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The influence of the sacrificial anode nature on the mechanism of electrochemical arylation and alkylation of white phosphorus

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The material of the sacrificial anode has a substantial effect on the nature and yield of the target products of electrochemical phosphorylation of organic halides by white phosphorus in the presence of the nickel complexes with 2,2´-bipyridine. The use of the zinc anode results in the products with tricoordinated phosphorus, *viz.*, triorganylphosphines, the reaction on the aluminum anode affords triorganylphosphine oxides, and the presence of Mg^{2+} ions in the reaction mixture provides the transformation of white phosphorus into cyclic phosphines $(PhP)_5$.

Key words: white phosphorus, nickel, zinc, 2,2´-bipyridine, organic halide, electrochemical catalysis, sacrificial anode.

The problem of selective tetrahedron opening in white phosphorus (P_4) and its direct functionalization gains increasing significance due to a search for new ecologically safe routes of syntheses of organophosphorus compounds. It is known**[1—3]** that organometallic compounds, *e.g.*, RMgX and PhLi, cleave the P—P bond of the P_4 tetrahedron to form a mixture of organophosphorus products in 5—70% yields.

Undivided processes using easily oxidized metals, such as Mg, Al, or Zn, as anodes well recommended themselves for electrosyntheses, including electrocatalytic functionalization of organic halides (RX). In these processes, the nature of sacrificial anodes plays an important role and often determines the selectivity and mechanism of the process.**[4]** Studies of routes of electrocatalytic transformation of substrates involving sacrificial anodes have been started rather recently. Understanding of mechanisms of these reactions is necessary for the development of new methods for syntheses of various organic and organoelement derivatives.

This work is aimed at studying the route of P_4 transformation and the influence of the sacrificial anode nature on the mechanism of electrochemical arylation and alkylation of P_4 by electrochemically generated Ni^0 complexes in the presence of RX or related σ-organyl complexes.

Experimental

In cyclic voltammetric (CV) studies, a stationary disk-shaped glassy-carbon electrode with a working surface area of 3.14 mm^2 was used as a working electrode. Voltammograms were recorded on a PI-50-1 potentiostat with a PR-49 programmer and an electrochemical cell connected by the three-electrode scheme. The curves were detected with linear potential scan sweeps of 50 mV s^{-1} on a two-coordinate recorder. An Ag/0.01 *M* $AgNO_3$ system in MeCN served as a reference electrode. A Pt wire 1 mm in diameter was used as an auxiliary electrode. Measurements were performed in a cell with a constant temperature (25 °C) in an argon atmosphere.

Preparative electrolyses were carried out in a three-electrode 40-mL cell using a B5-49 constant-current power source. The potential of the working electrode was detected by a Shch50-1 constant-current voltmeter with respect to a reference electrode, Ag/0.01 *M* $AgNO_3$ in MeCN. The working surface of a cylindrical Pt cathode was 20.0 cm^2. Zinc, aluminum, and magnesium rods, whose working surfaces were thoroughly cleaned with an emery paper before electrolysis, were used as anodes. During electrolysis the electrolyte was stirred with a magnetic stirrer in an argon flow.

^{31}P NMR spectra were recorded on a Bruker CXP-100 high-resolution spectrometer (Germany) at a frequency of 40.5 MHz relatively to the external standard (85% H_3PO_4) with positive downfield chemical shifts. ^1H NMR spectra were obtained on a Varian T-60 instrument (60 MHz) using Me_4Si as the internal standard. ESR spectra were detected on a Radiopan SE/X-2544 X-range electronic spectrometer (Poland) using diphenylpicrylhydrazyl (DPPH, $g = 2.0036$) as the external standard.

The solvent MeCN was purified by triple fractional distillation above P_2O_5 with an addition of $KMnO_4$. The concentration of residual water was $1 \cdot 10^{-3}$ mol L^{-1}. Dimethylformamide was purified by triple vacuum distillation with intermediate drying above calcined K_2CO_3 and molecular sieves. In order to prepare the supporting electrolyte, twice recrystallized salts (Et_4NBr, from MeCN and Et_4NBF_4, from EtOH) were used, which were dried for 2 days in a vacuum desiccator at 100 °C. Benzene and diethyl

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ether were dehydrated by distillation above Na, and $CHCl_3$ was dehydrated by boiling above P_2O_5 followed by distillation.

