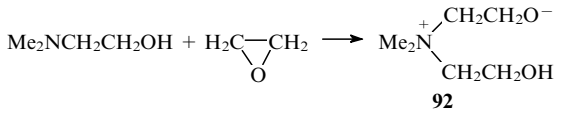
A method for the preparation of methylphosphonic acids, which have found wide use as fire retardants, has been developed on the basis of the reaction of white phosphorus with methyl chloride in the presence of KOH. Phosphonium salts were employed as phase transfer catalysts.[170]

By using organic bases (first of all, primary and secondary amines), one can prepare a series of organic phosphorus derivatives under mild conditions. For instance, white phosphorus reacts with formaldehyde in the presence of piperidine, giving rise to a mixture of tris(piperidinomethyl)phosphine oxide (**89**), bis(piperidinomethyl)phosphinic acid (**90**) and piperidinomethylphosphonic acid (**91**).[171,172]

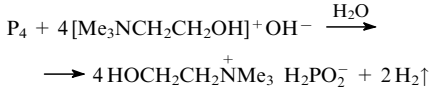


When linear amines, for example, Me_2NH and Et_2NH, are used, the reaction affords also tertiary phosphine.[102] The product yields depend on the starting reactant ratio, the nature of the solvent and the pH of the medium. It was found[102] that P_4 reacts with *N*-hydroxymethyldialkylamine, formed in the primary reaction between amine and aldehyde. The process starts with nucleophilic attack by the R_2NCH_2O on the white phosphorus molecule, and is accelerated by the presence of basic catalysts.

This hypothesis has been confirmed in a study of the chemical behaviour of white phosphorus towards alcohol–oxirane mixtures in the presence of inorganic and organic bases.[173–176] The reactions of oxiranes (in particular, ethylene oxide) with *N,N*-dimethylethanolamine were found to afford betaine **92**, which can react with white phosphorus.



β-Hydroxyethyltrimethylammonium hydroxide (choline) was used as the model compound in the reaction with P_4; this gave β-hydroxyethyltrimethylammonium hypophosphite.[177]



If ethylene oxide and trimethylamine are added consecutively to white phosphorus, the same products are formed as in the reaction with choline.[177]

4. Reactions of white phosphorus with alkyl halides

Since elemental phosphorus has weak nucleophilic properties, the reaction of both of its allotropes with organic halides usually take place under drastic conditions.

White phosphorus reacts with alkyl or aryl halides at a temperature of >250 °C to give phosphorus halides and phosphonium salts.[178]

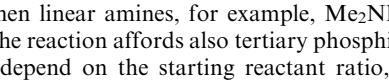
X = Cl, Br.

The introduction of alkyl iodides into this reaction, or conducting the process in the presence of elemental iodine, increases the yield of the target products.

Heating red phosphorus and lower alkyl iodides RI (R = Me, Et, Bu^n) in an autoclave at 200 °C in the presence of traces of iodine or diphosphorus tetraiodide, followed by treatment of the reaction mixture with dilute nitric acid, affords tertiary phosphine oxides: Me_3PO (yield 54%), Et_3PO (56%) and Bu_3PO (66%).[179–181] The separation of this process into two steps, that is, heating of catalytic amounts of alkyl iodide with red phosphorus in the presence of I_2 or the salt $[IR_3PP^+R_3]I_5^-$ to 180–230 °C and the subsequent addition of excess alkyl iodide, increases the yield of trialkylphosphine oxides.[179] For example, the yield of triethylphosphine oxide reaches 88%. The researchers believe that the process follows an ionic mechanism as no free radicals were detected during the reaction and UV irradiation or the addition of benzoyl peroxide did not influence the reaction rate.

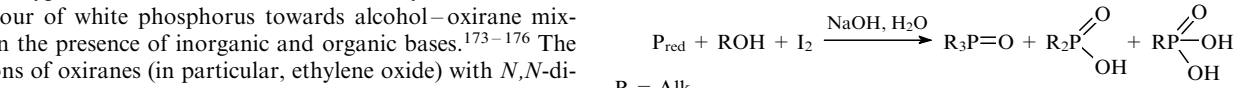
R = Me, Et, Bu^n.

Alcohols are suitable as alkylating agents for red phosphorus. The reaction occurs in the presence of iodine under drastic conditions. After treatment of the reaction mixture with an aqueous solution of sodium sulfite, the yield of phosphine oxide reaches 80%.[182]



R = Alk.

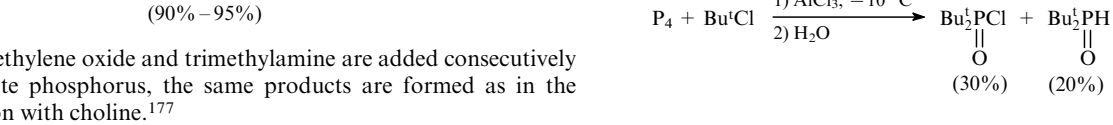
Under alternative conditions, for example, refluxing the reaction mixture in aqueous alkali, phosphinic and phosphonic acids are formed together with phosphine oxides.[183]



R = Alk.

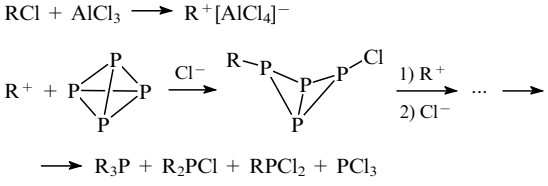
A similar reaction carried out using unsaturated compounds (fluorinated acetylene and ethylene derivatives) as the alkylating agents affords tertiary phosphines — diphosphabicyclooctatrienes (yields <30%).[183]

In the presence of catalysts (aluminium halides), the reactions between alkyl halides and white phosphorus can be carried out under mild conditions.[184] For example, white phosphorus dissolved in carbon disulfide reacts with *tert*-butyl chloride in the presence of Lewis acids, even at −10 °C. After hydrolysis of the reaction mixture, di(*tert*-butyl)phosphine oxide and di(*tert*-butyl)phosphinic acid chloride were isolated.



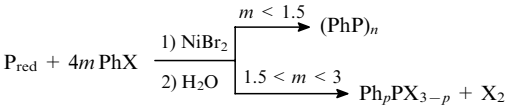
Other alkyl chlorides have also been used in this reaction. It has been suggested[184] that aluminium chloride polarises the C–Cl bond leading to the formation of a carbocation. The addition of the carbocation to a white phosphorus molecule results in a new cation, in which the phosphorus–phosphorus

bond is polarised and capable of adding chloride ions. Repetition of these steps would be expected to yield a mixture of tertiary phosphine, dialkylchlorophosphine, alkyldichlorophosphine and phosphorus trichloride.



However, only products containing alkyl groups at phosphorus were isolated from the reaction mixture,[184] which is inconsistent with this hypothesis.

Nickel bromide has been studied as the catalyst of reaction of alkyl (or aryl) halides with red phosphorus. It was shown [185] that the reaction of red phosphorus with the aromatic derivatives takes place at 200 °C and affords a mixture of arylation products. In the researchers' opinion, nickel bromide activates both red phosphorus and the aryl halide, the overall process being a redox reaction. If the molar ratio [phosphorus] : [aryl halide] > 6, free halogen is formed.



X = Cl, Br; p = 1, 2, 3.

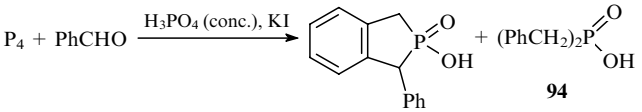
In the case of iodobenzene, mild hydrolysis afforded a mixture of the corresponding phosphonium salt and triphenylphosphine oxide.



On hydrolysis of the reaction mixture in the presence of an alkali, the yield of Ph_3PO reaches 95%.[185]

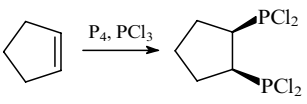
Dialkyl sulfides can be used as alkylating reagents. They react with red phosphorus at 200–400 °C, giving rise to tertiary phosphine sulfides R_3PS (R = Me, Et, Bu^n, Ph).[186] Dimethyl ether Me_2O enters into a similar reaction, resulting in trimethylphosphine oxide Me_3PO.[186]

Several other synthetic approaches to the formation of P–C bonds based on chemical transformations of the phosphorus molecule deserve attention. A simple one-step method for the preparation of isophosphindolines by the reduction of aromatic aldehydes under the action of white phosphorus has been reported.[187] Thus the reaction of P_4 with benzaldehyde in the presence of potassium iodide in concentrated phosphoric acid gave 1-phenyl-1,3-dihydro-2λ^5-benzophospholine acid (**93**) and a small amount of dibenzylphosphinic acid (**94**).



93 (23%)

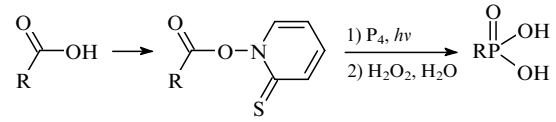
1,2-Bis(dichlorophosphino)ethane, an important precursor of chelating diphosphines, has been prepared by the reaction of white phosphorus with ethylene and PCl_3.[188, 189] This method has been successfully used to prepare 1,2-bis(dichlorophosphino)cyclopentane, which is a basic reagent in the synthesis of chiral chelating ligands.[190]



5. Free-radical alkylation of white phosphorus

The reactions of white phosphorus with alkyl halides occurring *via* a free-radical mechanism have scarcely been studied. Only two reactions of carbon-centred radicals with elemental phosphorus resulting in organophosphorus compounds are known to date.

For instance, white phosphorus is smoothly alkylated on treatment with the radicals generated by photolysis of activated carboxylic acid esters.[191] The process is initiated by traces of oxygen and results in phosphonic acids.



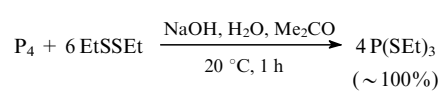
R = Bu^{t}CH$_2$CH$_2$, PhCH$_2$CH$_2$, Cy, 1-adamantyl.

