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Highly reactive σ-organonickel complexes in electrocatalytic processes

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Abstract

The electrochemical reduction of nickel complexes with 2,2′-bipyridine in the presence of *ortho*-substituted organic halides or white phosphorus yields the highly reactive σ-organonickel complexes. These complexes selectively react with organic halides forming cross-coupling products. The mechanism of these processes was investigated using the method of cyclic voltammetry and preparative electrolysis. The key intermediates of electrochemical functioning of white phosphorus in conditions of metallocomplex catalysis were detected. © 2001 Elsevier Science B.V. All rights reserved.

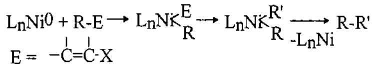
Keywords: Homogeneous redox catalysis; Cross-coupling; Ni(0) complexes; σ-Organonickel complexes; White phosphorus; Organic halides; Electrochemistry

1. Introduction

The elaboration of the ecologically safe and resource-saving chemical and engineering processes is one of the strategic directions in the development of science and technology. In this context, homogeneous catalysis has been increasingly used due to the valuable advantages, involved notably in terms of selectivity and efficiency. Electrochemistry is related to this field in many ways. For example, the synthesis of many organometallic compounds is performed electrochemically, with electrochemistry contributing to the investigation of the reactivity of coordination compounds and highlighting the possible reaction mechanisms.

This communication seeks to demonstrate some novel possibilities of obtaining highly reactive σ-aryl nickel complexes by electrochemical methods and using them in electrocatalytical reactions yielding compounds with various C–C and C–P bonds.

Organic σ-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 (epoxide deoxygenation, dibenzothiophene desulfurization, cross-coupling according to the Kumada reaction) [1–5]:



$$L_nNi^0 + R\text{-}E \longrightarrow L_nNi{<}^{E}_{R} \longrightarrow L_nNi{<}^{R'}_{R} \xrightarrow[-L_nNi]{} R\text{-}R'$$

$$E = -\overset{|}{C}{=}\overset{|}{C}\text{-}X$$

These compounds are of special interest, because they just border on the limits of stability and as a rule decompose on attempted isolation. The metal–carbon bond is rather reactive, and only several organonickel σ-complexes are yet described.

The application of electrochemistry allowed to make the process of elaborating new synthetic reactions proceed via Ni complexes. The advantages of the approach proposed for their synthesis and investigation are as follows:

- organonickel σ-complexes are electrochemically simple to synthesize in mild conditions;
- they enter into various reactions in situ;
- they are intermediates in electrocatalytic reactions of cross-coupling, transformation of olefins, aldehydes, etc. with a Ni(0) catalyst;

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- they are poorly known σ-complexes of metals which may, when necessary, be studied both on their own and as model compounds to gain an insight into the mechanisms of organometallic synthesis;
- the possibility to exist in various oxidation states was found for some Ni σ-complexes, e.g. RNiXbipy, RNibipy, R_2NiXbipy, R_2Nibipy with various reactivities.

We proposed a novel method to transform halogenated organic and organoelemental compounds and also white phosphorus with Ni(0) complexes under conditions of electrochemical catalysis and investigated the mechanism of the process, the nature of intermediates and the synthetic possibilities of these reactions. Organonickel σ-complexes have been found to be the key intermediates in these transformations.

2. Results and discussion

Voltammetric behaviour of Nibipy$_n$X$_2$ ($n = 1$–3, X = Br, BF_4) (bipy = 2,2′-bipyridine) complexes with various RX concentrations was studied to establish: the potentials of catalytic regeneration of Ni complexes in the presence of organohalides RX, the reduction potentials of the products of the RX oxidative addition to Ni(0) complexes and to estimate the reactivity of Ni(0)bipy complexes relative to various substrates, the stability of intermediates in the catalytic cycle.

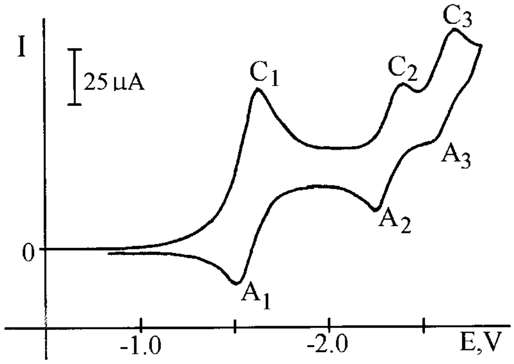


Fig. 1. Cyclic voltammograms for Ni$(BF_4)_2$bipy$_3$ (10^{-2} M) in DMF + Et_4NBF_4 (10^{-1} M).

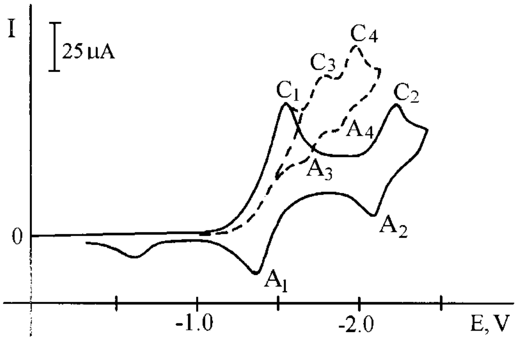


Fig. 2. Cyclic voltammograms for $NiBr_2$bipy (10^{-2} M) in the absence (1) and presence (2) of aryl bromides.