White phosphorus was purified using the following procedure: P_4 (10 g) was placed in a flask containing a mixture of benzene (10 g) and Py (10 g), and the resulting mixture was refluxed for 2 h in a box in an argon atmosphere. Then the procedure was repeated with the next portion of solvents, after which P_4 was refluxed for 2 h more in distilled water (20 g). For convenience, purified P_4 was molded from a melt using a glass syringe to form small rods with a weight of ~1 g each. Prior to the reaction, P_4 was twice successively washed with anhydrous acetone, EtOH, and Et_2O.

The $NiBr_2bpy$ and $Ni(BF_4)_2bpy_3$ complexes were synthesized from the corresponding nickel salt and a required amount of 2,2´-bipyridine in EtOH. Organic halides used as substrates were commercial reagents (reagent grade) purified by distillation to unchanged physicochemical constants. The purification of $(BuO)_3PO$ used as a label was carried out by heating to 100 °C with Na for 4 h followed by triple vacuum distillation.

Electrochemical reduction of $Ni^{II}bpy_3$ in the presence of white phosphorus and organyl halide. A working solution 40 mL in volume was prepared by dissolution of $Ni(BF_4)_2bpy_3$ (0.35 g, $5 \cdot 10^{\hbar-4}$ mol), organyl halide (RX, 0.03 mol), and Et_4NBF_4 (0.87 g, $4 \cdot 10^{-3}$ mol) in DMF (or MeCN). Phosphorus (0.186 g, $6 \cdot 10^{-3}$ mol) was emulgated to the resulting solution on heating to 50 °C in an argon atmosphere. Electrolysis was carried out in an undivided electrochemical cell with the Mg, Al, or Zn anode under thermostatic conditions with a current density on the cathode of 5—10 mA cm^{-2} and a controlled cathodic potential of −1.60 V (*vs.* Ag/0.01 *M* $AgNO_3$ in MeCN) corresponding to the reduction of the $Ni^{II}bpy_3$ complex to the Ni^0bpy_2 complex. An amount of electricity of 1 A h (6 *e* per P atom) was passed through the electrolyte. After the end of electrolysis, the reaction mixture was treated with a 2 *M* solution of HCl; electrolysis products were extracted with ether, and the ether was evaporated. In some experiments with the Mg anode, the treatment of the reaction mixture with a 2 *M* solution of HCl resulted in the formation of a precipitate, which was filtered off and analyzed by elemental analysis and spectroscopy. The relative content of organophosphorus compounds in the ether extract was estimated from the integral intensity of ^{31}P NMR spectral signals relatively to the $(BuO)_3PO$ label. The percentage yield of each compound was calculated from the overall preparative yield of the products. Triorganylphosphines and triorganylphosphine oxides were separated by recrystallization from EtOH. The yields of the isolated products are presented in Table 1. The physicochemical characteristics of the obtained compounds correspond to published data.

Electrochemical reduction of the nickel complexes in the presence of white phosphorus. A working solution (catholyte) 30 mL in volume was prepared by the dissolution in DMF of the nickel complex ($5 \cdot 10^{-4}$ mol) with 2,2´-bipyridine (0.1875 g of $NiBr_2bpy$ or 0.35 g of $Ni(BF_4)_2bpy_3$) and a supporting electrolyte ($5 \cdot 10^{-3}$ mol), *viz.*, 1.05 g of Et_4NBr (in the case of $Ni(BF_4)_2bpy_3$, 1.085 g of Et_4NBF_4). In the resulting solution, phosphorus (0.062 g, $2 \cdot 10^{-3}$ mol) was emulgated in an argon atmosphere at 50 °C. Electrolysis was carried out in a divided cell in the potentiostatic regime at −1.52 or −1.60 V (*vs.* Ag/0.01 *M* $AgNO_3$ in MeCN) at 50 °C in an argon atmosphere. During electrolysis the catholyte was stirred with a magnetic stirrer. A saturated DMF solution of the supporting electrolyte, which was used in the catholyte, served as an anolyte. After the end of electrolysis (2 *e* electricity per Ni atom corresponding to 27 mA h passed through the solution), the precipitate was filtered off, washed with diethyl ether, and dried in a vacuum desiccator at 30 °C.