Organic complexes of cobalt(III) with either dimethylglyoxime (dmgH) [EtCo(dmgH)$_2$(Py)], or a tridentate ligand [EtCo(7-Me-salen)(quil)] (quil is 8-hydroxyquinoline) were used as sources of C-radicals.[192] On exposure to visible light or on treatment with acids, these complexes effectively generate carbon-centred free radicals. After acid hydrolysis of the reaction mixtures, it is possible to identify the alkylation products containing one or two ethyl groups at the phosphorus atom: ethylphosphonic, ethylphosphinous, diethylphosphonic and diethylphosphinous acids (overall yields 30%–70%). The researchers assume the formation of new cobalt complexes containing unknown polyphosphorus fragments which are relatively stable under the reaction conditions, but which decompose during hydrolysis.

6. The synthesis of compounds with a P–heteroatom bond

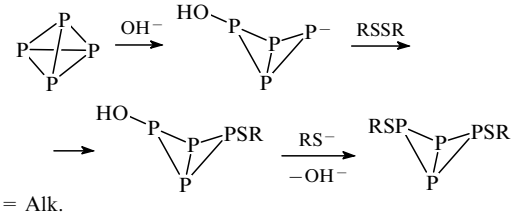
Phosphorus derivatives containing a P–heteroatom (O, S, N) bond are the most important reagents in the chemistry of phosphorus. They are intermediates for the preparation of a broad range of substances possessing practically useful properties. For this reason, the development of methods for the preparation of these compounds directly from white phosphorus to avoid the step of phosphorus chlorination is a topical subject.

A study of the reaction of white phosphorus with disulfides has shown [103] that they proceed only at high temperatures and follow a free-radical mechanism. Mixtures of trithiophosphites and tetrathiophosphates are formed. A change in the reaction conditions, in particular, using aprotic solvents and basic catalysts (hydroxides, mercaptides, amides or hydrides), sharply increases the process efficiency and selectivity. Indeed, the reaction of white phosphorus with diethyl disulfide in acetone in the presence of a catalytic amount of aqueous alkali affords triethyl thiophosphite in almost quantitative yield.[103]



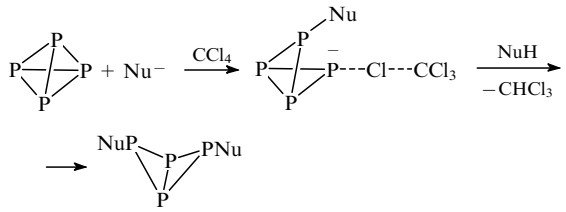
This reaction was successfully used to prepare phosphorous thioesters containing an organometallic fragment (ferrocenyl or cymantrenyl).[193] The products represent a convenient model for the synthesis of polynuclear complexes and various clusters.

The formation of trithiophosphites can be interpreted as being due to bimolecular nucleophilic substitution at phosphorus and sulfur atoms proceeding in the following steps:



R = Alk.

A more efficient procedure for the preparation of phosphorus derivatives with P—heteroatom bonds has been proposed by Lemann [194] and by Brown and Hudson.[93–96] It is based on the assumption that the reaction of white phosphorus with disulfides can be considered as a redox process. Since the forward reaction of white phosphorus with disulfides takes place only under drastic conditions, the reaction is carried out in CCl_4 in the presence of strong nucleophiles. Tetrachloromethane is known to form charge transfer complexes (CTC) with nucleophiles. White phosphorus possesses weak nucleophilic properties; therefore, before introduction into the reaction with CCl_4, it was converted into a rather stronger nucleophile [194] by treatment with, for example, alkoxide anions. The bicyclotetraphosphide type anion **73**, formed during this process, forms a CTC with CCl_4. On treatment with protic reagents, this complex decomposes to give chloroform and bicyclotetraphosphine.



By repeating this process several times, consecutive rupture of all P—P bonds in the P_4 tetrahedron can be attained to give trivalent phosphorus derivatives.

$$P_4 + 6\,Nu^- + 6\,NuH + 6\,CCl_4 \longrightarrow 4\,PNu_3 + 6\,CHCl_3 + 6\,Cl^-$$

If the PNu_3 derivatives are relatively strong nucleophiles, they can be oxidised by CCl_4 in the presence of protic reagents to give four-coordinate phosphorus compounds.[194]

The side reactions in the synthesis of trialkyl phosphites or trialkyl trithiophosphites can be suppressed by using a two-fold excess of alkoxide or thiolate ion with respect to the stoichiometric amount. The use of an equivalent amount of alkoxide decreases the yields of trialkyl phosphite due to the formation of dialkyl phosphite $(RO)_2PHO$. The formation of dialkyl phosphite can be attributed to either protonation of the initial phosphide anion or cleavage of trialkyl phosphite to dialkyl phosphite and alkyl halide on treatment with acids.[96] The optimal reaction conditions are as follows: a large excess of CCl_4, a two-fold amount of the alkoxide, room temperature, vigorous stirring and a short residence time.

$$P_4 + 6\,RX^- + 6\,RXH + 6\,CCl_4 \longrightarrow 4\,P(XR)_3 + 6\,CHCl_3 + 6\,Cl^-$$

X = O: R = Me (82%), Et (76%), Bu^n (58%) (see [101]);
X = S: R = Alk (< 90%) (see [94]).

The key problem faced by this procedure is related to the purification of trialkyl phosphites, which form stable azeotropic mixtures with excess alcohol and CCl_4. On repeated distillation of these mixtures, products of decomposition of trialkyl phosphites are formed.

An increase in the residence time results in the formation of trialkyl phosphate *via* the reaction of phosphite and CCl_4 in alcohol.[96]

$$(RO)_3P + CCl_4 \longrightarrow [(RO)_3\overset{+}{P}Cl]\,CCl_3^- \xrightarrow{ROH} \longrightarrow (RO)_4P^+Cl^- + CHCl_3 \longrightarrow (RO)_3P{=}O + RCl.$$

Under similar conditions, P_4 does not react with phenoxide and thiophenoxide ions. Relying on this fact, Brown *et al.*[93–96] made an unreasonable assumption that transformations of white phosphorus could be induced only by highly basic nucleophiles. Lemann and co-workers [194] demonstrated that it is nucleophilicity of the PhO^- and PhS^- anions rather than their basicity that plays the crucial role, the variation in the anion concentration having only a minor influence on the reaction rate. The use of bipolar aprotic solvents and a base (for example, Et_3N) to increase the nucleophilicity of these anions allowed the researchers to synthesise triphenyl phosphite (yield < 50%) and triphenyl trithiophosphite (< 80%).[194]

Despite the formal resemblance of the reactions giving trialkyl phosphite and its thio analogue in the P_4–CCl_4–RXH–NEt_3 system (X = O, S), these reactions were found to be quite different,[194, 195] the rate of reaction of P_4 with thiols proving to be much higher. The difference between the reaction mechanisms is due to the fact that thiol can be rapidly oxidised to form disulfide. This species is not nucleophilic enough to cleave the P—P bond but it can be involved in the acid–base reaction with triethylamine to generate thiolate ions, which initiate the decomposition of P_4.

The method based on the reaction of white phosphorus with proton-containing compounds in the presence of CCl_4 and a nucleophilic reagent has been successfully used to prepare triaminophosphines. A secondary amine functions as both a proton-donating reagent and a base.[194]

$$P_4 + 18\,R_2NH + 6\,CCl_4 \longrightarrow 4\,P(NR_2)_3 + 6\,CHCl_3 + 6\,(R_2NH)\cdot HCl$$

R = Alk.

The target product, tris(dialkylamino)phosphine, is a strong base and can form stable quasi-phosphonium salts with $[(R_2N)_3PCl]^+$ and $[(R_2N)_3PCCl_3]^+$ cations.

Phosphoramidates were prepared by the reaction of white phosphorus with a mixture of dialkylamine and alcohol.[194]

$$P_4 + 10\,ROH + 10\,R_2NH + 10\,CCl_4 \longrightarrow \longrightarrow 4\,R_2NP(O)(OR)_2 + 10\,CHCl_3 + 10\,(R_2NH)\cdot HCl + 4\,RCl$$

Due to the formation of by-products $(R_2N)_2P(O)(OR)$, $(RO)_3PO$ and $(R_2N)_3PO$, the yield of the target phosphoramidates did not exceed 50%.[194]

An original method has been proposed for the preparation of phosphorus derivatives with P—X bonds (X = S, O and N) using transition metal, first of all copper(II), salts as oxidants.[196–206]

As shown above (see Section II), the white phosphorus molecule can be either a η^1- or η^2 ligand. In the former case, the P_4 tetrahedron is converted into a trigonal pyramid arranged with its vertex towards the metal atom, which is manifested by an increase in the P_α—P_β bond length to 2.20 Å compared to the P_β—P_β bond lengths (2.09 Å). In the latter case, the length of the P—P bond that is coordinated to the metal atom (2.46 Å) increases to a greater extent than the bond length in the free phosphorus molecule, thus providing more appreciable loosening of the orbitals of the P_4 molecule. It has been suggested [2] that coordinatively saturated Cu(II) compounds containing donor ligands such as Cl^-, Br^-, SO_4^{2-} and RCO_2^-, incapable of the η^2-coordination of tetraphosphorus, possess lower catalytic activities than the coordinatively unsaturated complexes that display η^1- and η^2-binding modes.[196–199] This hypothesis is confirmed by the fact that the addition of pyridine to the former compounds sharply increases the reaction rate.

It was found [196–199] that the reaction of white phosphorus with alcohols proceeds selectively. The reaction takes place in the presence of copper(II) salts on moderate heating of the reactants dissolved in an aromatic hydrocarbon under an O_2 atmosphere.

$$P_4 + O_2 + R^1OH \xrightarrow[50-100\ ^\circ C]{[Cu]} \begin{cases} \xrightarrow{a} (R^1O)_3P{=}O + (R^1O)_2P(O)H + H_2O \\ \xrightarrow{b} (R^1O)_3P + H_2O \end{cases}$$

R^1 = Me, Et, Pr^n, Bu^n, Bu^i, n-C_5H_{11}, iso-C_5H_{11}, Ph, *p*-Tol.
(*a*) [Cu] = $CuCl_2$, $CuBr_2$; (*b*) [Cu] = $CuSO_4$, $Cu(O_2CR^2)_2$
(R^2 = Me, Pr^n, n-$C_{17}H_{35}$, Ar).