Electroreduction of Ni(II) complexes with 2,2′-bipy (L) occurs via three reversible successive stages of electron transfer (Fig. 1) [6–9]:

$$\mathrm{Ni(II)L_3} + 2e \rightleftharpoons \mathrm{Ni(0)L_2} + \mathrm{L}, \quad E_p^{C_1}$$

$$\mathrm{Ni(0)L_2} + e \rightleftharpoons [\mathrm{Ni(0)L_2}]^{-\bullet}, \quad E_p^{C_2}$$

$$\mathrm{L} + e \rightleftharpoons \mathrm{L}^{-\bullet}, \quad E_p^{C_3}$$

The anodic component of the first wave (C_1) $NiBr_2$bipy reduction disappeared, and two new waves (C_3 and C_4) emerged at more negative potentials in the presence of aryl bromides (Fig. 2).

The waves C_3 and C_4 in one form or another correspond to the reduction of the products of oxidative addition, i.e. nickel σ-aryl complexes [9]. We succeeded in determining the nature of σ-aryl complexes reduced at the $E_p^{C_3}$ and $E_p^{C_4}$ potentials by methods of preparative electrolysis and cyclic voltammetry. The instability of nickel σ-phenyl complexes makes it impossible to use them in the modelling of more complicated processes of cross-coupling of organohalides. A σ-complex from 2-Br-toluene synthesized according to reaction (2) is sufficiently stable in solution, and can be used to study the mechanism of cross-coupling of organic halides or other processes.

$$\mathrm{NiBr_2bipy} + 2e \underset{A_1}{\overset{C_1}{\rightleftarrows}} \mathrm{Ni^0bipy} + 2\mathrm{Br}^- \qquad (1)$$

$$\mathrm{Ni^0bipy} + \mathrm{TolBr} \rightarrow \underset{\text{stable in solution}}{\mathrm{TolNiBrbipy}} \qquad (2)$$

$$\mathrm{TolNi^{II}Brbipy} + e \underset{\leftarrow}{\overset{C_3}{\longrightarrow}} \mathrm{TolNi^{I}bipy} + \mathrm{Br}^- \qquad (3)$$

$$\mathrm{TolNi^{I}bipy} + \mathrm{TolBr} \rightarrow \underset{\text{stable on air}}{\mathrm{Tol_2NiBrbipy}} \qquad (4)$$

The enhanced stability of *ortho*-substituted phenyl complexes is attributed to steric factors, hindering the rotation around the σ-bond of Ar–metal and the attack of reagents at the axial site of the complex.

The reduction of the $NiBr_2$bipy complex in the presence of 2-Br-Tol (1:2) results in the formation of a red σ-complex TolNiBrbipy (after 2*F* passes through the electrolyte at $E_p^{C_1}$ potential (Fig. 3). The C_1 wave on the voltammogram disappears, and only the C_3 and C_4 waves with the 2e total current remain.

The reduction of TolNi^{II}Brbipy at $E_p^{C_3}$ (1*F*) results in claret–lilac coloured Tol_2NiBrbipy which was separated and characterized by spectral methods. The isolated dry complex is characterized by one reversible one-electron reduction wave with $E_p^{C_4} = -1.96$ V and one one-electron oxidation wave (Br^-) at $+0.12$ V (Fig. 4). It is assumed that the electron in the radical–anion formed is located on the ligand, because similar cases are cited in literature [10,11]. Radical–anion $[Tol_2NiBrbipy]^{-\bullet}$ is decomposed in solution, resulting in Tol_2:

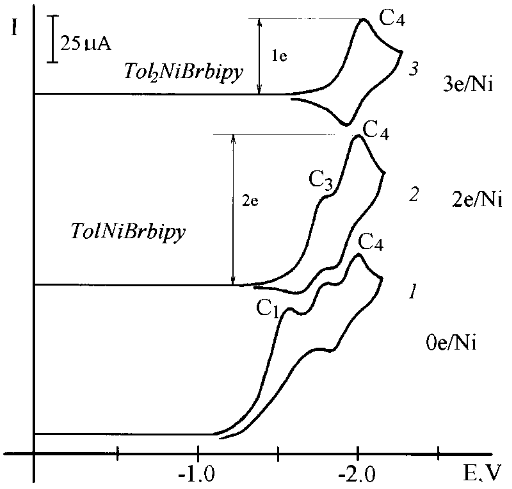


Fig. 3. Cyclic voltammograms for $NiBr_2bipy$ (10^{-2} M) with 2-BrTol (2×10^{-2}M) before electrolysis (1); after 2*e* per molecule of Ni complex (2); and 3*e* per molecule of Ni complex (3).