Table 1. Products of electrochemical functionalization of white phosphorus by the Ni^0 complexes with bpy obtained from $Ni(BF_4)_2bpy_3$

RX	Anode/solvent	Product	Yield by P (%)
PhI	Zn/DMF	Ph_3P	65
		Ph_2PH	12
		$PhPH_2$	10
	Mg/DMF	Ph_3P	50
		Ph_3PO	10
	Al/DMF	Ph_3P	40
		Ph_3PO	18
PhBr	Zn/DMF	Ph_3P	50
		Ph_3PO	10
		Ph_2PH	9
	Mg/DMF	$(PhP)_5$	60
		Ph_3P	15
	Al/DMF	Ph_3P	38
		Ph_3PO	10
	Al/MeCN	Ph_3P	8
		Ph_3PO	60
BuBr	Mg/DMF	Bu_3P	11
		Bu_3PO	55
	Al/MeCN	Bu_3PO	38
HexI*	Al/MeCN	Hex_3PO	46

* Hex is *n*-C_6H_{13}.

The $[NiP_3Nibpy]Br_2$ complex (0.11 g) was obtained from $NiBr_2bpy$ in 84% yield, m.p. 154 °C (decomp.). Found (%): C, 21.69; H, 2.03; Br, 31.78; N, 4.52; Ni, 21.90; P, 16.65. $C_{10}H_8Br_2N_2Ni_2P_3$. Calculated (%): C, 22.79; H, 1.52; Br, 30.40; N, 5.32; Ni, 22.29; P, 17.67. ^{31}P NMR, δ: −335.8. ^1H NMR ($CDCl_3$), δ: 6.63—8.82 (m, 8 H, 2,2´-bipyridine).

The $[NiP_3Nibpy](BF_4)_2$ complex (0.12 g) was obtained from $Ni(BF_4)_2bpy_3$ in 88% yield, m.p. 148 °C (decomp.). Found (%): C, 21.50; H, 1.98; B (was not determined); F, 27.2; N, 6.01; Ni, 19.34; P, 17.60. $C_{10}H_8B_2F_8N_2Ni_2P_3$. Calculated (%): C, 22.22; H, 1.48; B, 4.01; F, 28.15; N, 5.19; Ni, 21.74; P, 17.22. ^{31}P NMR, δ: −334.6. ^1H NMR ($CDCl_3$), δ: 6.63—8.82 (m, 8 H, 2,2´-bipyridine).

Results and Discussion

Electrolyses of solutions of RX in DMF or MeCN in the presence of the $Ni^{II}bpy_3$ complex and an emulsion of P_4 showed that the electrochemically generated catalysts (the Ni^0 complexes with bpy) can transform P_4 into compounds bearing P—C bonds, that is, phosphines and phosphine oxides (see Table 1). The following reactions are known[4,5] to occur at the electrodes during electrolysis (Scheme 1).

By analogy to the previously studied functionalizations of P_4 by the Grignard reagents, we can assume that the key step of the process is the interaction of P_4 with the

Scheme 1

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

$$\text{Anode: } \mathrm{M} - n\,e \longrightarrow \mathrm{M}^{n+},\ n = 2, 3;\ \mathrm{M} = \mathrm{Mg, Zn, Al}$$

$$\mathrm{P_4} + \mathrm{RX} \xrightarrow[-\mathrm{X^-}]{\mathrm{Ni^0L_2}} \mathrm{>P{-}R}$$

organonickel compound $\mathrm{RNi^{II}Xbpy}_n$ (n = 1, 2), which includes the sequence of reactions (Scheme 2).

Scheme 2

$$\mathrm{Ni^0bpy}_n + \mathrm{RX} \longrightarrow \mathrm{RNi^{II}bpy}_{n-1}\mathrm{X} \xrightarrow{1/4\ \mathrm{P_4}}$$

$$\longrightarrow \mathrm{>P{-}R} + \mathrm{Ni^{II}bpyX}$$

n = 1, 2

Depending on the RX nature and experimental conditions, the nickel(II) complex is completely or partially regenerated during preparative electrolysis. For example, when the Al anode is used, a portion of nickel removes from the reaction due to the formation of insoluble nickel phosphides, whose elemental composition is close to $\mathrm{Ph_2PNiBr \cdot NiBr_2}$. The treatment with concentrated acids can completely transfer these precipitates to a solution to form diorganylphosphinic acid.

$$\mathrm{Ph_2PNiBr(NiBr_2)} + \mathrm{HCl} + \mathrm{O_2^{\cdot}} \to$$

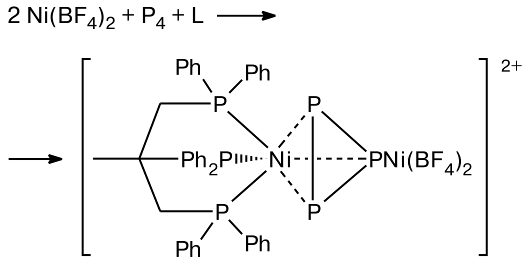
$$\to \mathrm{Ph_2P(O)OH} + 2\,\mathrm{Ni^{II}} + 3\,\mathrm{Br^-} + \mathrm{Cl^-}.$$

In this study, we have chosen PhBr, o-$\mathrm{BrC_6H_4Me}$ (o-BrTol), and $\mathrm{Me_3C_6H_2Br}$ (MesBr) as model ArX. The use of such a series of substrates makes it possible to model and compare the reaction routes involving intermediates ($\mathrm{Ni^0}$ complexes), which differ in stability due to the presence or absence of the Me group in the *ortho*-position of the benzene ring.

In order to confirm the sequence of reactions (see Scheme 2), the step of electrochemical formation of the organonickel compound $\mathrm{RNi^{II}Xbpy}_n$ (n = 1, 2) and the step of functionalization of $\mathrm{P_4}$ by the latter were separated. It was found that the products of phosphorus arylation formed by the treatment of $\mathrm{P_4}$ with a minor excess of $\mathrm{PhNi^{II}Xbpy}_n$ (obtained by the two-electron reduction of the $\mathrm{Ni^{II}bpy}$ complex from $\mathrm{NiBr_2bpy}$ in the presence of PhBr with a Ni : PhBr molar ratio of 1 : 2). In particular, the products with three P—C bonds, *viz.*, a mixture of $\mathrm{Ph_3P}$ and $\mathrm{Ph_3PO}$ (1 : 1), and a small amount on insoluble nickel phosphides with the elemental composition close to that given above are formed. However, $\mathrm{PhNi^{II}Xbpy}_n$ decomposes rapidly, and its concentration in a solution cannot be monitored. Rather stable σ-complexes obtained from o-$\mathrm{MeC_6H_4Br}$ and MesBr are more convenient for studying. A mixture of phosphines and phosphine oxides was also obtained when o-$\mathrm{MeC_6H_4NiBrbpy}$ and MesNiBrbpy were used as model compounds. It is of interest that in the absence of o-$\mathrm{MeC_6H_4Br}$ the reaction of o-$\mathrm{MeC_6H_4NiBrbpy}$ or MesNiBrbpy with $\mathrm{P_4}$ in DMF affords one compound probably containing low-coordination phosphorus: ArP=Nibpy (δ_P 204), which was not isolated, however, because of its low stability. A similar compound forms by the electroreduction of $\mathrm{PhPCl_2}$ in the presence of $\mathrm{Ni^{II}bpy_3}$ (from $\mathrm{Ni(BF_4)_2bpy_3}$) (δ_P 206). The attempt to isolate this compound from a solution results in its decomposition to ArP(O)(OH)H (δ_P 20, $J_\mathrm{P,H}$ = 531 Hz).

The $\mathrm{P_4}$ tetrahedron opening and the cleavage of other P—P bonds occur, most probably, by the $\mathrm{Ni^0}$ (or $\mathrm{Ni^{II}}$) complexes to form nickel phosphides and polyphosphides. For example, it is known**[6]** that the $\mathrm{[NiL]^{2+}}$ complex (L is $\mathrm{MeC(CH_2PPh_2)_3}$) is a sufficiently strong base to substitute one of the P atoms in the tetrahedral cluster of $\mathrm{P_4}$ to form the $\mathrm{[LNi(P_3)NiL](BF_4)_2}$ complex (**1**) stable in the air and containing the δ-$\mathrm{P_3}$ cyclotriphosphorus group (Scheme 3).

Scheme 3



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Subsequent reactions of P—C bond formation should occur similarly , as in the case of the primary attack to $\mathrm{P_4}$ of the organonickel compound $\mathrm{PhNi^{II}Xbpy}_n$ (n = 1, 2).

In order to consider other possible routes of appearance of the P—R bonds, we studied the interaction of $\mathrm{P_4}$ with the $\mathrm{Ni^{II}}$ and $\mathrm{Ni^0}$ complexes in the absence of RX.

It is known that the nonpolar tetrahedral molecule $\mathrm{P_4}$ is characterized by a weak nucleophilicity (due to the lone electron pairs at the P atoms) and a weak electrophilicity (due to the vacant low-lying d-orbitals**[7]**). It was established**[8,9]** that $\mathrm{P_4}$ can act as the η^1- or η^2-ligand. A tetrahedral molecule is activated during η^1-coordination to transform into a trigonal pyramid, whose vertex is directed toward the metal atom. As a result of η^2-coordination, the edge bound to the metal elongates by ~0.25 Å compared to the P—P bond in the free molecule (2.21 Å). The bidentate coordination of $\mathrm{P_4}$ favors a stronger activation of the molecule than the monodentate coordination does. For bidentate bonding of $\mathrm{P_4}$ the P—P distance is 0.14 Å longer than that for monodentate bonding, providing a considerable loosening of the $\mathrm{P_4}$ tetrahedron. Therefore, the coordinationally saturated metal complexes (in our case, nickel complexes) incapable of η^2-coordination of $\mathrm{P_4}$ are characterized by a lower catalytic activity than the coordinationally unsaturated complexes, which are capable of both η^1- and η^2-coordination.[9] According to the quantum-chemical calculations,[10] the nonpolar molecule is activated due to coordination: the energy of the P—P bonds decreases nonuniformly, and effective charges appear on the P atoms. Coordinated P_4 (unlike free P_4) becomes a stronger electron acceptor and is readily reduced by the Ni^0 complexes.

The behavior of $NiBr_2bpy$ and $Ni(BF_4)_2bpy_3$ in the presence of P_4 was studied to evaluate the complex-forming properties of the P_4 molecule and its reactivity toward the bipyridine complexes of nickel in different oxidation states. On adding a saturated solution of P_4 in benzene to a solution of the $Ni^{II}bpy$ complex in DMF, the second reversible peak ($E = -2.2$ V) disappears and the first peak of reduction of the nickel complex is divided into two peaks. The potential of the first of them $E_p^{C_1} = -1.38$ V shifts to -1.29 V on storing the solution for 1 day. The second peak $E_p^{C_2} = -1.52$ V corresponds to the reduction of the initial $NiBr_2bpy$ complex (Fig. 1). An increase in the P_4 concentration in a solution results in an increase in the current at potentials of the electrochemically irreversible first cathodic peak (C_1) and a proprotional decrease in the current of the second peak (C_2) with a simultaneous decrease in its anodic component (A_2). However, a new anodic peak appears at $E_p^{A_1} = -0.35$ V. The change in the morphology of the voltammetric curves can be explained as follows. In the general case, if both the initial compound and reduction product are complexes of nickel in different oxidation states and the overall reduction process is close to reversible or quasi-reversible, the direction and value of the shift of the peak should depend on the relative stability of components of this redox pair, the difference in their coordination numbers, and the equilibrium constant. It is known[11,12] that in the presence of organophosphorus ligands the reduction peaks of the Ni^{II} complex shift toward negative potentials. This is assumed to indicate that the reduced form of the metal produces a stronger complex than the oxidized form does. The reversible process

$$Ni^{2+}(P_4)bpy + 2\,e \rightleftharpoons Ni^0(P_4)bpy$$

becomes irreversible (the disappearance of the anodic component of the peak), probably, due to the fast subsequent chemical reduction of P_4 coordinated to Ni^0, which acts as the electron donor

$$Ni^0(P_4)bpy \rightarrow Ni^{n+}[P_4]^{n-}bpy.$$

This fast reaction shifts the reduction potential of the $Ni^{II}bpy$ complex from its standard reduction potential toward less negative potentials. As shown below, the preparative reduction of P_4 by the electrochemically generated Ni^0bpy complexes corroborated this assumption. The products of P_4 cathodic reduction, $[P_4]^{n-}$, are oxidized probably at a potential of -0.35 V (see Fig. 1).

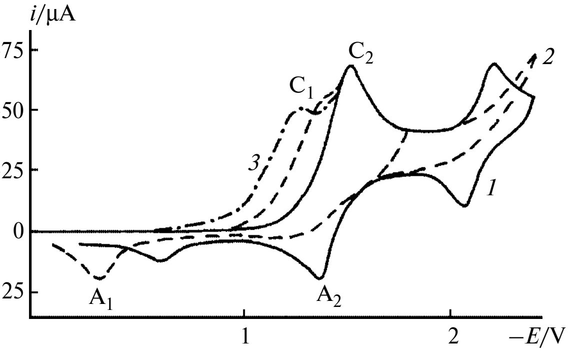
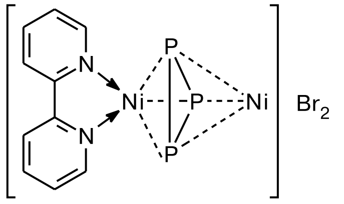


Fig. 1. Cyclic voltammetry of the electrochemical reduction of $NiBr_2bpy$ (0.01 mol L^{-1}) in DMF with Et_4NBF_4 (0.1 mol L^{-1}) as a supporting electrolyte in the absence (*1*) and presence of P_4 (0.01 mol L^{-1}) (*2*) and of the latter solution after its storage in an argon atmosphere for 1 day (*3*).

The solution blackens rapidly upon the preparative electrochemical reduction of $Ni^{II}bpy$ (from $NiBr_2bpy$) to Ni^0bpy in the presence of P_4. After exhaustive electrolysis (2 *e* per Ni^{II} complex molecule), a black amorphous precipitate forms in an electrolyte solution. This precipitate is poorly soluble in organic solvents and has the elemental composition $C_{10}H_8Br_2N_2Ni_2P_3$. We believe that it represents binuclear complex **2**.



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Compound **2** was characterized by the ^{31}P (δ_P −335) and ^1H NMR spectra in $CDCl_3$ (the spectrum consists of a complicated multiplet in the region of signals from aromatic protons δ_H 6.8—8.9). The ESR spectrum of this complex shows that this compound is paramagnetic: the signal has a broad maximum.

The single irreversible cathodic peak in the CV curve of a saturated solution of the isolated $[NiP_3Nibpy]Br_2$ complex in DMF (~$3 \cdot 10^{-4}$ mol L^{-1}) (Fig. 2) at $E_p^C = -1.67$ V ($E_p - E_{p/2} = 250$ mV) lies in the region of reduction potentials of the Ni^{II} and Ni^I complex with bpy. The reverse potential scan results in the appearance of a small poorly reproducible anodic peak at −0.9 V.

Since the reduction potential of compound **2** is somewhat more negative than that of $NiBr_2bpy$ and its solubility in DMF is low (a considerable portion of compound **2** precipitates during electrolysis), high yields of the nickel complex with cyclotriphosphorus can be achieved in the reaction of the Ni^0 complex with P_4. This complex reacts rapidly with RX. For example, the treatment with PhI affords a new orange-brown complex (δ_P −293), which is

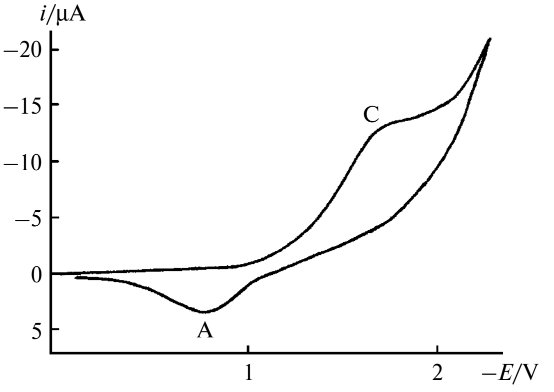
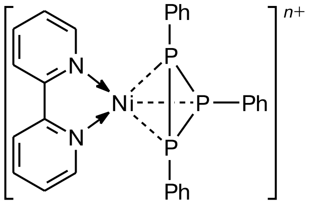


Fig. 2. Cyclic voltammetry of a saturated solution of $[NiP_3Nibpy]Br_2$ ($3 \cdot 10^{-4}$ mol L^{-1}) in DMF with Et_4NBF_4 (0.1 mol L^{-1}) as a supporting electrolyte.

also poorly soluble in organic solvents and, being isolated from a solution, decomposes to form PhP(O)(OH)H (δ_P 27, $J_{P,H}$ = 530 Hz). This fact confirms indirectly that the reaction of complex **2** with PhI involves the phenylation of the cyclotriphosphorus fragment with a probable formation of mononuclear complex **3**.



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This is another possible route for the formation of the P—Ph bonds, which is alternative to the reaction of the σ-aryl $PhNiXbpy_n$ complex with P_4.

The results of preparative electrosyntheses show that the nature of the sacrificial anode substantially affects the nature of organophosphorus compounds (OPC). The use of the Zn anode results in the complete conversion of P_4 to soluble phosphorus compounds, mainly to tertiary phosphines (R_3P) and, to a less extent, to diaryl- and monoarylphosphines (see Table 1). In the case of the Al anode, the general yield of soluble OPC is lower and a considerable part of them is presented by phosphine oxides. Such an occurrence of the process is probably associated with the possibility of formation in the solution of strong Lewis acids. In this case, the anodically generated Al^{3+} ions can act as strong Lewis acids (as shown[13] for the reaction of Bu^tCl with P_4 in the presence of $AlCl_3$). The magnesium anode, like the zinc anode, favors the formation of tricoordinated phosphorus compounds in a high yield. However, in the presence of PhBr, the cyclic polyphosphorus compound $(PhP)_5$ with the less strained cycle is mainly formed. It is known[2,14,15] that the Mg^{2+} ions favor the formation of the $(PhP)_5$ fragments due to the stabilization of cyclic polyphosphines. For example, the reaction of dihalophosphines with metallic Mg affords[14] cyclic structures $[R—P<]_n$, and the chemical functionalization of P_4 by the Grignard reagents in the presence of RX (see Refs. 2 and 15) also gives polycyclic phosphines $(R—P)_n$, the most stable of which are the compounds with five P atoms (Scheme 4).

Scheme 4

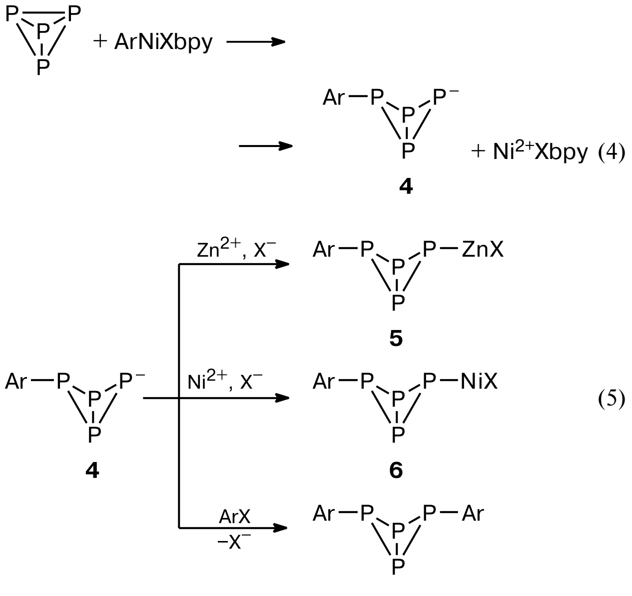
$$P_4 + R—MgBr + R—Br \xrightarrow[-2\,MgBr_2]{THF} (R—P)_n$$

When PhI is used (see Table 1), phosphine $(PhP)_5$ does not form as the final product. Cyclic polyphosphines probably form in this case as well. However, due to a higher reactivity of PhI (compared to PhBr), the intermediate products are further functionalized to form additional two P—C bonds at the P atom.

Thus, the experimental data point to the important role of metal ions in the mechanism of phosphorus tetrahedron opening and transformation of phosphorus oligomers into the final products. Let us consider in which steps of the overall process (Scheme 5) the anodically generated Zn^{2+}, Mg^{2+}, and Al^{3+} ions can be involved. It can be assumed that the metal ions act as electrophilic reagents, thus stabilizing phosphide anions **4** formed by the P—P bond cleavage (Eqs. (1)—(4)). This reaction competes with the reactions of phosphide anion **4** with the Ni^{2+} ions or organic halide ArX (see Scheme 5, Eq. (5)). The Ni^{2+} ions are present in minor amounts and, hence, their role is substantial mainly at the initial steps of elec-

Scheme 5

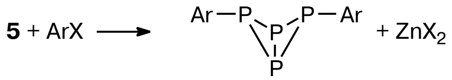
Anode: $Zn - 2e \longrightarrow Zn^{II}$ (1)
Cathode: $Ni^{II}bpy + 2e \rightleftharpoons Ni^0bpy$ (2)
$Ni^0bpy + ArX \longrightarrow ArNiXbpy$ (3)



trolysis when the concentration of the Zn^{2+} (Mg^{2+}, Al^{3+}) ions is low. The reaction of the phosphide anion with RX ($[RX] \gg [M^{2+}]$) affords products with the P—C bonds and is one of the main routes of P_4 functionalization.

Among known metal phosphides, only phosphides of Zn and alkaline metals react[16] efficiently with RX. Nickel phosphides, as well as Al and Mg phosphides, are much less reactive. Therefore, the contribution of formation of nickel phosphide **6** to the P_4 tetrahedron opening is likely rather small. Zinc phosphides **5** react readily with various RX *via* nucleophilic substitution (Scheme 6). This results in the successive cleavage of the P—P bonds in phosphorus oligomers to afford aryl(alkyl)phosphines as the final products.

Scheme 6

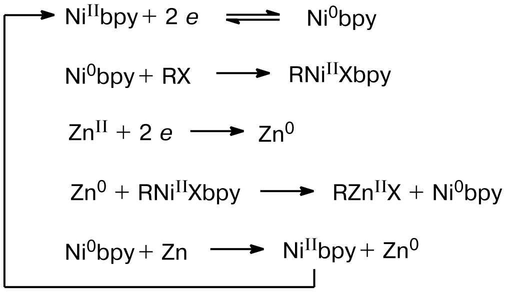


Another possibility of participation of the Zn^{2+}, Mg^{2+}, and Al^{3+} ions generated at the anode in the catalytic transformation of P_4 is transmetallation, *i.e.*, substitution of nickel in σ-organyl complexes. For example, cross-coupling reactions of RX involving the stage of catalytic formation of organozinc compounds were described[17]:

$$RNi^{II}Xbpy + Zn^{II} \rightarrow RZn^{II}Xbpy + Ni^{II}.$$

However, published proofs of the occurrence of this reactions are unavailable. Nevertheless, the preparation of organozinc compounds from RX and zinc salts catalyzed by the Ni^0 complex is doubtless because the RZnXbpy complex was multiply used for the functionalization of various substrates.[17—19] The transmetallation mechanism will be described in detail elsewhere. Here we would like to note that we proposed the mechanism of formation of organozinc compounds on the basis of the data of cyclic voltammetry and preparative electrolysis (Scheme 7).

Scheme 7



The Ni^0bpy complex can react with RX in the bulk solution to yield RNiXbpy and thus close the catalytic cycle. The reaction of the organozinc complex RZnXbpy with P_4 should result in the cleavage of the P—P bonds and in further transformations similar to those described above involving RNiXbpy.

Thus, the electrolysis in an undivided electrochemical cell with the sacrificial anode of Mg, Al, or Zn allows the functionalization of P_4 under mild conditions to form compounds with the P—C bonds. The purposeful choice of the material of the sacrificial anode makes it possible to influence, to some extent, on the nature and yield of the final products of electrochemical arylation and alkylation of P_4.

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