The reaction products depend on the copper(II) salt used. In the case of halides, phosphates and dialkyl (or diaryl) phosphites are mainly formed, while in the case of sulfates or carboxylates, the reaction gives trialkyl (or triaryl) phosphites.[200]

Under an inert atmosphere, copper(II) compounds react with white phosphorus in arene–alcohol solutions and are reduced to copper(I) salts or copper metal, which, in turn, can be oxidised by air oxygen to divalent copper.

Copper(II) complexes exhibit high catalytic activities in the oxidative coupling of P_4 with primary and secondary amines[201,202] to give phosphaazo compounds. Amines react with P_4 one or two orders of magnitude faster than alcohols. Under an argon atmosphere, white phosphorus reduces Cu(II) to Cu(0).

$$P_4 + 16\,R^1R^2NH + 5\,O_2 \xrightarrow{[Cu]}$$

$R^1 = H$: $\rightarrow 4\,(R^2NH)_3P{=}NR^2 + 10\,H_2O$

$R^1 = R^2$: $\rightarrow 4\,(R^2_1N)_3P{=}NR^1 + 6\,H_2O + 4\,R^1OH$

$R^1 = H$: R^2 = Et, Cy, $PhCH_2$; $R^1 = R^2$ = Et, Cy, $PhCH_2$.

The reactions of red phosphorus with alcohols in the presence of copper(II) salts afford trialkyl phosphates and dialkyl phosphates.[202–205] The process is carried out either under an inert gas or in the presence of atmospheric oxygen. In the latter case, oxygen and red phosphorus are consumed only by the formation of organic phosphates, whose yields based on the reactants are ~100%. The oxidative P–O coupling of red phosphorus with glycols in dioxane results in linear and cyclic alkylene phosphates.

Subsequently, other procedures for oxidative alkoxylation of white phosphorus have been proposed.[206] In these reactions, a co-oxidant and a catalyst are used in addition to the oxidant (oxygen or $NaBrO_3$).

$$P_4 + ROH \xrightarrow{[O],\,Cat} (RO)_3P \longrightarrow$$

$\rightarrow (RO)_3P{=}O$

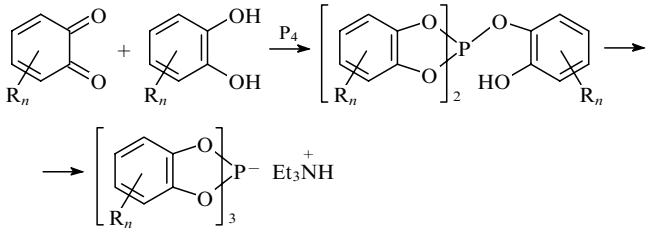
$\xrightarrow{H_2O,\,H^+} (RO)_2P(O)H \xrightarrow{[O]} (RO)_2P(O)OH$

[O] = O_2, $NaBrO_3$ + co-oxidant ($CuCl_2$, $NaNO_2$, $FeCl_3$, $C_6H_4O_2$); Cat = $PdCl_2$, $Ru(OH)Cl_3$, $RuCl_3 \cdot 6\,H_2O$.

The oxidation of elemental phosphorus with oxygen in the presence of organic compounds yields a number of derivatives. In a study of the oxidation mechanism of white phosphorus in the presence of phenol in water, 17 reaction products have been detected, phosphonic acids being the major components.[206,207] In some cases, the researchers were able to attain selectivity in the formation of particular compounds. For example, white phosphorus is rapidly and selectively oxidised by air oxygen to give trialkyl phosphate from benzene–alcohol mixtures in the presence of iodine and sodium nitrite at 20–60 °C.[208]

Slow oxidation of white phosphorus with oxygen in ethylenediamine results in ethylenediammonium monophosphite $[H_3NCH_2CH_2NH_3]^+[PHO_3]^-$ (see Ref. 209).

Benzoquinones can be used as oxidants in the synthesis of phosphoranes. For example, phosphoranes $P(O_2C_6R)_2X$ (R = Cl_4, Br_4, $Bu^n{}_2H_2$; X = Br, SePh) were formed as the major products in the reaction of white phosphorus with *o*-benzoquinones, performed in the presence of bromine or diphenyl diselenide.[210] Studies of these reactions by EPR spectroscopy showed the presence of *o*-semiquinone radicals. Exposure to UV radiation or thermolysis of a mixture of white phosphorus and substituted *o*-benzoquinone in the presence of catechol derivatives also yielded phosphoranes.[211]



R_n = H, 3,5-Bu^t_2, 3,6-Bu^t_2, 3,4,5,6-Cl_4, 4-Ph_3C.

The addition of anhydrous copper(II) chloride substantially accelerates this reaction and increases the yield of phosphoranes to 40%–60%; copper(II) being reduced to copper(I).

IV. Electrochemical methods for the synthesis of organophosphorus compounds from elemental phosphorus

Studies of the electrochemical behaviour of white phosphorus and the scope of applicability of electrochemistry for the synthesis of OPCs are in their infancy; therefore, the number of relevant papers is relatively small. The major contribution to the development of this line of chemistry was made by the Russian scientific groups headed by A P Tomilov and Yu M Kargin.

It has been shown[212] that electrochemical reduction of white phosphorus in an aprotic medium at a mercury dropping electrode is irreversible (half-wave potential $E_{1/2} = -1.55$ V *vs.* mercury pool in DMF). The calculated number of accepted electrons depends on the concentration of P_4. It was suggested that the first stage of reduction is a one-electron transfer to give a radical anion:

$$P_4 + e^- \longrightarrow P_4^{-\bullet}.$$

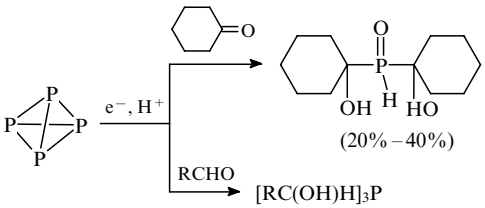
In the presence of active proton donors, which rapidly protonate the intermediate anions, all P–P bonds in the white phosphorus molecule are cleaved to give phosphine.

$$P_4 \xrightarrow{12\,H^+,\,12\,e^-} 4\,PH_3.$$

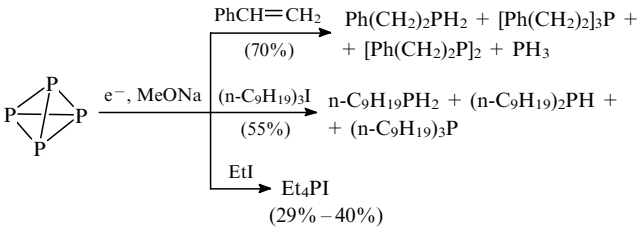
In alcohol solutions, white phosphorus is reduced *via* the intermediate chemisorbed product $P_4/(Hg)_x$.[213]

$$P_4Hg_x \xrightarrow{12\,H^+,\,12\,e^-} 4\,PH_3 + x\,Hg.$$

The electrochemical hydrogenation of white phosphorus is of practical interest as a method for the synthesis of phosphine. This process has been studied in detail using a lead cathode.[214,215] The results of the study initiated an important field of OPC electrosynthesis, namely reduction of white phosphorus in a proton-donating medium at a cathode with high hydrogen overvoltage (a mercury or lead cathode). The process consists of a number of successive steps giving highly reactive phosphorus hydrides of type $(PH)_x$ (see Ref. 214). The final phosphine and intermediate phosphorus hydrides can react with various compounds that have been added to the electrolyte and are electrochemically inactive in the potential region of the working electrodes; these include alkenes,[216] carbonyl compounds,[217,218] alkyl halides[219] and so on. These reactions yield mixtures of phosphines or individual phosphine oxides. Lower alkyl halides react with P_4 to give quaternary phosphonium salts.



R = Alk.



The electrolysis of an emulsion of P_4 in DMF in the presence of n-butyl bromide[220] furnishes a complex mixture of organic phosphines and phosphine oxides with an overall yield of 29%. At the cathode, hydrogen is apparently evolved and phosphorus and Bu^nBr are reduced.

In the above reactions, a substantial portion of elemental phosphorus polymerises and alkylation proceeds only partially (by 20% – 50%). The low yields and the complex compositions of the mixtures hamper the separation and purification of the products.

Electrochemical reduction of red phosphorus in alkaline solutions has been proposed for the synthesis of phosphine. It was found[221] that 15% – 25% solutions of NaOH and a temperature range of 70 – 100 °C were the conditions of choice for the synthesis of PH_3. In more concentrated solutions, phosphorous and hypophosphorous acids were mainly formed. When a lead cathode was used, the yield of phosphine varied from 60% to 83%.[221]

The electrochemical oxidation of white phosphorus supported on porous conductive substrates in neutral or acidic media results in phosphoric and phosphorous acids.[222] It has been suggested that the reaction is accompanied by oxidation of phosphine formed upon disproportionation of white phosphorus.

In aqueous solutions of hydrogen halides[223,224] (in some cases, with the addition of the organic solvents, benzene or chloroform[224]), indirect electrochemical oxidation of white phosphorus to phosphorous acid takes place. Apparently, in the first stage, phosphorus is oxidised by the elemental halogen evolved at the anode; this gives phosphorus halides, which are hydrolysed to give H_3PO_3.

The synthesis of phosphorous and hypophosphorous acids was performed by electrolysis of a suspension of red phosphorus in the presence of organic bases, ethylenediamine and triethylamine.[224] The influence of a number of parameters on the yield and product ratio, which depend on the amount of electricity passed, was studied. The process was intensive only at a temperature of > 70 °C, the degree of conversion of phosphorus being 40% – 45%.

Of interest from both theoretical and practical standpoints was a study of the anodic oxidation of a suspension of red phosphorus in alcohols in the presence of hydrogen chloride.[225] In these experiments, electrolysis was carried out in an undivided cell; hydrogen being evolved at the cathode, and trialkyl phosphate and alkyl chloride at the anode. The process can be represented as follows:

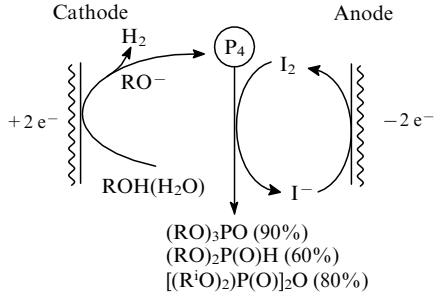
$$P + HCl + 4\,ROH \xrightarrow{5\,e^-} (RO)_3PO + \frac{5}{2}H_2 + RCl$$

R = Alk.