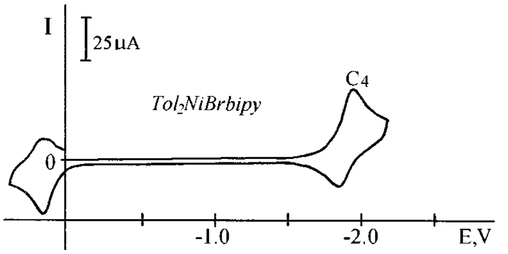


Fig. 4. Cyclic voltammograms for $Tol_2NiBrbipy$ (10^{-2} M) in DMF + Et_4NBF_4 (10^{-1} M).

$$Tol_2NiBrbipy + e \overset{C_4}{\rightleftharpoons} [Tol_2NiBrbipy]^{-\bullet} \quad (5)$$

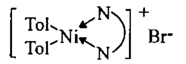
$$[Tol_2NiBrbipy]^{-\bullet} \rightarrow Tol_2 + Ni^0bipy + Br^- \quad (6)$$

$$[Tol_2NiBrbipy]^{-\bullet} \rightarrow Tol_2Nibipy + Br^- \rightarrow Tol_2 + Ni^0bipy + Br \quad (7)$$

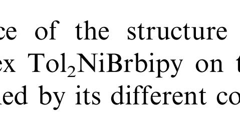
The mechanism of the formation of compound $Tol_2NiBrbipy$ is inadequately studied. The formal oxidation degree of nickel in this compound is + 3. However, such deep nickel oxidation is hardly possible in the electrolysis conditions, as this complex is formed and reduced at higher cathode potentials in comparison with the standard potential of the Ni(II)/Ni(III) system. Studies of this complex by methods of spectroscopy and elementary analysis confirm, that this individual compound conforms to the formula $Tol_2NiBrbipy$.

In order to determine the degree of nickel oxidation, ESR method was used at various temperatures. Ni(III) is known to have the $3d^7$ electronic configuration assuming the occurrence of both high-spin [↑↓|↑↓|↓|↓|↓] and low-spin [↑↓|↑↓|↑↓|↓|] states.

Thus, owing to unpaired electrons the nickel atom is paramagnetic in both states. These paramagnetic properties can be recorded as an ESR signal with an appropriate *g*-factor only at low temperatures, as the significant rate of inversion of the three unpaired electrons will result in the annihilation of each other of paramagnetic impulses at high temperatures. However no paramagnetic signal was detected at the temperature of liquid nitrogen. This supports the fact that the nickel atom does not exhibit paramagnetic properties in this σ-complex. Furthermore, the reduction potential of $Tol_2NiBrbipy$ is in a more negative region in comparison with the Ni(II) reduction potential. All these experimental facts demonstrate that degree of nickel oxidation in this compound cannot equal + 3. Therefore, one can assume that the organic fragments in this complex do not carry a negative anion charge. Probably, $Tol_2NiBrbipy$ is formed according to a mechanism different from the standard S_N2 oxidative addition which always changes the oxidation degree of the central ion by two units and proceeds through several transformations in the inner sphere of the initial complex $TolNi^Ibipy$. Further, the degree of nickel oxidation in the $Tol_2NiBrbipy$ complex under consideration equals + 2, and the coordination of Tol–Ni is different from simple σ-bonding.



One can make some assumptions on possible nickel coordination in this molecule. The $3d^8$ electronic configuration (Ni(II)) is known to assume the nickel coordination of 4 or 6, with the formation of either a planar square easily inverted in a tetrahedron or a tetrahedral bipyramid. In the first case it can be possible to assume, that Br^- is in the outer sphere of complex I. This assumption is confirmed by the presence of the oxidation wave of free Br^- anions on cyclic voltammograms. This coordination is stable in polar solvents, e.g. in DMF, which has strong donor properties. Nickel has probably six bonds in the solid state (without any solvent). In this case the structure of the complex is stabilized by the formation of binuclear structures II, connected via a halogen bridge. The structure is typical for nickel compounds.



The dependence of the structure of the obtained σ-organic complex $Tol_2NiBrbipy$ on the nature of the solvent is confirmed by its different colouring. Thus, in DMF, the colour is claret–violet, in hexane green, and in ether dark blue.

σ-Complex $MesNi^{II}Brbipy$ is more stable and can be exposed to air for an indefinite period of time. A reversible one-electron reduction wave C_3 corresponding to MesNiBrbipy, is observed on the voltammogram

(Fig. 5) after reduction of $NiBr_2bipy$ in the presence of MesBr (1:1) at the $E_p^{C_1}$ potential (−1.55 V), after passing of 2*F*. The reduction of MesNiBrbipy in the presence of some excess of bipy leads to the formation of paramagnetic particles of $MesNi^Ibipy$, i.e. this is the nickel-centred reversible transfer of an electron.

$$Ni^0bipy + MesBr \xrightarrow{C_1} \underset{\text{stable on air}}{MesNiBrbipy} \qquad (8)$$

$$MesNiBrbipy + e \overset{C_3}{\rightleftharpoons} [MesNiBrbipy]^{-\bullet} \rightleftharpoons MesNi^Ibipy + Br^- \qquad (9)$$

It should be noted that the availability of two methyl groups in *ortho*-position decelerates not only the reaction of reductive elimination, but also the reaction of oxidative addition with the nickel σ-mesityl complexes. Further reduction of the $NiBr_2bipy$ and MesBr solution (1:2) in DMF in a divided electrochemical cell has been investigated. Thus, two reversible one-electron reduction waves, C_3 and C_4, are observed on the voltammogram after 2*F* at $E_p^{C_1}$. This is analogous to the case of *o*-Br-toluene. Oxidative addition of $MesNi^Ibipy$ to MesBr proceeds more slowly, and the attempt to obtain $Mes_2NiBrbipy$ fails. However, the four-electron reduction of $NiBr_2bipy$ in the presence of MesBr (1:2) results in the selective formation of the nickel dimesityl complex, i.e. $Mes_2Nibipy$, reduced at the $E_p^{C_4}$ potential (Fig. 6). This complex was isolated from solution and characterized by methods of spectroscopy and elemental analysis.

$$Mes_2NiBrbipy + e \overset{C_4}{\rightleftharpoons} Mes_2Nibipy + Br^- \qquad (10)$$

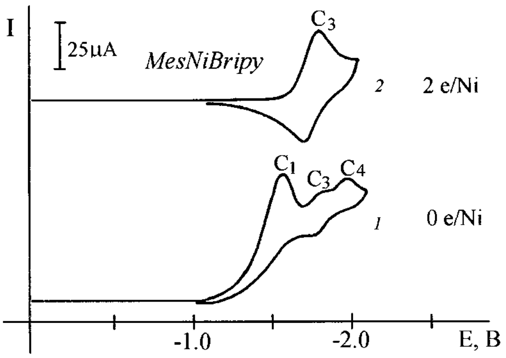


Fig. 5. Cyclic voltammograms for $NiBr_2bipy$ (10^{-2} M) with MesBr (10^{-2} M) before electrolysis (1) and after 2*e* per molecule of Ni complex (2). Ni^{2+}:MesBr = 1:1.

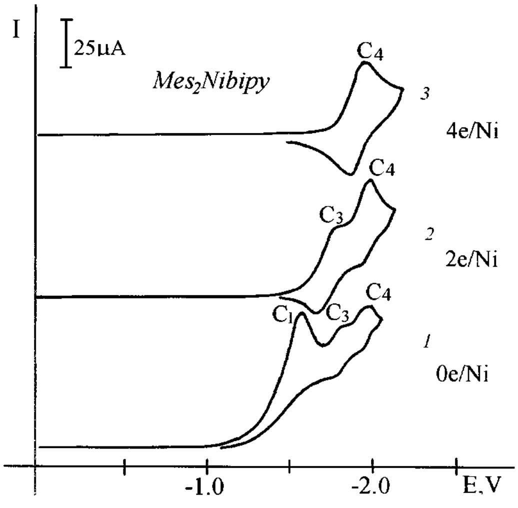
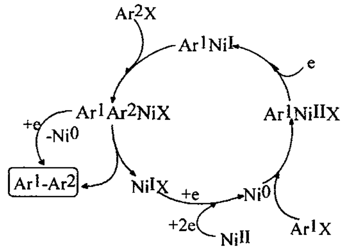


Fig. 6. Cyclic voltammograms for $NiBr_2bipy$ (10^{-2} M) with MesBr (2×10^{-2}M) before electrolysis (1); after 2*e* per molecule of Ni complex (2); and 4*e* per molecule of Ni complex (3). Ni^{2+}:MesBr = 1:2.

The importance attached to the intermediate σ-organyl complexes of nickel, produced in a multi-stage process, depends in many cases upon their key character, and by their ability to determine the further course of electrochemical and chemical transformations as a whole.

As the model *o*-Br-toluene is involved in all reactions of cross-coupling and as a result of oxidative addition forms a stable σ-complex, $TolNi^{II}Brbipy$. This was used to study the mechanism of electrocatalytic reactions. Thus, the course of a catalytic cycle for the cross-coupling process of aromatic and heteroaromatic halides was established [12–16]. The mechanism of this process includes the stages of oxidative Ni(0) addition to organic halide with the formation of σ-complex, $Ar^1NiXbipy$, its reduction to Ar^1Ni^Ibipy, and the reaction of the latter with another Ar^2X molecule yielding $Ar^1Ar^2NiXbipy$ and the reductive elimination to the cross-coupling product (in some cases induced by electron transfer):

$$Ar^1X + Ar^2X \xrightarrow{Ni^{II}bipy,\ e} Ar^1\text{–}Ar^2, \quad 58\text{–}78\%$$



The complex of Ni^I is always an active form of the nickel σ-complex, resulting in the target product.

Thus, the use of model nickel σ-aryl complexes, TolNiBrbipy and MesNiBrbipy, synthesized by electrochemical methods, allows to establish the key stage resulting in the products of cross-coupling (Ar–R), i.e. the interaction of $ArNi^Ibipy$ with RX and also to estimate the value of the rate constant for this process.

These investigations allowed to expand the range of reactions of organometallic synthesis with organonickel σ-complexes and to elaborate a convenient method for electrosynthesis of tertiary phosphines from organic

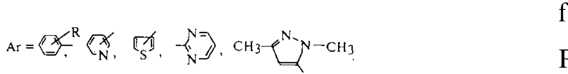
Table 1
Electrochemical functionalization of P_4 by alkyl and aryl halides catalysed by Ni(0)bipy {from $Ni(BF_4)_2bipy_3$}

R–X	Anode/solvent	Products	Yield (%)
Ph–I	Zn/DMF	Ph_3P	65
		Ph_2PH	12
		$PhPH_2$	10
	Mg/DMF	Ph_3P	50
		Ph_3PO	10
	Al/DMF	Ph_3P	12
		Ph_3PO	52
Ph–Br	Zn/DMF	Ph_3P	50
		Ph_3PO	10
		Ph_2PH	9
	Mg/DMF	$(PhP)_5$	60
		Ph_3P	15
	Al/MeCN	Ph_3P	8
		Ph_3PO	30
	Al/DMF	Ph_3P	15
		Ph_3PO	31
Bu–Br	Mg/DMF	Bu_3P	11
		Bu_3PO	55
Hex–I	Al/MeCN	Hex_3PO	47

halides and chlorophosphines catalysed by nickel complexes [17–20]. We suggested a new universal and simple method for the synthesis of unsymmetrical tertiary phosphines in mild conditions with rather high yields [17–20]. Some of these compounds are not easily accessible and/or are expensive when obtained by usual classical methods (including ligands for heterobinuclear and water-soluble complexes). The method involves the electroreduction of organic halide in the presence of mono- or dichlorophenyl phosphine added gradually using a Ni–bipy catalytic system in an undivided cell:

$$ArX + Ph_nPC_{3-n} \underset{\text{DMF, anode}-\text{Mg, Zn}}{\overset{\text{NiBr}_2\text{bipy, e}}{\rightarrow}} Ar_{3-n}Ph_nP,$$

$$n = 1{,}2 \text{ Yields } 50-87\%$$



$R = CH_3, CH_3O, (CH_3)_2N, CN, CO_2Et, CH_3C(O).$

The product of cross-coupling with the P–C bond is formed by the following substitution reaction: ArNiBr-bipy + $Ph_nPCl_{3-n} \rightarrow Ar_{3-n}Ph_nP$ + NiBrClbipy (at the initial stages of electrolysis with magnesium anode when the reaction proceeds only at the potential of the Ni(II)/Ni(0) system). After passing of one half of the calculated amount of electricity through the electrolyte, there is no initial form of the catalyst, $NiBr_2bipy$, in the solution, and electrolysis is carried out at larger cathodic potentials (−1.8 to −1.9 V, depending on the nature of Ar), but the product of cross-coupling is formed even more vigorously than at the initial stages of the electrolysis.

$$ArNiX + e \rightarrow ArNi^Ibipy + X^- \quad (-1.65\ V)$$

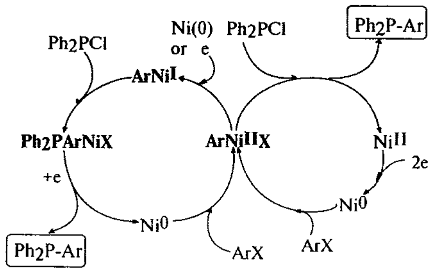
$$ArNibipy + Ph_2PCl \rightarrow ArPh_2PNibipy$$

$$ArPh_2PNiClbipy + e \rightarrow [ArPh_2PNiClbipy]^{-\bullet}$$

$$\rightarrow ArPh_2P + Ni(0) + Cl^-$$

$$(-1.8 \text{ to } -1.9\ V)$$

The proposed method of triorganyl phosphine synthesis is efficient both for aromatic halides with acceptor and donor substituents in the ring and for heteroaromatic halides (pyridine, thiophene, pyrimidine and pyrazole halides). The advantages are the single-stage character and mild conditions (room temperature) of the process performance. Electrocatalytic cycle is presented in the following scheme:



One of the problems in our investigations involves the study of the possibility of obtaining compounds with P–C bonds directly from white phosphorus and organic halides under the action of electrochemically generated Ni(0) complexes or organyl σ-complexes, obtained on their basis [21,22]. For this purpose, electrolyses of solutions of organic halides in DMF or acetonitrile in the presence of tetraphosphorus emulsion and Ni–bipy complex as a catalyst were performed.

When acted upon by electrochemically generated nickel complexes as catalysts (Table 1), it is possible to convert white phosphorus to compounds with P–C bonds, phosphines and phosphine oxides, according the following scheme:

$$P_4 + RX \underset{-X^-}{\overset{Ni(0)L_2}{\rightarrow}} >P\text{–}R$$

$$\text{Cathode:}\quad Ni(II)L + 2e \rightleftharpoons Ni(0)L,\ L = \text{bipy}$$

$$\text{Anode:}\quad M - ne \rightarrow M^{n+}\quad M = Mg, Zn$$

The interaction of organonickel compound, $RNi^{II}XL_m$, with white phosphorus was a key stage

$$Ni(0)L + RX \rightarrow RNiXL \overset{P_4}{\rightarrow} >P\text{–}R + Ni(II)$$

It should be noted that in the absence of o-TolBr the reaction of σ-complex with P_4 results only in compounds of, probably, low-coordinated phosphorus, ArP=Nibipy:

$$P + ArNiBr \rightarrow [ArP{=}Nibipy] \quad (\delta P = 204\ ppm).$$

Upon attempted isolation it proved unstable. We studied the possibility of white phosphorus interacting directly with Ni(II) and Ni(0) complexes, in order to consider other ways of formation of P–Ar bonds.

Some theoretical approaches to the activation of white phosphorus tetrahedron in complex formation have been considered. The non-polar tetrahedral molecule of P_4 is characterized by weak nucleophilicity, due to the unshared electron pairs of the phosphorus atoms, and weak electrophilicity, caused by the lowest unoccupied anti-bonding d orbitals. According to the data obtained recently, P_4 is liable to show itself as an η^1- or as an η^2-ligand. Coordinated P_4, contrary to free phosphorus, becomes more stronger acceptor of electrons and is easily reduced under the action of Ni(0) complexes.

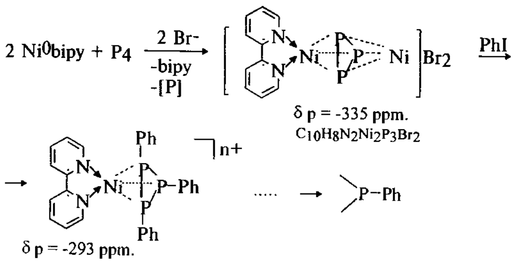
A voltammetric study of $NiBr_2$bipy and $Ni(BF_4)_2bipy_3$ behaviour in the presence of white phosphorus demonstrated that tetraphosphorus is coordinated with nickel complexes, and a reduced form of the metal yields a more stable complex than an oxidative form. The irreversibility of the process as a whole

$$Ni^{2+}(P_4)bipy + 2e^- \rightleftarrows Ni^0(P_4)bip$$

may be caused by the fast subsequent chemical reaction of P_4 reduction under the action of Ni(0) complex as an electron donor, for example

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

The fast subsequent reaction leads to a shift of the reduction curve of $NiBr_2$bipy from the standard Nernst potential to less negative potentials (Fig. 7). It was found that Ni(0)bipy reacts with tetraphosphorus, probably with the formation of binuclear complex (I), which reacts fast with organic halides, leading to the functionalization of cyclo-P_3-fragment and formation of mononuclear complex with Ph_3P_3 ligand [23]



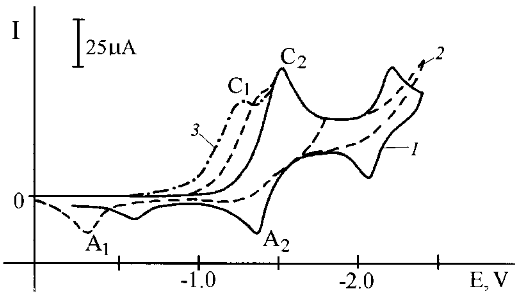


Fig. 7. Voltammograms for $NiBr_2$bipy (10^{-2} M) without (1) and with (2) white phosphorus (10^{-2} M). The same solution after keeping in argon atmosphere for 1 day (3).

Consequently, such a path to the P–Ph bond formation is competitive with the interaction of the σ-aryl complex, PhNiXbipy, with P_4. Thus, white phosphorus functionalization can be carried out by an electrochemical method with formation of compounds with P–C bonds under mild conditions.

It should be noted that electrochemical methods allow not only to carry out these processes under mild conditions at a high rate, but in many cases also to control them with a high selectivity.

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

3. Experimental

3.1. General procedures

All manipulations and reactions were carried out under dry Ar atmosphere. All solvents employed were purified and dried prior to use. Acetonitrile was purified by triple fractionation distillation over phosphorus anhydride with the addition of $KMnO_4$. The concentration of residual water was 10^{-3} M. *N*,*N*-Dimethylformamide was purified according to the method in Ref. [24], enabling to reach the residual water content of 0.01–0.005% (weight). Supporting salts were recrystallized twice: Et_4NBr from MeCN, Et_4NBF_4 from EtOH and were dried in vacuum at 70 °C for 2 days. Alcohols were refluxed with BaO for 5 h and then distilled. The white phosphorus was purified by recrystallization from benzene and pyridine mixtures and later it was washed out of absolute Me_2CO and EtOH and by ether. $NiBr_2$bipy and $Ni(BF_4)_2bipy_3$ were prepared according to the method in Ref. [25]. Preparative electrolysis at a constant current density, NMR spectroscopy of ^{31}C, ^1H, chromatographic analysis, elemental analysis and ESR were used for the establishment of structure and yields of electrosynthesis products.

Cyclic voltammograms were recorded at glassy carbon electrode with a 1.5 mm diameter in a thermostatically controlled cell in argon atmosphere. Silver electrode $Ag/AgNO_3$ (0.01 mol l^{-1} solution in MeCN) served as a reference electrode and platinum wire served as an auxiliary electrode. Curve registration was performed with potentiostat PI-50-1 (USSR). Scan rate was 50 mV s^{-1}.

Preparative electrolyses were performed by means of the direct current source B5-49 in thermostatically controlled cylindrical undivided electrolyser (a three-electrode cell) with a 40 cm^3 volume. Silver electrode Ag/AgNO$_3$ (0.01 mol l^{-1} solution in MeCN) served as a reference electrode. Platinum with surface areas of 20 cm^2 was used as a cathode. The argon flow was bubbled through the electrolyte in the course of electrolysis. During electrolysis, the electrolyte was stirred with a magnetic stirrer. The saturated solution of Et$_4$NCl in MeCN was used as anolyte, and the membrane was made of paper.

Chromatographic analysis of the reaction mixtures and synthesized compounds was carried out on a Chrom-4 gas-liquid chromatograph using helium as a carrier gas and a flame ionization sensor-detector. Glass columns filled with a 5% Silicone SE-30 packing on chromaton N-AW (0.0125–0.160) were used. NMR spectra were registered in CDCl$_3$ using a Varian T-60 spectrometer with the working frequency 60 MHz and Me$_4$Si was used as the internal standard. The ^{31}P-NMR spectra were recorded using a CXP-100 Bruker spectrometer (85% H$_3$PO$_4$ as an external standard) with and without decoupling of protons. ESR signals were recorded using the RADIOPAN (Polish electronic spectrometer of a X-range SE/X-2544) and calculated according to the method in Ref. [26]; 1,1-diphenyl-2-picrylhydrazyle ($g = 2.0036$) was used as the external standard.

3.2. Preparative electrolyses

3.2.1. Electrochemical reduction of NiBr$_2$bipy in presence of aromatic bromides

A solution for electrolysis was prepared by mixing 0.1875 g (0.5 mmol) NiBr$_2$bipy and 1 mol of aromatic bromide in DMF. 2-BrTol (0.12 ml, 1 mmol) and MesBr (0.075 ml, 0.5 mol or 0.15 ml, 1 mmol) were used for the preparation of Tol$_2$NiBrbipy, MesNiBrbipy and Mes$_2$Nibipy, respectively. Electrolysis was carried out in an electrochemical cell both with separation, and without separation of anode and cathode compartments at ambient temperature at the potential of a working electrode − 1.52 V. The amounts of electricity passed through the electrolyte were 3*e*, 2*e* or 4*e* per molecule of nickel complex for the preparation of Tol$_2$NiBrbipy, MesNiBrbipy and Mes$_2$Nibipy, respectively. After completing the electrolysis, the solution was hydrolysed and extracted with ether; the organic layer was washed with water and dried; and the solvent was evaporated.

3.2.1.1. Bis-ortho-tolyl-nickel-bromide-2,2′-bipyridine. ^{1}H-NMR (CDCl$_3$, ppm): δ 8.56–8.57 (m, 2H), 8.33–8.37 (d, 2H), 7.79–7.82 (m, 2H), 7.28–7.31 (m, 2H), 7.10–7.14 (m, 6H, C$_6$H$_4$), 6.92–6.92 (m, 2H, C$_6$H$_4$), 1.91 (s, 6H, CH$_3$). Anal. Found: C, 60.34; H, 5.23; Br, 16.58; N, 6.03; Ni, 12.37. Calc. for C$_{24}$H$_{22}$NiN$_2$Br: C, 60.38; H, 4.61; Br, 16.77; N, 5.87; Ni, 12.37%. M.p. (dec.) 145 °C; yield 90%.

3.2.1.2. Mesityl-nickel(II)-bromide-2,2′-bipyridine. ^{1}H-NMR (CDCl$_3$, ppm): δ 8.56–8.57 (m, 2H), 8.33–8.37 (d, 2H), 7.79–7.82 (m, 2H), 7.28–7.31 (m, 2H), 6.45 (m, 2H, C$_6$H$_2$), 2.59 (s, 6H, CH$_3$), 2.17 (s, 3H, CH$_3$). Anal. Found: C, 55.03; H, 4.60; Br, 18.90; N, 6.03; Ni, 14.16. Calc. for C$_{19}$H$_{19}$NiN$_2$Br: C, 55.14; H, 4.59; Br, 19.31; N, 6.77; Ni, 14.18%. M.p. (dec.) 149 °C; yield 85%.

3.2.1.3. Bis-mesityl-nickel-2,2′-bipyridine. ^{1}H-NMR (CDCl$_3$, ppm): δ 8.56–8.57 (m, 2H), 8.33–8.37 (d, 2H), 7.79–7.82 (m, 2H), 7.28–7.31 (m, 2H), 6.45 (m, 4H, C$_6$H$_2$), 2.59 (s, 12H, CH$_3$), 2.17 (s, 6H, CH$_3$). Anal. Found: C, 74.08; H, 6.83; N, 6.28; Ni, 12.37. Calc. for C$_{28}$H$_{30}$NiN$_2$: C, 74.19; H, 6.62; N, 6.18; Ni, 12.96%. M.p. (dec.) 215 °C; yield 81%.

3.2.2. Nickel catalysed electrosynthesis of triorganyl phosphines from organic halides and chlorophosphines

The anode was a magnesium or zinc cylindrical rod (diameter 1.3 cm) surrounded by a cylindrical nickel grid. The electrosyntheses were carried out according to the following procedure. The solution of Bu$_4$NBF$_4$ (0.005 mmol), NiBr$_2$bipy (1 mmol), aryl or heteroaryl halide (15 mmol) in DMF (40 ml) was electrolysed at $i = 500$ mA under argon until the whole ArX was consumed. During the electrolysis the chlorophosphine was continuously added dropwise with the rate of 1 mol of phosphine per 2*F* of electricity (Ph$_2$PCl) or 1 mol of phosphine per 4*F* of electricity (PhPCl$_2$). The progress of the reaction was checked by GC analysis of samples. The solution was hydrolysed using 0.1 N NH$_4$Cl and extracted with ether; the organic layer was washed with water and dried; and the solvent was evaporated. The products were purified by column chromatography on silica gel with pentane–ether mixtures as eluent.

3.2.3. Nickel catalysed electrosynthesis of organophosphorus compounds with P–C bonds from white phosphorus and organic halides

The single-compartment cell was fitted with a cylindrical magnesium, zinc or aluminium rod (diameter 1.3 cm) as an anode, surrounded by a platinum cylinder as a cathode. The solution of Bu$_4$NBF$_4$ (0.005 mmol), NiBr$_2$bipy or Ni(BF$_4$)$_2$bipy (0.5 mmol), organic halide (35 mmol) and 7 mmol of white phosphorus dispersed in DMF (100 ml) was electrolysed at 0.5 mA cm^{-2}

cathodic current density in an atmosphere of argon until the whole RX was consumed. The solution was hydrolysed using 0.1 N NH_4Cl and extracted with ether; the organic layer was washed with water and dried; and the solvent was evaporated. Individual products were isolated from the mixture by column chromatography on silica gel and were identified by measuring physical constants and spectra according to appropriate literature data. In some experiments the relative content of organophosphorus compounds was estimated according to the integral intensity of the ^{31}P-NMR spectrum.

3.2.4. *Electrochemical reduction of nickel complexes in the presence of white phosphorus*

The process solution (catholyte) with a total volume of 30 ml was prepared by dissolving 0.5 mmol of a nickel complex (0.1875 g $NiBr_2bipy$ or 0.35 g $Ni(BF_4)_2bipy_3$) and 0.5 mol of supporting electrolyte 1.05 g Et_4NBr (in the case of $NiBr_2bipy$) or 1.085 g Et_4NBF_4 (in the case of $Ni(BF_4)_2bipy_3$) in DMF. In the resulting solution, 0.062g (2 mmol) of white phosphorus was dispersed under argon when heated to 50 °C. The electrolysis has been carried out in a two-compartment electrochemical cell in potentiostatic regime (-1.52 or -1.60 V). The amounts of electricity passed through the electrolyte were $2e$ per molecule of nickel complex. After completing the electrolysis, the precipitate was filtered, washed out by ether and dried in vacuum at a temperature of 30 °C.

3.2.4.1. Complex [$NiP_3Nibipy$]Br_2. Anal. Found: C, 21.69; H, 2.03; Br, 31.78; N, 4.52; Ni, 21.90; P, 16.65. Calc. for $C_{10}H_8N_2Ni_2P_3Br_2$: C, 22.79; H, 1.52; Br, 30.40; N, 5.32; Ni, 22.29; P, 17.67%. ^{31}P-NMR: -335.8 (s). ^1H-NMR ($CDCl_3$, ppm): δ 6.63–8.82 (m, 8H, 2,2′-bipy). M.p. (dec.) 154° C; yield 0.11 g (84%).

3.2.4.2. Complex [$NiP_3Nibipy$]$(BF_4)_2$. Anal. Found: C, 21.50; H, 1.98; B, not determined; F, 27.2; N, 6.01; Ni, 19.34; P, 17.60. Calc. for $C_{10}H_8N_2Ni_2P_3B_2F_8$: C, 22.22; H, 1.48; B, 4.01; F, 28.15; N, 5.19; Ni, 21.74; P, 17.22%. ^{31}P-NMR ^{31}P: -334.6 (s). ^1H-NMR ($CDCl_3$, ppm): δ 6.63–8.82 (m, 8H, 2,2′-bipy). M.p. (dec.) 148 °C; yield 0.12 g (89%).

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References

[1] J.J. Eisch, S.R. Sexsmith, Res. Chem. Intermed. 13 (1990) 149.
[2] J.J. Eisch, K.R. Im, J. Organomet. Chem. 139 (1977) C45.
[3] J.J. Eisch, L.E. Hallenbeck, K.I. Han, J. Am. Chem. Soc. 108 (1986) 7763.
[4] T. Hayashi, M. Kumada, Acc. Chem. Res. 15 (1982) 395.
[5] J.J. Eisch, Y. Quian, M. Singh, J. Organomet. Chem. 512 (1996) 207.
[6] M. Troupel, Y. Rollin, O. Sock, G. Meyer, J. Perichon, Nouv. J. Chim. 10 (1986) 593.
[7] Y.H. Budnikova, O.E. Petrukhina, Y.M. Kargin, Zh. Obsh. Chim. (Russ.) 66 (1996) 605.
[8] