



# Electrocatalytic eco-efficient functionalization of white phosphorus

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## Abstract

The novel eco-efficient methods to transform white phosphorus into the esters of phosphoric, phosphorous and phosphonic acids, tertiary phosphines and other organophosphorus compounds under conditions of electrochemical catalysis were elaborated. The mechanism of these processes was investigated using the method of cyclic voltammetry and preparative electrolysis.

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*Keywords:* White phosphorus; Electrosynthesis; Nickel complex; Copper complex; Esters of phosphorous acid; Tertiary phosphines

## 1. Introduction

A longstanding aim of electrochemical research has been to develop a clean, selective method for carrying out organic synthesis. The only limitation of electrochemical techniques to organic synthesis is aversion of organic chemists to electrodes [1]. The renaissance of electrochemistry has come with the general realization of its ubiquity. In some cases, the oxidizing or reducing power can be controlled by the electrical potential of the electrode providing functional group differentiation. Electrochemical methods are particularly “green” (electrons as reagents) and the lack of byproducts makes them attractive for synthesizing pharmaceuticals and fine chemicals. Electrochemistry offers access to the synthesis of valuable compounds including fine chemicals, pharmaceuticals, agrochemicals, complex natural products and a wide variety of interesting intermediates and precursors such as chiral drug intermediates. The interest to direct synthesis of organophosphorus compounds (OPCs) from white phosphorus, escaping the traditional stages of its chlorination, is connected to

the increase of the requirements of ecological safety and low-waste production [2–4].

A replacement of the present-day processes for preparation of basic organophosphorus compounds based now on reactions of phosphorus chlorides rises in importance. The existing processes are environmentally dangerous, energy-consuming and multiple-waste. The evolved hydrogen chloride accounting, by mass, for three quarters of initial phosphorus trichloride is their key disadvantage. This makes inaccessible a large-capacity of the organophosphorus compounds production based on the chlorine technology from the viewpoint of environmental safety. The creation of chlorine- and waste-free processes to obtain some starting compounds, namely, phosphites, phosphates, amides, tertiary phosphines, etc., based on elemental (white) phosphorus is an alternative of the organophosphorus compounds synthesis.

Some progress in this area was observed during last years. It is connected with the use of either the reagents combination (nucleophiles–electrophiles) [5–7] or catalysts [3] allowing to get better results under mild conditions. In our opinion, however, non-traditional methods for the organophosphorus compounds synthesis based on elemental phosphorus and electrochemical techniques first of all are the most challenging now.

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We represent in this review last results made within last 10–15 years in our laboratory in the field of electro-synthesis on the basis of white phosphorus [8–30].

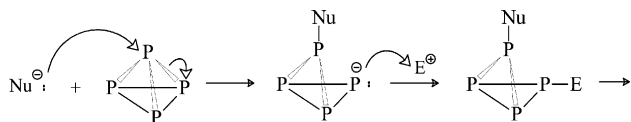
This paper is devoted to consideration of electrochemical methods for synthesis of the most significant types of industrially important OPC. Esters of phosphorus acids and tertiary phosphines holds a particular position among these substances. Many of them play a key role in biochemical processes and are applied as plasticizers, inhibitors of combustion, insecticides, ligands, extragents of heavy metals and so on.

## 2. Results and discussion

### 2.1. Synthesis of phosphorous esters containing P–O, P–N and P–S bonds

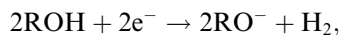
The instant analysis of electrochemical behaviour of white phosphorus and the possibilities of application of electrochemical methods for synthesis on P<sub>4</sub> basis is in its early stage at present, and only a number of publications in this area are available. Reduction and oxidation of white phosphorus and at the various electrodes (graphite, platinum, mercury) in water and non-aqueous solvents (aqueous solutions of sulfuric acid and sodium hydroxide, ethanol) were investigated by methods of cyclic voltammetry, but for preparative synthesis were not used, as are accompanied by passivation of an electrode in many cases [31–35].

The most promising approach involving a joint action of nucleophilic and electrophilic reagents on the molecule of white phosphorus gives the basis for electro-synthesis of esters of phosphorus acid. The consecutive repetition of the stages of nucleophile attack on phosphorus and phosphide anion capture by electrophilic agent allows to obtain various organophosphorus products under mild conditions [5–7].



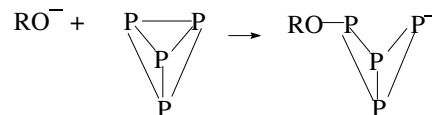
Combining the advantages of usual homogeneous chemistry in solution and electrochemistry, when the reagents (both nucleophiles and electrophiles) are generated on electrodes directly in the reactions system, we succeeded in gaining high conversion of white phosphorus to target products and choosing conditions of high selectivity of the process [8–22].

It is known that an alkoxy ion is formed on cathodes with low hydrogen overvoltage when tetraalkylammonium halides are used as supporting electrolytes.



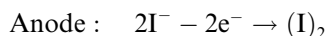
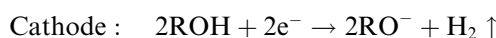
$$E_{1/2} = -2.2\text{--}2.4 \text{ V (ref. Ag/AgNO}_3, 10^{-2}\text{M)}$$

This reaction was supposed be used to disclose the P<sub>4</sub> tetrahedron.

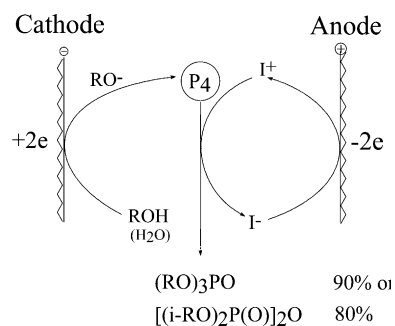


The halogen generated at the anode during the oxidation of the halide ions of supporting electrolyte plays the role of necessary electrophile. The joint action of alkoxy anion and halide on the white phosphorus molecules results in various derivatives of phosphorus acids (phosphates, pyrophosphates, phosphites), depending on electrolysis conditions (Scheme 1) [8–17].

A mixture of organophosphorus products was obtained after full dissolution of all phosphorus oligomers at 25–50 °C in a non-aqueous solution of alcohol and acetonitrile (Table 1) [8–10]. Their composition and percentage depend on the alcohol structure and temperature of the process. Each intermediate was detected and confirmed spectroscopically. Alkyl iodide is reduced at the cathode and was detected in the electrolyte only in minor quantities. Hence, some by-products other than trialkyl phosphate are formed under these conditions. The yield of trialkyl phosphates did not exceed 70% in all cases. On the basis of these data it is possible to suggest the general next processes (Scheme 2) [8–10,13–17].



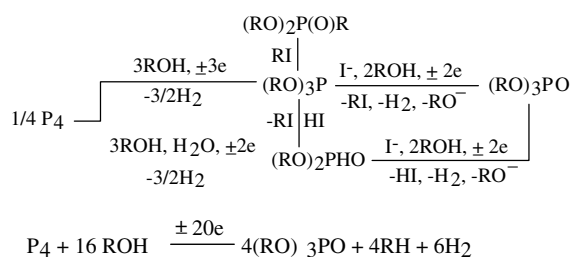
It is feasible to obtain a single ultimate product for certain limits of the molar ratio of water and alcohol [11,29]. A comprehensive study of the reaction mechanism allowed to make a conclusion about the influence of hydroxide ions, arising during electrochemical process on the course of this interaction. Indeed, the



Scheme 1. Electrochemical processes in the synthesis of the phosphorus acids derivatives from P<sub>4</sub>.

Table 1  
Products of alcohols electrolysis in acetonitrile solution in the presence of  $P_4(M(P):M(ROH) = 1:20, Q = 5.2F)$

| ROH  | T (°C) | Product                   | Yield on P (%) |
|------|--------|---------------------------|----------------|
| MeOH | 18     | (MeO) <sub>2</sub> PHO    | 11             |
|      |        | (MeO) <sub>3</sub> PO     | 70             |
|      |        | (MeO) <sub>2</sub> P(O)Me | 3              |
|      | 50     | (MeO) <sub>3</sub> PO     | 51             |
|      |        | (MeO) <sub>2</sub> P(O)Me | 28             |
| EtOH | 20     | (EtO) <sub>2</sub> PHO    | 9              |
|      |        | (EtO) <sub>3</sub> PO     | 69             |
|      | 56     | (EtO) <sub>3</sub> PO     | 65             |
|      |        | (EtO) <sub>2</sub> P(O)Et | 14             |
| BuOH | 25     | (BuO) <sub>2</sub> PHO    | 7              |
|      |        | (BuO) <sub>3</sub> PO     | 66             |
|      | 56     | (BuO) <sub>3</sub> PO     | 60             |
|      |        | (BuO) <sub>2</sub> P(O)Bu | 15             |



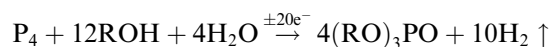
Scheme 2.

electrolysis carrying out in water–alcohol solutions under optimal conditions and reagents ratio allows to obtain trialkyl phosphates practically with a quantitative yields both in the base of the phosphorus and electric current (see Table 2) [11,29]. As a result of successive reactions dialkylphosphite is formed, which is unstable under electrolysis conditions and may be transformed to trialkylphosphate with an excess of alcohol. It is possible to direct the process towards formation in high

Table 2  
Yields of trialkyl phosphates in electrolysis of water–alcohol solutions in the presence of  $P_4 \{M(P):M(H_2O):M(ROH) = 1:(1-1.1):(20-50)\}; CH_3CN, 50^\circ C, Et_4NI, I_a = 10-30 \text{ mA cm}^{-2}$

| (RO) <sub>3</sub> P=O            | Yield on P (%) |
|----------------------------------|----------------|
| (MeO) <sub>3</sub> PO            | 93             |
| (EtO) <sub>3</sub> PO            | 92             |
| (PrO) <sub>3</sub> PO            | 89             |
| ( <i>i</i> -PrO) <sub>3</sub> PO | 80             |
| (BuO) <sub>3</sub> PO            | 95             |
| ( <i>s</i> -BuO) <sub>3</sub> PO | 83             |
| (AmO) <sub>3</sub> PO            | 89             |

yield of trialkyl phosphate by adequate selection of the molar ratio of the reagents. Only hydrogen is the by-product in this case. The overall equation for the process is [11,13–17,29]:



Therefore, this variant of the synthesis method is practically wasteless and allows to avoid difficulties in the modern production of trialkyl phosphates.

Nevertheless, it is necessary to suppress parallel reactions that produce the formation of indeliberate products. The selective transformation of white phosphorus in trialkylphosphate is possible by using the catalytic amounts of transition metal complexes that accelerate the oxidation of phosphorus and all phosphoric intermediates into derivatives of four-coordinated phosphorus. The complexes NiBr<sub>2</sub>bipy and CuBr<sub>2</sub>bipy were selected for this purpose [22]. Activation of P<sub>4</sub> molecule by interaction with the catalytic metal complex is favored the breaking of the P–P bonds and therefore the P<sub>4</sub> reduction. Results obtained by electrolyses of the P<sub>4</sub> emulsion in ethanol in presence of these complexes show that the catalytic electro-synthesis of trialkylphosphates is possible. The complex of nickel allows to obtain triethylphosphate as the sole product, whereas the complex of copper gives the mixture of products under the same conditions. In the latter case the increase of the electricity intensity allows to synthesized (EtO)<sub>3</sub>PO from (EtO)<sub>2</sub>PHO, but (EtO)<sub>2</sub>P(O)Et still remains as a by-product [22]. The overall reaction of the electro-synthesis with the use of metal complex became as following (Scheme 3).

It is obvious, that the complex of nickel allow to prepare triethyl phosphate as the sole product, whereas the complex of copper gives mixture of products in the same conditions (Table 4) [22].

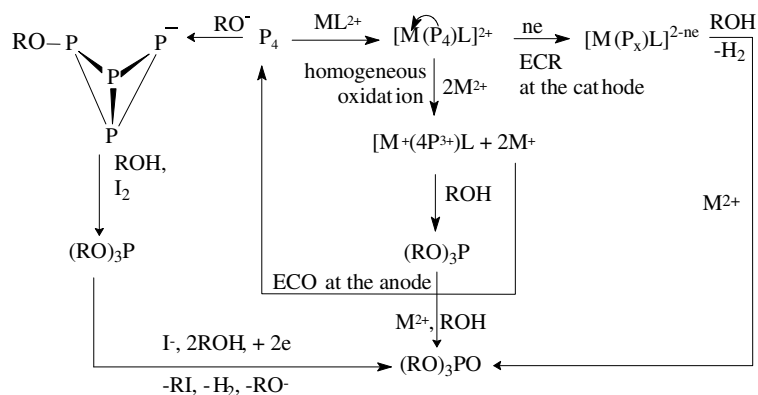
L = bipy, M = Ni, Yield = 95%

M = Cu, Yield = 78%

It was determined that the redox-properties of copper catalysts vary in the presence of white phosphorus, the potential of a reduction wave of Cu<sup>I</sup>/Cu<sup>0</sup> being displaced to more positive values. The complex Cu<sup>I</sup>–P<sub>4</sub> is characterized by a smaller value of an electrochemical gap, which is polarized easier and more reactive than initial Cu<sup>I</sup> [22].

Thus, the increasing of the process selectivity of trialkylphosphate synthesis can be reached in two ways. The first one using a water/P<sub>4</sub> definite ratio [8–11,29], the second one by introducing a metallocomplex catalyst that accelerates the processes via oxidation of the P(III) intermediates, avoiding their isomerisation stage and other three-coordinated phosphorus intermediates [22].

For a more complete study of synthetic possibilities and limitations of this reaction, it is necessary to clarify



Scheme 3.

the conditions of successive breaking of the P–P bonds in  $P_4$  molecule, its oligomerization and the nature of electrochemically generated nucleophilic and electrophilic reagents. The presence of water is fundamental for these processes. A comprehensive study of the reaction mechanism allowed us to conclude about the influence of hydroxide ions.

When water and alcohol content in the electrolyte decreases comparing white phosphorus, a general direction of electrochemical process changes leading to tetraalkyl pyrophosphate as a main product. Its yield depends on the aliphatic alcohol (Table 3) and reaches 80% in the case of iso-alcohols [12,17,29].

Table 3

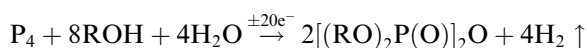
Products from the electrolysis of the  $P_4$  emulsion in alcohol–water solution ( $M(P):M(ROH):M(H_2O) = (1:(4-6):(0.8-1.5))$ ), alcohol and water lack with 0.01 M  $Et_4NI$

| ROH            | $I$ (mA cm <sup>-2</sup> ) | $T$ (°C) | Products             | Yield on P (%) |
|----------------|----------------------------|----------|----------------------|----------------|
| PrOH           | 3.2                        | 52       | $[(PrO)_2P(O)]_2O$   | 52             |
|                |                            |          | $(PrO)_3PO$          | 17             |
| <i>i</i> -PrOH | 4.0                        | 51       | $[(i-PrO)_2P(O)]_2O$ | 80             |
|                |                            |          | $(i-PrO)_3PO$        | 5              |
| <i>i</i> -AmOH | 5.5                        | 55       | $[(AmO)_2P(O)]_2O$   | 79             |
|                |                            |          | $(AmO)_3PO$          | 4              |
| <i>i</i> -BuOH | 4.7                        | 50       | $[(i-BuO)_2P(O)]_2O$ | 81             |
|                |                            |          | $(i-BuO)_3PO$        | 4              |

Table 4

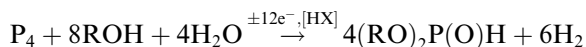
Products from the electrolysis of the  $P_4$  emulsion in ethanol solution in the presence of metalcomplex catalysts in the undivided cell

| Products        | Yield on P (%)                     |           |      |  |
|-----------------|------------------------------------|-----------|------|--|
|                 | CuCl <sub>2</sub> bpy <sub>3</sub> |           |      | Ni(BF <sub>4</sub> ) <sub>2</sub> bpy <sub>3</sub> |
|                 | DMF–EtOH                           | MeCN–EtOH | EtOH | DMF–EtOH   |
| $(EtO)_2P(O)Et$ | 5.4                                | 15.5      | 17.5 | 0  |
| $(EtO)_2PHO$    | 15.3                               | 29.5      | 16.0 | 0  |
| $(EtO)_3PO$     | 79.3                               | 55.0      | 28.5 | 90   |
| Total yield     | 90                                 | 81        | 62   | 90   |



These investigations allowed not only to recognize a scheme of white phosphorus reacting during electrolysis of water–alcohol solutions in the aprotic solvents with tetraethylammonium iodide as a supporting electrolyte, but to control this complicated process. In the system under study, a nucleophile generated on cathode acts as an initiator for disclosure of white phosphorus tetrahedron, and a product of iodide ion oxidation promotes the process completion being regenerated during the electrolysis. The high selectivity and rate of electrosynthesis allow to carry out this process with high conversion of white phosphorus to target organophosphorus products.

It is possible to change a state of reagent generated at the cathode and, therefore, a direction of white phosphorus transformation by changing the pH of an electrolyte containing alcohol and water [16,17]. Acidolysis reaction of the obtained trialkyl phosphites leading to appropriate dialkyl phosphates begins to prevail in acidic solutions (yields up to 65%):

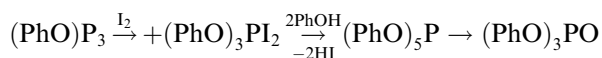


Thus, it is clearly demonstrated, using a simple system including white phosphorus, alcohol and water as an example, that electrochemistry is a powerful synthetic method offering few advantages over some classical methods of organophosphorus chemistry, namely, mild conditions of the process, its high rate and selectivity; environmental safety (electrophilic component is cyclically regenerated at the anode); purposeful synthesis of desired products only by the variation of electrosynthesis conditions.

An interesting result shown that it is possible to use the radicals–cations of phenothiazine or triarylamine generated at the anode in alcohol solution for disclosing the white phosphorus and formation of trialkyl phosphates [14].

It was demonstrated that triaryl phosphites, triaryl phosphates [17–19], triamido phosphates [17,20,21] and their sulfurous analogs, triamidothio phosphates [17,21], are electrosynthesized easily from white phosphorus.

Thus, the study of phenol electrolysis in acetonitrile solution in the presence of white phosphorus emulsion confirms the general regularities of the process. At the same time, some differences were found in proceeding its separate stages which determined a formation of the mixture of appropriate triphenyl phosphites and triphenyl phosphates [17,18]. The authors succeeded in establishing that pentaphenoxyphosphorane and  $(\text{PhO})_3\text{PI}_2$  are the intermediates in the transformation process of triphenyl phosphite to phosphate, by the following reactions:

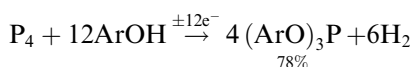
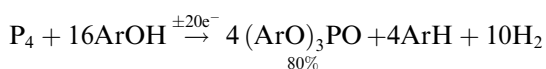


The last results are of special interest, because data about possible routes and conditions for the transformation of phosphorane to phosphate under similar conditions were virtually non-existent in the literature.

Pentaphenoxyphosphorane is reduced irreversibly at the platinum electrode in acetonitrile to triphenyl phosphate at less negative potentials than phenol.

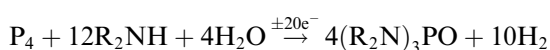


Varying the electrolysis conditions, from white phosphorus either triarylphosphate or predominantly triaryl phosphite (with pyridine addition) can be obtained as the main product [17,18].



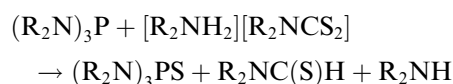
## 2.2. Electrochemical synthesis of phosphorus derivatives containing P–N bonds

It was assumed that the successive cleavage of P–P bonds with the subsequent substitution of the halogen by an amido group proceeds such as studied in the presence of alcohol or phenol. Thus, triamidophosphite is produced as a result of the main reaction (yields up to 62%) [17,20,21]. Probably, transformation of white phosphorus to phosphate occurs by the hydrolysis of unstable iodine derivatives by water. The overall scheme of the process is given below:



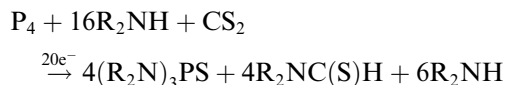
Formation of triamidophosphite as an intermediate product was detected as the whole cleavage of phosphorus P–P bonds is produced, according to the characteristic signal  $\delta^{31}\text{P}$  in the NMR  $^{31}\text{P}$  spectrum [17,21].

The white phosphorus can be transformed into sulfide phosphorus derivative through the reaction of  $(\text{R}_2\text{N})_3\text{P}$  by carbon disulfide into the electrolyte [17,21]. This acts as a sulfur source under the electrosynthesis conditions giving  $(\text{R}_2\text{N})_3\text{P}$  to  $(\text{R}_2\text{N})_3\text{P}=\text{S}$  (yields up to 68%), thioformamide being a by-product. The following reaction scheme is proposed. The phosphorous triamide reacts with thiocarbamate, yielding triamidothio phosphate:



The occurrence of these processes was substantiated by independent experiments. Thus, synthesized  $(\text{Et}_2\text{N})_3\text{P}$  reacted easily with thiocarbamate resulting in  $(\text{Et}_2\text{N})_3\text{PS}$ , and in the absence of amine under the same conditions no changes are found.

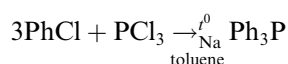
The overall equation of the process is as follows [17,21]:



Thus, cathodic electrochemical activation of white phosphorus in presence of amines allows the preparation of amides of phosphorus acids. Triamidophosphite is the primary product after cleavage of P–P bonds. It undergoes further transformations to triamidophosphate or to triamidothio phosphate.

## 2.3. Synthesis of compounds with P–C bonds

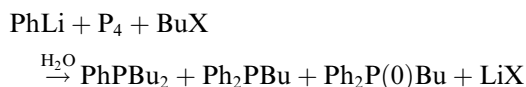
Electrochemical generation of alcoxide or amide anions on cathode and iodine on anode in the presence of white phosphorus offers a novel approach to the synthesis of the appropriate esters or amides of phosphorus acids. But this electrochemical method is unsuitable to prepare compounds with the phosphorus–carbon bond, which are the most important in phosphorus chemistry, for example, tertiary phosphines or their oxides which are the most widespread ligands in metal complex catalysts, including the industrial ones, and used widely also as extractants of heavy metal ions (uranium and technetium first of all). An industrial method for triphenyl phosphine preparation is based on high-temperature reaction of chlorobenzene with phosphorus trichloride in the presence of smelt sodium.



The ways of selective synthesis for compounds with three P–C bonds starting from white phosphorus at room temperature with high rate are not described.

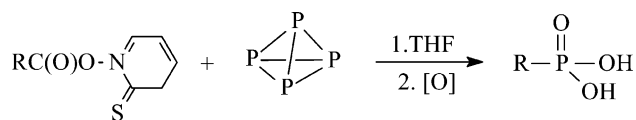
The reaction, in which a P–C bond is formed from P–P bonds is a very rare process, notwithstanding the ubiquitous role played by phosphines and by phosphorus compounds in both organometallic and coordination chemistry.

It is known that rupture of the phosphorus tetrahedron  $P_4$  under the action of organometallic compounds, e.g.,  $RMgX$  and  $PhLi$ , takes place by cleavage of P–P bonds leading to formation of a mixture of organophosphorus products in yields from 5% to 70% [36]:



The opportunity of white phosphorus alkylation by organometallic complexes of the trivalent cobalt with Co–C  $\sigma$ -bond ( $RCo^{III}$ ) was shown [37]. The last, due to the propensity to homolytic cleavage are convenient sources of carbon-centered free radicals  $R\cdot$ . As a result of acid hydrolysis of reactionary mixes, the alkylation products, containing one and two ethyl groups at phosphorus atom, namely, ethylphosphonic, ethylphosphinous, diethylphosphonic and diethylphosphinous acids, with a total yield of 30–70% were identified.

A convenient route for conversion of carboxylic acids into the corresponding phosphonic acids was proposed on the basis of reaction of white phosphorus with carbon radicals. Thus, white phosphorus in tetrahydrofuran under argon reacts in a long radical chain reaction with carbon radicals derived from Barton PTOC esters (*N*-hydroxy-2-thiopyridone) with irradiation by white light [38,39].



Inaccessible precursors are lack of this way.

The  $\sigma$ -alkyl or -aryl complexes  $[MeC(CH_2PPh_2)_3]RhR(\eta^2-C_2H_4)$  ( $R = Me, Ph$ ) rapidly react with white phosphorus, to form the  $P_4R$  complexes  $[MeC(CH_2PPh_2)_3]Rh(\eta^3-P_4R)$  with ethene elimination [40,41]. When the Rh-hydride complex  $[MeC(CH_2PPh_2)_3]RhH(\eta^3-P_4R)$  is reacted with  $P_4$ , the ethyl compound  $[MeC(CH_2PPh_2)_3]Rh(\eta^3-P_4Et)$  is selectively obtained by insertion of coordinated ethene into the Rh–H bond with subsequent P–C bond formation. These reactions represent the first examples of transition metal-mediated P–C bond formation starting from white phosphorus and also the first examples of direct metal mediated transfer of an organyl fragment to the

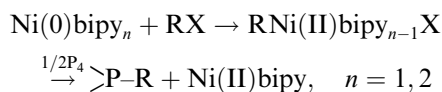
coordinated tetrahedral unit of elemental phosphorus [40,41].

To investigate the opportunity of the transformation of  $P_4$  into P–C derivatives, an electrochemical alternative of the reaction of oxidative addition was considered. Under favorable conditions single bonds of a tetraphosphorus molecule could also be involved in the above reaction and new effective way of selective electrosynthesis of compounds with P–C bonds from white phosphorus in mild conditions of metal complex catalysis was elaborated. We supposed that white phosphorus can be involved to the reaction with alkyl and aryl halides under conditions of cyclic regeneration of metallocomplex catalyst at the electrode [23–27,30].

Cathode:  $Ni(II)L_3 + 2e^- \rightleftharpoons Ni(0)L_2 + L$ ,  $L = bipy$

Anode:  $M - ne^- \rightarrow M^{n+}$   $n = 2, 3$ ;  $M = Mg, Zn, Al$

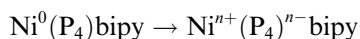
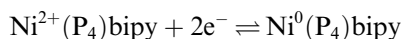
By analogy with the white phosphorus functionalization process by Grignard reagents, it is proposed that a key stage of the reaction consists in the interaction of organonickel compound,  $[RNi^{II}XL_n]$ , with white phosphorus according to the following scheme [23–27,30]:



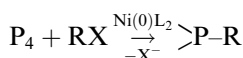
In order to support the reaction path depicted above, the stages of the electrochemical formation of organonickel complex  $[RNi^{II}XL_n]$ , and the stage of functionalization of white phosphorus by this compound were studied separately. It was found that a small excess of  $[PhNi^{II}Xbipy_n]$  ( $n = 1, 2$ ), which were obtained by two-electron reduction of  $NiBr_2bipy$  in the presence of  $PhBr$ , leads to the phosphorus arylation. Phosphine and phosphine oxide were prepared also by using  $[Ni-o-TolBrbipy]$  or  $[NiMesBrbipy]$ . In the absence of *o*- $TolBr$ , the reaction of  $[Ni-o-TolBrbipy]$  (or  $[NiMesBrbipy]$ ) with  $P_4$  in DMF leads only to compounds containing low-coordinated phosphorus,  $[ArP = Nibipy]$ , which proved unstable on attempted isolation. Evidently, cleavage of P–P bonds and as a result rupture of the  $P_4$  tetrahedron occurs also under the action of  $Ni(0)bipy$  or  $Ni(II)bipyX_2$  complexes with formation of phosphides or polyphosphides of nickel.

It was studied the reaction between tetraphosphorus with complexes  $Ni(II)X_2bipy$  and  $Ni(0)bipy$ , in order to design new pathways to obtain phosphorus derivatives containing P–Ar bonds.

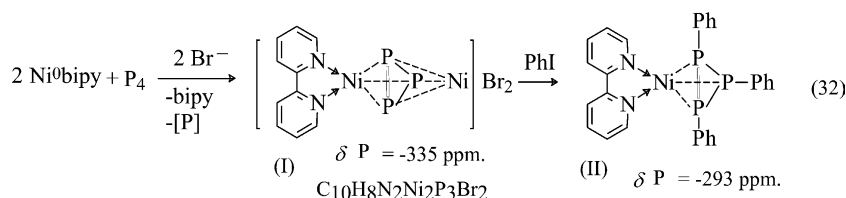
Coordinated  $P_4$ , contrary to free phosphorus, becomes more stronger acceptor of electrons and is easily reduced under the action of  $Ni(0)$  complexes. A voltammetric study of  $NiBr_2bipy$  and  $Ni(BF_4)_2bipy_3$  behaviour in the presence of white phosphorus demonstrated that tetraphosphorus is coordinated with nickel complexes, and a reduced form of the metal yields a more stable complex than an oxidative form:



It is possible to converse white phosphorus to compounds with P–C bonds, phosphines and phosphine oxides, according to the following scheme:

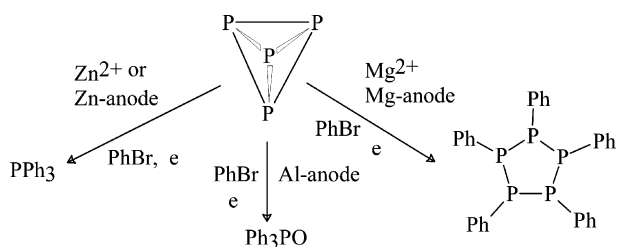


Cyclic regeneration of Ni-catalyst takes place at the cathode, reactive  $\sigma$ -complex forms in the bulk of the



solution. The  $\sigma$ -complex attacks the  $\text{P}_4$  molecule resulting in tertiary phosphines as target product (see Scheme 4).

It should be noted that the yields of products and their ratio depend on metal used as the anode material and a nature of solvent. The essential influence of the sacrificial anode on the nature and the yield of the target products of electrochemical phosphorylation of organic halides by white phosphorus was shown. Zinc anode yield to three-coordinated phosphorus – triorganylphosphines, aluminium anode – triorganylphosphine oxides, and the magnesium anode promotes the transformation of white phosphorus into cyclic phosphines  $(\text{PhP})_5$  (Table 5). The last reaction is very unusual.



The mechanism of the electrocatalytic arylation of white phosphorus was investigated using the method of preparative electrolysis and cyclic voltammetry.

For analysis of paths of transformation of white phosphorus we have divided the process into separate stages and have simulated them. We have investigated the interaction of all initial and electrogenerated reagents, mutually, in the system. The key intermediates of electrochemical functioning of white phosphorus, such as phosphinidenes and phosphorus cycles, in condi-

tions of metallocomplex catalysis were detected (Scheme 5). The interaction of organonickel compound,  $\text{RNi}^{\text{II}}\text{XL}_m$ , with white phosphorus was a key stage:

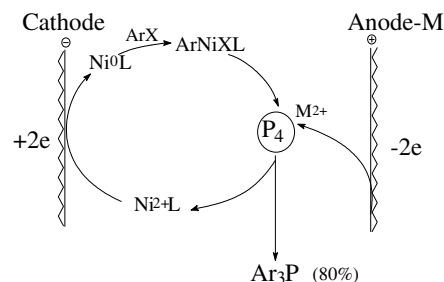
For a consideration of alternative pathways of P–R bond formation, we studied a possibility of white phosphorus reacting directly with Ni(II) and Ni(0) complexes.

It was found that Ni(0)bipy reacts with tetraphosphorus, probably, with formation of binuclear complex (I), which reacts fast with organic halides, leading to functionalization of *cyclo*- $\text{P}_3$ -fragment and formation of mononuclear complex with  $\text{Ph}_3\text{P}_3$ -ligand:

Compound (I) was characterized by spectroscopy on nuclei of  $^{31}\text{P}$  ( $\delta^{31}\text{P} = -335 \text{ ppm}$ ) and  $^1\text{H}$  (the spectrum consists of a complex multiplet in the region of the signals of aromatic protons, 6.8–8.9 ppm). The EPR spectrum shows that the isolated compound is paramagnetic. So, e.g., a new mononuclear complex, orange-brown in color, with a  $[\text{Ph}_3\text{P}_3]$ -ligand (II) is produced, and, i.e., arylation of the *cyclo*- $\text{P}_3$  fragment takes place. Consequently, such path to P–Ph bond formation is competitive with interaction of  $\sigma$ -aryl complex,  $\text{PhNiXbipy}$ , with  $\text{P}_4$ . Thus, white phosphorus functionalization can be carried out by electrochemical method with formation of compounds with P–C bonds under mild conditions.

The application of electrochemistry allowed to make the process of elaborating new synthetic reactions proceed via Ni complexes [23–27,30].

Organic  $\sigma$ -complexes of Ni are rather poorly investigated compounds though they have been reported to be crucial precursors and intermediates in a number of useful carbon-heteroatom bond cleavages. These compounds are of special interest, because they are just border on the limits of stability and as a rule decompose on attempted isolation. The metal–carbon bond is rather



Scheme 4. Electrosynthesis of triaryl phosphines from  $\text{P}_4$ .

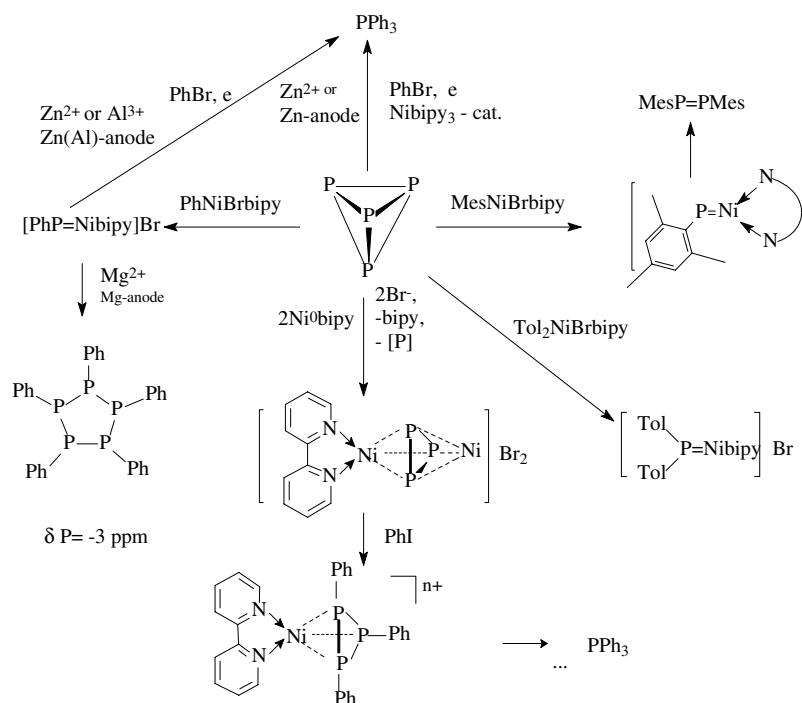
Table 5  
Products of electrochemical functionalization of P<sub>4</sub> catalyzed by Ni(0)bipy

| R–X                | Anode/solvent         | Products              | Yield on P (%)     |    |
|--------------------|-----------------------|-----------------------|--------------------|----|
| PhI                | Zn/DMF                | Ph <sub>3</sub> P     | 75                 |    |
|                    |                       | Ph <sub>2</sub> PH    | 10                 |    |
|                    |                       | PhPH <sub>2</sub>     | 5                  |    |
|                    | Mg/DMF                | Ph <sub>3</sub> P     | 50                 |    |
|                    |                       | Ph <sub>3</sub> PO    | 10                 |    |
|                    | Al/DMF                | Ph <sub>3</sub> P     | 40                 |    |
| Ph <sub>3</sub> PO |                       | 18                    |                    |    |
| PhBr               | Zn/DMF                | Ph <sub>3</sub> P     | 80                 |    |
|                    |                       | Ph <sub>3</sub> PO    | 10                 |    |
|                    |                       | Ph <sub>2</sub> PH    | 9                  |    |
|                    | Mg/DMF                | (PhP) <sub>5</sub>    | 60                 |    |
|                    |                       | Ph <sub>3</sub> P     | 15                 |    |
|                    | Al/DMF                | Ph <sub>3</sub> P     | 18                 |    |
|                    |                       | Ph <sub>3</sub> PO    | 60                 |    |
|                    | Al/CH <sub>3</sub> CN | Ph <sub>3</sub> P     | 0                  |    |
|                    |                       | Ph <sub>3</sub> PO    | 60                 |    |
|                    | BuBr                  | Mg/DMF                | Bu <sub>3</sub> P  | 11 |
|                    |                       |                       | Bu <sub>3</sub> PO | 55 |
|                    |                       | Al/CH <sub>3</sub> CN | Bu <sub>3</sub> PO | 38 |
| HexI               | Al/CH <sub>3</sub> CN | Hex <sub>3</sub> PO   | 46                 |    |
|                    | Zn/DMF                | Hex <sub>3</sub> P    | 75                 |    |

reactive, and only several organonickel  $\sigma$ -complexes are yet described. Organonickel  $\sigma$ -complexes have been found to be the key intermediates in these transformations [25].

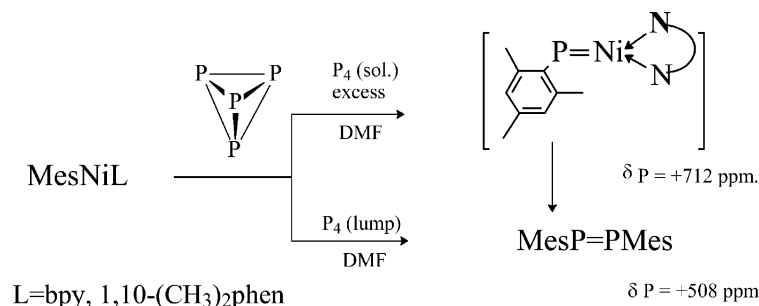
Phosphinidenes are the phosphorous analogues of carbenes, nitrenes and silenes and present the class of low-ligated phosphorus compounds. Although terminal phosphinidene complexes are receiving an increasing amount of attention, well characterized examples remain relatively rare. For some time now, transient electrophilic terminal phosphinidene complexes [RP=M] have been developed into a highly efficient tool for the synthesis of P–C heterocycles from alkenes, alkynes, dienes, etc. Despite the many investigations into the properties of these reactive intermediates, the pathways by which the phosphinidenes can be generated remain limited. Historically, the most suitable route, developed by Matey and co-workers [42], remains the cleavage of complexed phosphanorbornadienes. In search of alternative pathways for generating electrophilic phosphinidene complexes we were interested in using more readily available phosphorus compounds, such as chlorophosphines and white phosphorus.

The phosphinidene complexes from white phosphorus were obtained for the first time. It was supposed to use white phosphorus as the precursor of phosphinidene complexes, basing on its ability to react with nucleophiles, including the reagents of the Grignard and their analogues. The organonickel  $\sigma$ -complex obtained



Scheme 5.





Scheme 6.

electrochemically by oxidative addition was used for disclosure of a white phosphorus tetrahedron. The synthesis of the nickel–phosphinidenes from tetraphosphorus was investigated under different conditions. It has been established that the excess of white phosphorus is necessary for suppression of side reaction of diphosphene formation (Scheme 6).

Upon attempted isolation it proved unstable.

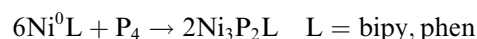
The use of electrochemical approach to generate Ni(0) and  $\sigma$ -organonickel complexes appears to have considerable promise. Firstly, this is a possibility to use a catalytic quantity of complex which will be regenerated on the electrode and, in such a way, will retreat a significant amounts of various substrates. Secondly, it is possible to estimate quantitatively a rate of catalytic reaction using an electrochemical approach, and, in some instances, to divide the summary process into separate stages and to evaluate reactivity of intermediates and stability of various forms of metal complex.

#### 2.4. Electrosynthesis of nickel phosphides

More and more interest has been focused on the preparation of transition-metal phosphides for their excellent properties and potential applications in the fields of electricity, mechanics, corrosion-resistance, etc. [43,44]. Nickel phosphides have received extensive attention because they are an excellent oxidation-resistant, wear-proof material [45,46] and an effective catalyst in hydro-processing [47,48]. All conventional synthesis routes of nickel phosphides preparation require high temperatures and/or high pressure, inert atmosphere and use of toxic initial phosphides or form toxic PH<sub>3</sub> as side product, etc. As the electrochemical reduction of Ni(II) complexes to Ni(0) complexes is a key stage in many electrocatalytic reactions, we have suggested using these highly reactive particles for the synthesis of nickel phosphides or other relative products of white phosphorus reduction under Ni<sup>0</sup>L in mild conditions.

Joint electrolysis of NiBr<sub>2</sub>, ligand (bipy, phen, PPh<sub>3</sub>) and of white phosphorus in dimethylformamide in cathode compartment of electrolyzer yields to black precipitate after the electrolysis is finished in a day. Elemental composition (using laser ionization EMAL 2 mass-spec-

trometer) and mass spectrum (using MALDI-TOF spectrometer) of this precipitate corresponds to Ni<sub>3</sub>P<sub>2</sub>L for L = bipy, phen, and Ni<sub>3</sub>P<sub>2</sub>DMF for L = PPh<sub>3</sub> [49].



The proposed synthetic procedure allows to obtain the ‘ultrafine materials’ with a very large surface area – 200 m<sup>2</sup>/g, hard to be proceeded in the regular way [50], what allows to use these materials as the basis for the development of new catalysts.

To summarise, there are many interesting promising synthetic applications combining electrochemistry with homogeneous catalysis.

The interest to the organophosphorus compounds electrosynthesis on the basis of white phosphorus is also caused by a number of advantages compared to common chemical methods:

- mild conditions of the process (normal pressure and temperature);
- a possibility to carry out the reaction in practically closed system with minimum amount of cyclically regenerated reagents;
- high environmental safety of synthesis, especially in comparison with the traditional procedures of organophosphorus chemistry. The supporting electrolyte is chemically passive and at the end of the process it must be recycled.

It is necessary to mention that the use of electrochemical methods provides a unique opportunity to study the reaction mechanisms of elemental phosphorus with various reagents generated on electrodes along with the solution of synthesis problems.

It is obvious that optimization of the methods for electrochemical functionalization of white phosphorus is a basis for realization of these processes on an industrial scale.

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