Chlorine evolved at the anode reacts with phosphorus and alcohol, giving the final products in 40% – 70% yields. This method is applicable only to primary aliphatic alcohols in an excess of hydrogen chloride; in other cases, the anodic process appears to yield compounds that cannot be isolated or identified.

An electrochemical procedure for the synthesis of OPCs from white phosphorus in an undivided cell was developed in the USA.[226,227] The process is carried out in solutions of alcohols, phenols or mercaptans in the presence of nitrates, bicarbonates, *etc*. as the supporting electrolytes, and using either a mercury[226] or ferrophosphorus anode.[227] Hydrogen is evolved at the cathode, and the metal cation formed upon anode dissolution serves as the oxidant. However, the yields of triorganyl phosphates are relatively low (45% – 50%). In addition, this method is environmentally unsafe due to its use of large amounts of mercury. No data on the mechanism of formation of the products have been reported in the publications cited.

In recent years, new approaches to the synthesis of OPCs have been developed. They combine the advantages of conventional (homogeneous) chemistry in solution with electrochemistry, in which the reagents are generated at the electrodes directly in the reaction system.[228 – 241]



R = Alk.

The following processes occur in an undivided cell: the formation of nucleophiles (alkoxide, hydroxide, phenoxide, amide or other anion) at the cathode and oxidation of halide ions (*e.g.*, iodide to iodine) at the anode.[228 – 238,240 – 243] The halogen, together with the nucleophile, reacts with the P_4 molecule to give various phosphorus compounds depending on the conditions of electrolysis. The general pattern of electrosynthesis of trialkyl phosphate from white phosphorus in anhydrous alcohol is as follows:

$$P_4 + 16\,ROH \xrightarrow{20\,e^-} 4\,(RO)_3PO + 4\,RH + 6\,H_2\uparrow$$

In the presence of water, optimal conditions are ensured and the yield of trialkyl phosphate becomes nearly quantitative.[231,233,235 – 238]

$$P_4 + 12\,ROH + 4\,H_2O \xrightarrow{20\,e^-} 4\,(RO)_3PO + 6\,H_2\uparrow$$

The proposed method for the electrosynthesis of trialkyl phosphates is almost waste-free. By varying the electrolysis conditions, the process can be directed towards the formation of other products, for example, tetraalkyl pyrophosphates.[230,232,236 – 238] The yield of these products depends on the structure of the aliphatic alcohol and the reactant ratio. In the case of linear aliphatic alcohols, a mixture of trialkyl phosphate and tetraalkyl pyrophosphate in ~2 : 3 ratio is formed, while the use of branched alcohols results in a similar mixture, but in a 1 : 9 ratio.

These studies provided an understanding of the mechanism of transformation of white phosphorus during the electrolysis of its solutions in aqueous alcohols in the presence of Et_4NI, and also made it possible to control this complex process. In the systems in question, cathodically generated nucleophile initiates the opening of the phosphorus rings, while halogen resulting from oxidation of the halide ion facilitates the replacement of the proton of the P – H bond. The halogen is regenerated during the electrolysis, and thus the cycle is completed. Owing to the high selectivity and rate of

these processes, phosphorus can be transformed into organophosphorus compounds with a high degree of conversion. Varying of the pH of the alcohol- and water-containing electrolyte can result in a substantial change in the composition of the cathodically generated species and, hence, in the routes of transformation of white phosphorus into target products.[236,237] For example, in acidic solutions, hydrogen ions are reduced at the cathode instead of alcohol; therefore, no opening of the phosphorus rings induced by nucleophiles (alkoxide ions) takes place. In addition, dealkylation of the esters of trivalent phosphorus acids readily occurs under these conditions. Indeed, electrolysis of aqueous alcohol solutions of HBr (or HI) over a broad concentration range in the presence of an emulsion of white phosphorus gives dialkyl phosphite as the major product (yield 70%).

It was found that anodically generated phenothiazine and triarylamine radical cations can be used to cleave P_4 in alcohol solutions.[234]

Thus, using the simple phosphorus–alcohol–water system as an example, a number of essential advantages of electrochemical methods over classical approaches of organic chemistry have been demonstrated. The use of electrochemistry allows one to synthesise OPCs from white phosphorus in high yields under mild conditions. This opens up the way to almost waste-free environmentally safe processes, allowing one to design a controlled chemical system in which the desired products can be obtained specifically by varying the conditions.

The oxidation of Cu(I) catalyst to Cu(II) during the preparation of trialkyl phosphates from white phosphorus,[196–206] considered above, can be carried out by an electrochemical process,[239] which would eliminate the explosion-prone oxidant O_2. The important advantages of the electrochemical regeneration of the catalyst include a decrease in the number of components to the reaction system, the elimination of side reactions and an increase in the yield of the target products. Studies of the Cu–ROH–P_4 ternary system revealed an analogy with the behaviour of white phosphorus in the coordination sphere of copper or nickel. The redox properties of copper catalysts were found to change in the presence of white phosphorus: the Cu^I/Cu^0 reduction wave shifting towards more positive potentials. The Cu^I–P_4 complex is characterised by a smaller electrochemical gap, *i.e.,* it is more polarisable and reactive than the initial Cu(I) compound. The possibility of electrosynthesis of phosphorus-containing acid derivatives from P_4 and alcohol, promoted by copper(II) compounds which serve as charge transferring catalysts, was also demonstrated.

$$P_4 + 20\,CuX_2 + 16\,ROH \longrightarrow 4\,(RO)_3PO + 20\,CuX + 4\,RX + 16\,HX$$

(Anode)

R = Alk.

The use of electrochemical methods has extended the range of compounds that can be prepared directly from white phosphorus. For example, aromatic esters of phosphorus acids have been synthesised in good yields.[237–242] By varying the conditions of electrolysis, one can obtain either triaryl phosphites (by adding pyridine to the electrolyte) or triaryl phosphates in nearly quantitative yields.

A study[237,240] of the decomposition routes of white phosphorus during the electrolysis of phenol solutions of Et_4NI has confirmed the general rules of behaviour of P_4 molecule in alcohol media. Characteristic features of the subsequent transformations of the organophosphorus intermediates were also elucidated. It was found that rupture of all the P–P bonds in phosphorus oligomers produced the phosphite $(PhO)_3P$. It was the first product formed in the reaction of white phosphorus with nucleophilic and electrophilic reagents generated at the electrodes.

$$P_4 + 12\,PhOH \xrightarrow{20\,e^-} 4\,(PhO)_3P + 6\,H_2\uparrow$$

It was shown experimentally for the first time[237,240] that pentaphenoxyphosphorane formed at intermediate stages of the process undergoes cathodic reduction to triphenyl phosphate. This accounts for the quantitative transformation of triphenyl phosphite into the corresponding phosphate.

$$(PhO)_3PI_2 \xrightarrow[-HI]{PhOH} (PhO)_5P \xrightarrow{e^-,\,H^+} (PhO)_3PO + PhH + PhO^-$$

This accumulated experience has been used to develop a procedure for the electrosynthesis of phosphorotriamidates and thiophosphorotriamidates from white phosphorus under the action of amide anions R_2N^-, generated by the reduction of amines at the cathode with a low hydrogen overvoltage.[237,242,243] The electrolysis of amine in the presence of an emulsion of white phosphorus gave the corresponding phosphorotriamidate; the yields in DMF (62%) were substantially higher than those in acetonitrile (12%). Presumably, phosphorotriamidate is formed by hydrolysis of the intermediate triamidoiodophosphoranes.[237,243]

$$P_4 + 12\,R_2NH \xrightarrow{12\,e^-} 4\,(R_2N)_3P + 6\,H_2\uparrow$$

$$(R_2N)_3P \xrightarrow{I_2} [(R_2N)_3PI_2] \xrightarrow{H_2O} (R_2N)_3PO$$

R = Alk.

Yet another route of transformation of $(R_2N)_3P$ formed initially has been accomplished by conducting the electrolysis in the presence of carbon disulfide. This compound acts as a sulfur donor, the reaction yielding thiophosphorotriamidate $(R_2N)_3P{=}S$ (major product) and thioformamide (minor product).[237,243]

$$P_4 + 16\,R_2NH + 4\,CS_2 \xrightarrow{20\,e^-} 4\,(R_2N)_3P{=}S + 4\,R_2NC(S)H + 6\,H_2\uparrow$$

The methods described above are based on the combined treatment of white phosphorus with nucleophilic and electrophilic reagents in an undivided cell. In these reactions, one can obtain only esters or amides of phosphorus acids but not compounds with P–C bonds.

In recent years, a new efficient method for the selective electrosynthesis of compounds with P–C bonds from white phosphorus, using metal complexes as catalysts, has been developed.[244–249] The activation of white phosphorus followed by rupturing of the P–P bonds takes place in a system that ensures cyclic regeneration of the catalyst at an electrode. It was shown that by treatment with organic halides in the presence of electrochemically generated catalysts, namely Ni(0) complexes with 2,2′-bipyridine (bipy) ligands, white phosphorus can be converted into organic phosphines and phosphine oxides. The process scheme is as follows:[246–249]

$$\text{Cathode: } Ni^{II}L_3 + 2\,e^- \rightleftharpoons Ni^0L_2 + L,$$

$$\text{Anode: } M - n\,e^- \longrightarrow M^{n+},$$

$$P_4 + RX \xrightarrow{Ni^0L_2} \diagup P{-}R,$$

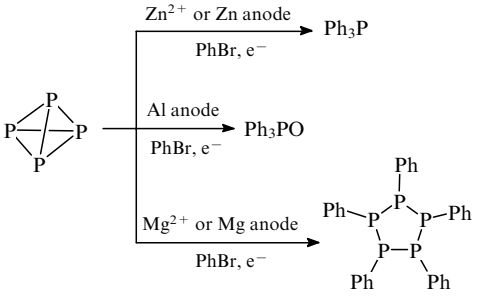
n = 2, 3; M = Mg, Zn, Al; L = bipy, Ph_3P.

The electrocatalytic arylation of white phosphorus has been studied using preparative electrolysis and cyclic voltammetry.[246–248] Some stages of the catalytic cycle were simulated and studied separately. Cathodically generated Ni(0) complexes were found to react with organic halides to give nickel organyl-σ-complexes, which are involved in the functionalisation of white phosphorus. The reaction of organonickel compound, $RNi^{II}XL_m$ with white phosphorus is the key step of the process.

$$Ni^0(bipy)_n + RX \longrightarrow RNi^{II}(bipy)_{n-1}X \xrightarrow{1/4\,P_4} \longrightarrow \text{>P—R} + Ni^{II}(bipy)$$

$n = 1, 2.$

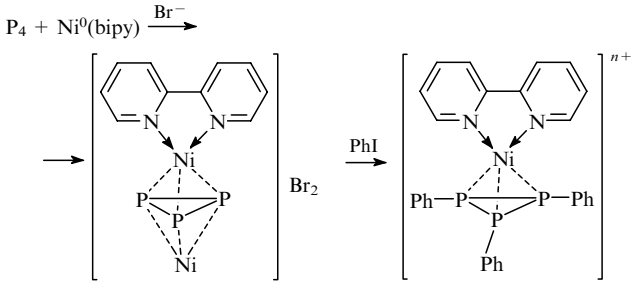
The reaction route and the yields of the final products of the electrochemical phosphorylation of organic halides with white phosphorus are considerably affected by the sacrificial anode material. The use of a zinc anode results in the synthesis of three-coordinate phosphorus compounds, triorganylphosphines, an aluminium anode stipulates the formation of triorganylphosphine oxides, and the presence of Mg(II) ions in the reaction mixture ensures the transformation of P_4 into cyclic polyphosphines $(PhP)_5$.



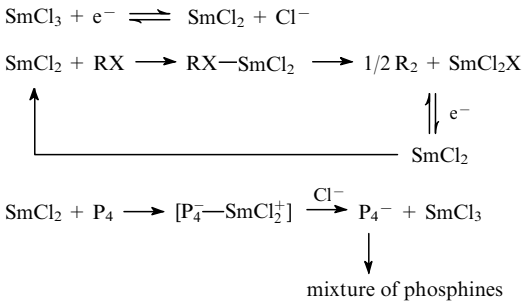
To elucidate the pathways leading to the formation of P—C bonds, an attempt has been made to cleave the white phosphorus molecule directly using Ni(II) and Ni(0) complexes.[246–248] Metal-coordinated white phosphorus becomes a stronger electron acceptor and is more readily reduced on treatment with Ni(0) complexes. A voltammetric study of the behaviour of Ni(II) complexes with bipyridine in the presence of white phosphorus has shown that the latter forms a more stable complex with Ni(0) than with Ni(II). The process irreversibility and the shift of the potential from the equilibrium value to less negative values are due to the subsequent fast chemical reduction of the P_4 molecule with the Ni^0 complex.

$$Ni^0(P_4)(bipy) \longrightarrow Ni^{n+}(P_4)^{n-}(bipy)$$

It was found that Ni^0(bipy) reacts with white phosphorus to give a binuclear complex with a cyclo-P_3 fragment. The arylation of the phosphorus fragment with aromatic halides results in a mononuclear complex with Ph_3P_3 ligand.



Among the numerous catalysts of OPC electrosynthesis, primary attention is attracted by samarium(II) derivatives, which possess strong reducing properties.[243] Electrochemical generation of these compounds from stable samarium(III) salts, in the presence of an emulsion containing a mixture of white phosphorus and iodobenzene, gives rise to products containing phosphorus–carbon bonds. If the hydrate $SmCl_3 \cdot 5\,H_2O$ is used, a mixture of phosphines, $PhPH_2$, Ph_2PH and Ph_3P, is formed predominantly, together with the phosphonium salt Ph_4PI. The anhydrous salt $SmCl_3$ catalyses the predominant formation of $PhPI_2$; some Ph_4PI was also isolated as a minor product.[244] The following scheme for the catalytic process was proposed:



Different routes for the activation of white phosphorus in the coordination sphere of nickel complexes, depending on the nature of the ligands, have been considered.[250] The first route is based on coordination of the P_4 molecule to the metal, resulting in a deformation of the tetrahedron without its destruction. This is the case with the NiX_2L complexes [where X = BF_4, Br, Cl; L = bipy (the solvents are DMF, MeCN, acetone); L = 2,9-dimethyl-1,10-phenanthroline (phen) or PPh_3 (the solvents are DMF or acetone)], which are reduced at the most negative potentials, $|E_{red}| > -0.9$ V. To cleave the P—P bonds in the complex formed, its electrochemical reduction is required.

The second route is oxidation of white phosphorus in the coordination sphere of a Ni(II) complex. This method is used when the NiX_2L complex exhibits relatively strong oxidative properties and is reduced readily ($|E_{red}| < -0.9$ V). When X = BF_4 and L = triphos, the reaction is carried out in acetone; for L = 1,1′,5,5′-bis[methylenedi(*p*-phenylene)]di(3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane) (n^2p^2), the reaction is carried out in DMF; for L = phen or PPh_3, the process is conducted in MeCN. In these cases, cleavage of the P_4 molecule affords a new Ni(I) complex, containing a P_3 fragment, for example, [(triphos)-$Ni(P_3)Ni$(triphos)]$(BF_4)_2$.

The reduction of white phosphorus in the coordination sphere of the electrochemically produced nickel(0) complex with a σ-donor ligand results in previously unknown nickel phosphides.

$$6\,Ni^0L + P_4 \longrightarrow 2\,Ni_3P_2L$$

L = bipy, phen.

A relatively high reactivity of these complexes, compared to the known nickel phosphides, has been demonstrated.[251]

To conclude this Section, it should be noted that electrochemical methods can be successfully used to synthesise a wide range of compounds containing P—O, P—N, P—C and P—S bonds from white phosphorus. These reactions usually proceed under mild conditions, at high rates and with high selectivities, providing a good base for consideration at an industrial level.

* * *

The information on the chemical properties of elemental phosphorus considered in this review is indicative of the keen attention given by researchers to this line of investigation, situated at the junction of different fields of chemistry. This is reflected in numerous publications on the subject. An important reason for this interest is the demand for new highly effective industrial processes for the production, direct from white phosphorus, of organophosphorus compounds which possess diverse useful properties. These compounds have found extensive use in various fields of human activity. Study of the chemical behaviour of white phosphorus with respect to transition metal complexes is the most convenient technique for investigation of the mechanisms of cleavage of the P_4 molecule and the stabilisation of the phosphorus-containing intermediates thus formed.

References

1. B A Trofimov, T N Rakhmatulina, N K Gusarova, S F Malysheva *Usp. Khim.* **60** 2619 (1991) [*Russ. Chem. Rev.* **60** 1360 (1991)]
2. Ya A Dorfman, M M Aleshkova, G S Polimbetova, L V Levina, T V Petrova, R R Abdreimova, D M Doroshkevich *Usp. Khim.* **62** 928 (1993) [*Russ. Chem. Rev.* **62** 877 (1993)]
3. D E C Corbridge *Phosphorus — an Outline of its Chemistry and Technology* (Amsterdam: Elsevier, 1995)
4. A P Tomilov, I M Osadchenko, A V Khudenko *Usp. Khim.* **65** 1080 (1996) [*Russ. Chem. Rev.* **65** 1001 (1996)]
5. M Scheer *Coord. Chem. Rev.* **163** 271 (1997)
6. N K Gusarova, S F Malysheva, S N Arbuzova, B A Trofimov *Izv. Akad. Nauk, Ser. Khim.* 1695 (1998) [a]
7. O J Scherer *Chem. Res.* **32** 751 (1999)
8. M Peruzzini, I de los Rios, A Romerosa, F Vizza *Eur. J. Inorg. Chem.* 593 (2001)
9. M Ehses, A Romerosa, M Peruzzini *Top. Curr. Chem.* **220** 107 (2002)
10. M Peruzzini *Spec. Chem. Mag.* 32 (2003)
11. B G Sukhov, N K Gusarova, S F Malysheva, B A Trofimov *Izv. Akad. Nauk, Ser. Khim.* 1172 (2003) [a]
12. M Peruzzini, R R Abdreimova, Y Budnikova, A Romerosa, O J Scherer, H Sitzman *J. Organomet. Chem.* **689** 4319 (2004)
13. R Hoffmann *Angew. Chem.* **94** 725 (1982)
14. K B Dillon, F Mathey, J F Nixon *Phosphorus: the Carbon Copy* (Chichester: Wiley, 1998)
15. O J Scherer *Angew. Chem.* **102** 1137 (1990
16. R G Pearson *Hard and Soft Acids and Bases* (Strousbourg: Dowden Hutchinson and Ross, 1973)
17. O J Scherer, H Swarowsky, G Wolmershiuser *Angew. Chem.* **100** 738 (1988)
18. O J Scherer, M Swarowsky, H Swarowsky, G Wolmershiuser, W Kaim, S Kohlmann *Angew. Chem.* **99** 1178 (1987)
19. E Hey, M F Lappert, J L Atwood, S G Bott *J. Chem. Soc., Chem. Commun.* 597 (1987)
20. M Herberhold, G Frohmader, W Milius *J. Organomet. Chem.* **522** 185 (1996)
21. O J Scherer, J Vondung, G Wolmershäuser *Angew. Chem.* **101** 1395 (1989)
22. O J Scherer, R Winter, G Wolmershäuser *Z. Anorg. Allg. Chem.* **619** 827 (1993)
23. O J Scherer, J Schwalb, H Swarowsky, G Wolmershäuser, W Kaim, R Gross *Chem. Ber.* **121** 443 (1988)
24. L Y Goh, C K Chu, R C S Wong, T W Hambley *J. Chem. Soc., Dalton Trans.* 1951 (1989)
25. O J Scherer, H Sitzmann, G Wolmershäuser *J. Organomet. Chem.* **268** C9 (1984)
26. M H Chisholm, K Folting, J C Huffman, J J Koh *Polyhedron* **4** 893 (1985)
27. M H Chisholm, J C Huffman, J W Pasterczyk *Inorg. Chim. Acta* **133** 17 (1987)
28. M H Chisholm, K Folting, J W Pasterczyk *Inorg. Chem.* **27** 3057 (1988)
29. J Wasserman, G J Kubas, R R Ryan *J. Am. Chem. Soc.* **108** 2294 (1986)
30. O J Scherer, J Schwalb, G Wolmershäuser, W Kaim, R Gross *Angew. Chem.* **98** 349 (1986)
31. J Schwalb, Ph.D. Thesis, University of Kaiserslautern, Kaiserslautern, 1988
32. P Jutzi, R Kroos *Chem. Ber.* **121** 1399 (1988)
33. O J Scherer, H Sitzmann, G Wolmershäuser *Angew. Chem.* **97** 358 (1985)
34. C Reddy, E D Jemmis, O J Scherer, R Winter, G Heckmann, G Wolmershiuser *Organometallics* **11** 3894 (1992)
35. W Tremel, R Hoffmann, M Kertesz *J. Am. Chem. Soc.* **111** 2030 (1989)
36. M Scheer, U Becker, J Magull *Polyhedron* **17** 1983 (1998)
37. M Scheer, E Herrmann, J Sieler, M Oehme *Angew. Chem.* **103** 1023 (1991
38. M E Barr, S K Smith, B Spencer, F L Dahl *Organometallics* **10** 3983 (1991)
39. L Y Goh *Coord. Chem. Rev.* **185–186** 257 (1999)
40. M Peruzzini, M Marvelli, A Romerosa, R Rossi, F Vizza, F Zanobini *Eur. J. Inorg. Chem.* 931 (1999)
41. P Bergamini, F F De Biani, L Marvelli, N Mascellani, M Peruzzini, R Rossi, P Zanello *New J. Chem.* 207 (1999)
42. M Di Vaira, L Sacconi *Angew. Chem.* **94** 338 (1982)
43. O J Scherer, M Ehses, G Wolmershäuser *J. Organomet. Chem.* **531** 217 (1997)
44. O J Scherer, M Ehses, G Wolmershäuser *Angew. Chem.* **110** 530 (1998)
45. M Peruzzini, S Masas, A Romerosa, A Vacca *Mendeleev Commun.* 134 (2000)
46. O J Scherer, G Kemény, G Wolmershäuser *Chem. Ber.* **128** 1145 (1995)
47. O J Scherer, G Schwarz, G Wolmershäuser *Z. Anorg. Allg. Chem.* **622** 951 (1996)
48. P Jutzi, S Opiela *J. Organomet. Chem.* **431** C29 (1999)
49. L Weber, U Sonnenberg *Chem. Ber.* **124** 725 (1991)
50. O J Scherer, T Hilt, G Wolmershäuser *Organometallics* **17** 4110 (1998)
51. O J Scherer, T Hilt, G Wolmershäuser *Angew. Chem.* **112** 1484 (2000)
52. O J Scherer, T Brück *Angew. Chem.* **99** 59 (1987)
53. O J Scherer, T Brück, G Wolmershäuser *Chem. Ber.* **121** 935 (1988)
54. G Friedrich, O J Scherer, G Wolmershäuser *Angew. Chem.* **107** 1454 (1995)
55. B Rink, O J Scherer, G Wolmershäuser *Chem. Ber.* **128** 71 (1995)
56. C Bianchini, C Mealli, M Peruzzini, F Zanobini *J. Am. Chem. Soc.* **114** 5905 (1992)
57. C Bianchini, D Masi, A Meli, M Peruzzini, F Zanobini *J. Am. Chem. Soc.* **110** 6411 (1988)
58. F Cecconi, C A Ghilardi, S Midollini, A Orlandini *Inorg. Chem.* **25** 1766 (1986)
59. M Di Vaira, L Sacconi, P Stoppioni *J. Organomet. Chem.* **250** 183 (1983)
60. A Vizi-Orosz , G Pályi, L Markó *J. Organomet. Chem.* **60** C25 (1973)
61. A Vizi-Orosz *J. Organomet. Chem.* **111** 61 (1976)
62. G Capozzi, L Chiti, M Di Viara, M Peruzzini, P Stoppioni *J. Chem. Soc., Chem. Commun.* 1799 (1986)
63. P Barbaro, M Peruzzini, J A Ramirez, F Vizza *Organometallics* **18** 4237 (1999)
64. M Peruzzini, J A Ramirez, F Vizza *Angew. Chem.* **110** 2376 (1998)
65. A P Ginsberg, W E Lindsell *J. Am. Chem. Soc.* **93** 2082 (1971)
66. A P Ginsberg, W E Lindsell, K J McCullough, C R Sprinkle, J Welch *J. Am. Chem. Soc.* **108** 403 (1986)
67. S Kang, T A Albright, J Silvestre *Croat. Chem. Acta* **57** 1355 (1984)
68. O J Scherer, M Swarowsky, H Swarowsky, G Wolmershäuser *Organometallics* **8** 841 (1989)
69. O J Scherer, G Berg, G Wolmershäuser *Chem. Ber.* **129** 53 (1996)
70. S Weigel, G Wolmershiuser, O J Scherer *Z. Anorg. Allg. Chem.* **624** 559 (1998)
71. O J Scherer, T Völmecke, G Wolmershäuser *Eur. J. Inorg. Chem.* 945 (1999)
72. O J Scherer, B Höbel, G Wolmershäuser *Angew. Chem.* **104** 1042 (1992)
73. M Detzel, Ph.D. Thesis, University of Kaiserslautern, Kaiserslautern, 1995
74. M Scheer, C Troitzsch, P G Jones *Angew. Chem.* **104** 1395 (1992)
75. M Scheer, U Becker *Phosphorus, Sulfur Silicon Relat. Elem.* **93–94** 257 (1994)
76. M Scheer, U Becker, M H Chisholm, J C Huffman, F Lemoigne, O Eisenstein *Inorg. Chem.* **34** 3117 (1995)
77. M Scheer, C Troitzsch, L Hilfert, M Dargatz, E Kleinpeter, P G Jones, J Sieler *Chem. Ber.* **128** 251 (1995)
78. M Scheer, U Becker, J C Huffman *J. Organomet. Chem.* **461** C1 (1993)
79. M Scheer, U Becker, E Matern *Chem. Ber.* **129** 721 (1996)

80. K H Whitmire *Adv. Organomet. Chem.* **42** 2 (1998)
81. M Scheer, E Herrmann *Z. Chem.* **29** 41 (1990)
82. O J Scherer *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds M Regitz, O J Scherer) (Stuttgart: Thieme, 1990)
83. O J Scherer *Angew. Chem.* **97** 905 (1985)
84. O J Scherer *Comments Inorg. Chem.* **6** 1 (1987)
85. M Di Vaira, P Stoppioni, M Peruzzini *Polyhedron* **6** 351 (1987)
86. P Dapporto, S Midollini, L Sacconi *Angew. Chem.* **91** 510 (1979)
87. P Dapporto, L Sacconi, P Stoppioni, F Zanobini *Inorg. Chem.* **20** 3834 (1981)
88. O J Scherer, J Braun, G Wolmershüuser *Chem. Ber.* **123** 471 (1990)
89. O J Scherer, J Braun, P Walther, G Wolmershüuser *Chem. Ber.* **125** 2661 (1992)
90. M Scheer, U Becker *Chem. Ber.* **129** 1307 (1996)
91. M Scheer, M Dargatz, K Schenzel *J. Organomet. Chem.* **435** 123 (1992)
92. M Scheer, M Dargatz *J. Organomet. Chem.* **440** 327 (1992)
93. C Brown, R F Hudson, G A Wartew *J. Chem. Soc., Chem. Commun.* 7 (1978)
94. C Brown, R F Hudson, G A Wartew *Phosphorus Sulfur* **5** 121 (1978)
95. C Brown, R F Hudson, G A Wartew *J. Chem. Soc., Perkin Trans. 1* 1799 (1979)
96. C Brown, R F Hudson, G A Wartew, H Coates *Phosphorus Sulfur* **6** 481 (1979)
97. C Brown, R F Hudson, G A Wartew *Phosphorus Sulfur* **5** 67 (1978)
98. E Fluck, C M E Pavlidou, R Janoschek *Phosphorus Sulfur* **6** 469 (1979)
99. V Auger *Compt. Rend.* **139** 639 (1904)
100. M M Rauhut, A M Semsel *J. Org. Chem.* **28** 471 (1963)
101. L Maier *Z. Anorg. Allg. Chem.* **394** 117 (1972)
102. M M Rauhut, R Bernheimer, A M Semsel *J. Org. Chem.* **28** 478 (1963)
103. C Wu. *J. Am. Chem. Soc.* **87** 2522 (1965)
104. BRD P. 246 544; *Chem. Abstr.* **104** 22 041 (1987)
105. M Baudler, D Düster *Z. Naturforsch., B* **42** 335 (1987)
106. M Baudler, C Adamek, S Opiela, D Ouzounis *Angew. Chem.* **100** 1110 (1988)
107. E Fluck, R Riedel, H-D Hausen, G Heckmann *Z. Anorg. Allg. Chem.* **551** 85 (1987)
108. A Schmidpeter *Nova Acta Leopoldina* **59** 69 (1985)
109. M Baudler, S Akpapoglou, D Ousounis, F Wasgestian, B Meinigke, H Budzikiewicz, H Muenster *Angew. Chem.* **100** 288 (1988)
110. M Baudler, D Ouzounis *Z. Naturforsch., B* **44** 381 (1989)
111. M Baudler, D Düster, D Ouzounis *Z. Anorg. Allg. Chem.* **544** 87 (1987)
112. Russ. P. 2 178 385; *Byull. Izobret.* (2) 122 (2002)
113. V A Miluykov, O G Sinyashin, O Scherer, E Hey-Hawkins *Mendeleev Commun.* 1 (2002)
114. I Maak, A Rabenau *Angew. Chem.* **72** 268 (1960)
115. J Ellermann, A M Demuth *Monatsh. Chem.* **118** 183 (1987)
116. G Becker, W Hoederich *Chem. Ber.* **108** 2484 (1975)
117. G Fritz, J Reuter *Z. Anorg. Allg. Chem.* **578** 27 (1989)
118. G Fritz, P Amann *Z. Anorg. Allg. Chem.* **535** 106 (1986)
119. N Wiberg, A Woerner, H Heinrich, K Karaghiosof, in *Organosilicon Chemistry* Vol. II (Eds N Auner, J Weis) (Weinheim: VCH, 1994) p. 195
120. G M Bogolyubov, A A Petrov *Dokl. Akad. Nauk SSSR* **173** 1076 (1967) [b]
121. M Baudler, D Düster *Z. Naturforsch., B* **42** 330 (1987)
122. S N Arbuzova, L Brandsma, N K Gusarova, B A Trofimov *Recl. Trav. Chim. Pays-Bas* **113** 575 (1994)
123. L Brandsma, J A Van Doorn, R-J de Lang, N K Gusarova, B A Trofimov *Mendeleev Commun.* 14 (1995)
124. T L Schull, S L Brandow, W J Dressick *Tetrahedron Lett.* **42** 5373 (2001)
125. S N Arbuzova, S F Malysheva, N I Ivanova, N A Belogorlova, L Brandsma, N K Gusarova, B A Trofimov *Zh. Obshch. Khim.* **67** 1907 (1997) [c]
126. S N Arbuzova, L Brandsma, N K Gusarova, A H T M van der Kerk, M C J van Hooijdonk, B A Trofimov *Synthesis* 65 (2000)
127. E R Bornancini, R A Alonso, R A Rossi *J. Organomet. Chem.* **270** 177 (1984)
128. M Baudler, H Jachow, B Lieser, K-F Tebbe, M Feher *Angew. Chem.* **101** 1245 (1989)
129. M Baudler *Angew. Chem.* **99** 428 (1987)
130. M Baudler, H Jachow *Z. Anorg. Allg. Chem.* **580** 27 (1990)
131. M Baudler, H Jachow, A Floruss, J Hasenbach *Chem. Ber.* **124** 1153 (1991)
132. M Baudler, V Arndt *Z. Naturforsch., B* **39** 275 (1984)
133. M Baudler, H Jachow, J Germeshausen *Z. Anorg. Allg. Chem.* **553** 15 (1987)
134. M Baudler, Y Aktalay, V Arndt, K-F Tebbe, M Feher *Angew. Chem.* **95** 1005 (1983)
135. M Baudler, H Jachow, K-F Tebbe *Z. Anorg. Allg. Chem.* **593** 9 (1991)
136. M Baudler, H Jachow, K-F Tebbe *Z. Anorg. Allg. Chem.* **614** 17 (1992)
137. M Baudler, H Jachow, J Hasenbach *Z. Anorg. Allg. Chem.* **608** 28 (1992)
138. M Baudler, W Oehlert, A Kmieciak, A Floruss *Z. Anorg. Allg. Chem.* **611** 43 (1992)
139. M Baudler, W Oehlert, A Kmieciak, A Floruss *Z. Anorg. Allg. Chem.* **616** 19 (1992)
140. M Baudler, B Koll, V Arndt *Z. Naturforsch., B* **45** 1517 (1990)
141. B A Trofimov, L Brandsma, S N Arbuzova, N K Gusarova *Zh. Obshch. Khim.* **67** 343 (1997) [c]
142. B A Trofimov, L Brandsma, S N Arbuzova, N K Gusarova *Izv. Akad. Nauk, Ser. Khim.* 884 (1997) [a]
143. C Sharrier, N Maigrot, L Ricard, P Le Floch, F Mathey *Angew. Chem., Int. Ed. Engl.* **35** 2133 (1996)
144. L Maier *Top. Curr. Chem.* **19** 1 (1971)
145. BRD P. 2840147; *Chem. Abstr.* **93** 28728 (1980)
146. BRD P. 2632316; *Chem. Abstr.* **88** 173 006 (1978)
147. BRD P. 2549084; *Chem. Abstr.* **87** 55236 (1977)
148. US P. 4207300; *Chem. Abstr.* **93** 116696 (1980)
149. S D Gokhale, W L Jolly *Inorg. Synth.* **9** 56 (1967)
150. B A Trofimov, N K Gusarova, S F Malysheva, T N Rakhmatulina, M G Voronkov, V I Dmitriev, S I Shaikhudinova *Phosphorus, Sulfur Silicon Relat. Elem.* **55** 271 (1991)
151. N K Gusarova, B A Trofimov, S F Malysheva, T N Rakhmatulina, E P Vyalykh, M G Voronkov *Izv. Akad. Nauk SSSR, Ser. Khim.* 488 (1989) [a]
152. B A Trofimov, S F Malysheva, N K Gusarova, V I Dmitriev, S I Shaikhudinova, T N Rakhmatulina, V I Donskikh, M G Voronkov *Zh. Obshch. Khim.* **59** 1894 (1989) [c]
153. N K Gusarova, B A Trofimov, S F Malysheva, T N Rakhmatulina, M G Voronkov *Dokl. Akad. Nauk SSSR* **305** 355 (1989) [b]
154. B A Trofimov, N K Gusarova, S F Malysheva, E P Vyalykh, T N Rakhmatulina, M G Voronkov *Izv. Akad. Nauk SSSR, Ser. Khim.* 1449 (1988) [a]
155. B A Trofimov, L Brandsma, S N Arbuzova, S F Malysheva, N A Belogorlova, N K Gusarova *Zh. Obshch. Khim.* **67** 695 (1997) [c]
156. B A Trofimov, N K Gusarova, S F Malysheva, V I Dmitriev, S I Shaikhudinova, T N Rakhmatulina *Zh. Org. Khim.* **25** 1563 (1989) [d]
157. N K Gusarova, B A Trofimov, T N Rakhmatulina, S F Malysheva, A A Tatarinova, L M Sinegovskaya, M G Voronkov *Zh. Obshch. Khim.* **60** 300 (1990) [c]
158. B A Trofimov, N K Gusarova, S F Malysheva, T N Rakhmatulina, A V Polubentsev, M G Voronkov *Zh. Obshch. Khim.* **60** 456 (1990) [c]
159. S F Malysheva, Z M Garashchenko, S N Arbuzova, M V Nikitin, N K Gusarova, B A Trofimov *Zh. Obshch. Khim.* **67** 1905 (1997) [c]
160. V A Potapov, S V Amosova, A V Khangurov *Izv. Akad. Nauk SSSR, Ser. Khim.* 208 (1989) [a]

161. N K Gusarova, S I Shaikhudinova, N I Ivanova, A M Reutskaya, A I Albanov, B A Trofimov *Zh. Obshch. Khim.* **71** 765 (2001) [c]
162. N K Gusarova, B A Trofimov, T N Rakhmatulina, S F Malysheva, S N Arbuzova, S I Shaikhudinova, A I Albanov *Izv. Akad. Nauk, Ser. Khim.* 1680 (1994) [a]
163. B A Trofimov, N K Gusarova, S I Shaikhudinova, T N Rakhmatulina, S F Malysheva, L A Oparina, V I Dmitriev, M G Voronkov *Izv. Akad. Nauk SSSR, Ser. Khim.* 2870 (1990) [a]
164. B A Trofimov, V I Dmitriev, T I Kazantseva, S I Shaikhudinova, S F Malysheva, M V Sigalov, N K Gusarova *Zh. Obshch. Khim.* **60** 2174 (1990) [c]
165. B A Trofimov, N K Gusarova, L Brandsma *Main Group Chem. News* **4** 18 (1996)
166. N K Gusarova, Yu V Smetannikov, B G Sukhov, S F Malysheva, N P Tarasova , B A Trofimov *Zh. Obshch. Khim.* **71** 688 (2001) [c]
167. B A Trofimov, B G Sukhov, N K Gusarova, S F Malysheva, V V Tirskii, L I Ruzhnikov, E F Martynovich *Dokl. Akad. Nauk* **382** 214 (2002) [b]
168. B G Sukhov, N K Gusarova, S F Malysheva, T I Vakul'skaya, V V Tirskii, L I Ruzhnikov, E F Martynovich, B A Trofimov, in *Lyuminestsentsiya i Soputstvuyushchie Yavleniya* (*Tez. Dokl. VII Vseross. Shkoly-seminara), Irkutsk, 2001* [Luminescence and Accompanying Phenomena (Abstracts of Reports of the VIIth All-Russian School-seminar), Irkutsk, 2001] p. 75
169. N K Gusarova, S I Shaikhudinova, T I Kazantseva, S F Malysheva, B G Sukhov, N A Belogorlova, V I Dmitriev, B A Trofimov *Zh. Obshch. Khim.* **72** 399 (2002) [c]
170. BRD P. 19923830; *Chem. Abstr.* **132** 12410 (2000)
171. L Maier *Helv. Chim. Acta* **50** 1723 (1967)
172. L Maier *Angew. Chem.* **77** 549 (1965)
173. E Y Boros, W M Lanham, C Wu *Ind. Eng. Chem. Prod. Res. Develop.* **12** 221 (1973)
174. US P. 3644595; *Chem. Abstr.* **76** 99821 (1972)
175. BRD P. 1913644; *Ref. Zh. Khim.* 18H157 (1975)
176. B E Ivanov, N S Fridland, A G Abul'khanov, S S Krokhina, A V Il'yasov *Izv. Akad. Nauk SSSR, Ser. Khim.* 1399 (1987) [a]
177. N S Fridland, B E Ivanov *Zh. Obshch. Khim.* **63** 2668 (1993) [c]
178. K A Petrov, V V Smirnov, V I Emel'yanov *Zh. Obshch. Khim.* **31** 3027 (1961) [c]
179. N G Feshchenko, T I Alekseeva, A V Kirsanov *Zh. Obshch. Khim.* **38** 122 (1968) [c]
180. L Maier *Fortschr. Chem. Forsch.* **19** 1 (1971)
181. BRD P. 2620847; *Chem. Abstr.* **88** 89840 (1980)
182. N G Feshchenko, T I Alekseeva, A V Kirsanov *Zh. Obshch. Khim.* **33** 1013 (1963) [c]
183. N G Feshchenko, L F Irodionova, O I Korol', A V Kirsanov *Zh. Obshch. Khim.* **40** 773 (1970) [c]
184. H P Angstadt *J. Am. Chem. Soc.* **86** 5040 (1964)
185. H-J Christau, J Pascal, F Plenat *Tetrahedron Lett.* **31** 5463(1992)
186. US P. 4052463; *Chem. Abstr.* **88** 7056 (1978)
187. E Fluck, R Riedel, P Fischer *Phosphorus Sulfur* **33** 115 (1987)
188. US P. 3976690; *Chem. Abstr.* **85** 192889 (1976)
189. R J Burt, J Chatt, W Hussain, G J Leigh *J. Organomet. Chem.* **182** 203 (1979)
190. D L Allen, V C Gibson, M L H Green, J F Skinner, J Bashkin, P D Grebenik *J. Chem. Soc., Chem. Commun.* 895 (1983)
191. D H R Barton, R F V Embse *Tetrahedron* **54** 12475 (1998)
192. M V Tsikalova, M E Lobanov, I Ya Levitin, P V Petrovskii, M E Vol'pin, M I Kabachnik *Dokl. Akad. Nauk SSSR* **38** 386 (1989) [b]
193. V A Milyukov, A V Zverev, S M Podlesnov, D B Krivolapov, I A Litvinov, A T Gubaidullin, O N Kataeva, A G Ginzburg, O G Sinyashin *Eur. J. Inorg. Chem.* 225 (2000)
194. G A Lemann, in *Khimiya i Primenenie Fosfororganicheskikh Soedinenii (Trudy VI Konf.)* [The Chemistry and Applications of Organophosphorus Compounds (Proceedings of the VIth Conference)] (Kiev: Naukova Dumka, 1981) p. 194
195. R Riedel, Ph.D. Thesis, University of Stuttgardt, Stuttgardt, 1986
196. R R Abdreimova, F K Faizova, D N Akbayeva, G S Polimbetova, S M Aibasova, A K Borangazieva, M B Aliev *Eurasian Chem. Tech. J.* **4** 11 (2002)
197. Ya A Dorfman, R R Abdreimova, L V Levina, T V Petrova *Kinet. Katal.* **30** 1484 (1989) [e]
198. Ya A Dorfman, R R Abdreimova, L V Levina, T V Petrova *Zh. Obshch. Khim.* **59** 481 (1989) [c]
199. Ya A Dorfman, R R Abdreimova, D M Doroshkevich *Teoret. Eksp. Khim.* 659 (1991) [f]
200. Ya A Dorfman, L V Levina, T V Petrova, M M Aleshkova, R R Abdreimova, G S Polimbetova, V S Emel'yanova *Zh. Obshch. Khim.* **60** 1275 (1990) [c]
201. Ya A Dorfman *Katalizatory Organicheskogo Sinteza* (Catalysts of Organic Synthesis) (Alma-Ata: Nauka, 1992) Vol. 2
202. Ya A Dorfman, M M Aleshkova, A S Karinskaya, A K Barangazieva, M M Kebekbaeva *Zh. Obshch. Khim.* **61** 1101 (1991) [c]
203. Ya A Dorfman, M M Aleshkova, A S Karinskaya *Kinet. Katal.* **32** 188 (1991) [e]
204. Ya A Dorfman, M M Aleshkova, M M Kebekbaeva *Kinet. Katal.* **32** 1349 (1991) [e]
205. Ya A Dorfman, D M Doroshkevich, M M Aleshkova *Kinet. Katal.* **32** 1357 (1991) [e]
206. R R Abdreimova, D N Akbayeva, G S Polimbetova, A-M Caminade, J-P Majoral *Phosphorus Sulfur Silicon* **156** 239 (2000)
207. X Miao, S Chu, X Xu, K Hu *Zhongguo Huanjing Kexue* **16** 373 (1996)
208. Ya A Dorfman, R R Abdreimova, G S Polimbetova, S M Aibasova, D N Akbaeva *Kinet. Katal.* **37** 183 (1996) [e]
209. W Hoenle, L Walz, H G Von Schnering *Z. Naturforsch., B* **45** 1251 (1990)
210. T A Annan, Z Tian, D G Tuck *J. Chem. Soc., Dalton Trans.* 19 (1991)
211. M I Kabachnik, D I Lobanov, N V Matrosova, P V Petrovskii *Zh. Obshch. Khim.* **56** 1464 (1986) [c]
212. I N Brago, A P Tomilov *Elektrokhimiya* **4** 697 (1968) [g]
213. A P Tomilov, I N Brago, I M Osadchenko *Elektrokhimiya* **4** 1153 (1968) [g]
214. N Ya Shandrinov, A P Tomilov *Elektrokhimiya* **4** 237 (1968) [g]
215. I M Osadchenko, A P Tomilov *Zh. Prikl. Khim.* **43** 1255 (1970) [h]
216. L V Kabak, N Ya Shandrinov, A P Tomilov *Zh. Obshch. Khim.* **40** 584 (1970) [c]
217. I M Osadchenko, A P Tomilov *Zh. Obshch. Khim.* **39** 469 (1969) [c]
218. I M Osadchenko, A P Tomilov *Zh. Obshch. Khim.* **40** 698 (1970) [c]
219. L F Filimonova, L V Kaabak, A P Tomilov *Zh. Obshch. Khim.* **39** 2174 (1969) [c]
220. L V Kaabak, M I Kabachnik, A P Tomilov, S A Varshavskii *Zh. Obshch. Khim.* **36** 2060 (1966) [c]
221. I M Osadchenko, A P Tomilov *Elektrokhimiya* **29** 406 (1993) [g]
222. M L Varry, C W Tobias *Electrochim. Technol.* **4** 502 (1966)
223. US P. 4021321; *Chem. Abstr.* **87** 13505 (1977)
224. US P. 4021322; *Chem. Abstr.* **87** 13506 (1977)
225. S P Varshavskii, A P Tomilov *Zh. Vses. Khim. O-va im D I Mendeleeva* 598 (1962) [i]
226. US P. 4337125; *Chem. Abstr.* **97** 81757 (1982)
227. US P. 4338166; *Chem. Abstr.* **97** 127818 (1982)
228. A S Romakhin, Yu G Budnikova, I M Zaripov, Yu M Kargin, E V Nikitin, A P Tomilov, Yu A Ignat'ev, V V Smirnov *Izv. Akad. Nauk, Ser. Khim.* 1322 (1992) [a]
229. A S Romakhin, I M Zaripov, Yu G Budnikova, Yu M Kargin, E V Nikitin, A P Tomilov, Yu A Ignat'ev *Izv. Akad. Nauk, Ser. Khim.* 1328 (1992) [a]
230. Yu G Budnikova, Yu M Kargin, I M Zaripov, A S Romakhin, Yu A Ignat'ev, E V Nikitin, A P Tomilov, V V Smirnov *Izv. Akad. Nauk, Ser. Khim.* 2033 (1992) [a]
231. USSR P. 1494492; *Byull. Izobret.* (26) 269 (1989)
232. USSR P. 1594951; *Byull. Izobret.* (35) 280 (1990)
233. A S Romakhin, I M Zaripov, Yu G Budnikova, Yu A Ignat'ev, E V Nikitin, Yu M Kargin *Elektrokhimiya* **25** 780 (1989) [g]

234. Yu G Budnikova, Yu M Kargin *Zh. Obshch. Khim.* **65** 566 (1995) [c]
235. Yu H Budnikova, Yu M Kargin, O G Sinyashin *Phosphorus, Sulfur Silicon Relat. Elem.* **144–146** 565 (1999)
236. Yu H Budnikova, Yu M Kargin, O G Sinyashin *Phosphorus, Sulfur Silicon Relat. Elem.* **144–146** 51 (1999)
237. Yu M Kargin, Yu H Budnikova, B I Martynov, V V Turygin, A P Tomilov *J. Electroanal. Chem.* **507** 157 (2001)
238. Russ. P. 2199545; *Byull. Izobret.* (6) 27 (2003)
239. Yu G Budnikova, A G Kafiyatullina, O G Sinyashin, R R Abdreimova *Izv. Akad. Nauk, Ser. Khim.* 882 (2003) [a]
240. Yu G Budnikova, Yu M Kargin, I M Zaripov, A S Romakhin, Yu A Ignat'ev, E V Nikitin, A P Tomilov *Izv. Akad. Nauk, Ser. Khim.* 2039 (1992) [a]
241. USSR P. 1582580; *Byull. Izobret.* (28) 256 (1990)
242. USSR P. 1602015; *Byull. Izobret.* (39) 241 (1990)
243. Yu G Budnikova, Yu M Kargin *Zh. Obshch. Khim.* **65** 1663 (1995) [c]
244. Yu G Budnikova, D G Yakhvarov, Yu M Kargin *Zh. Obshch. Khim.* **68** 603 (1998) [c]
245. Yu H Budnikova, D G Yakhvarov, Yu M Kargin *Mendeleev Commun.* 67 (1997)
246. Yu H Budnikova, J Perichon, D G Yakhvarov, Yu M Kargin, O G Sinyashin *J. Organomet. Chem.* **630** 185 (2001)
247. Yu M Kargin, Yu G Budnikova *Zh. Obshch. Khim.* **71** 1472 (2001) [c]
248. D G Yakhvarov, Yu G Budnikova, D I Tazeev, O G Sinyashin *Izv. Akad. Nauk, Ser. Khim.* 1903 (2002) [a]
249. Russ. P. 2221805; *Byull. Izobret.* (2) 20 (2004)
250. Yu G Budnikova, A G Kafiyatullina, A S Balueva, R M Kuznetsov, V I Morozov, O G Sinyashin *Izv. Akad. Nauk, Ser. Khim.* 2289 (2003) [a]
251. Yu H Budnikova, D I Tazeev, B A Trofimov, O G Sinyashin *Electrochem. Commun.* **6** 700 (2004)

[a] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[b] — *Dokl. Chem. (Engl. Transl.)*
[c] — *Russ. J. Gen. Chem. (Engl. Transl.)*
[d] — *Russ. J. Org. Chem. (Engl. Transl.)*
[e] — *Kinet. Catal. (Engl. Transl.)*
[f] — *J. Theor. Exp. Chem. (Engl. Transl.)*
[g] — *Russ. J. Electrochem. (Engl. Transl.)*
[h] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[i] — *Mendeleev Chem. J. (Engl. Transl.)*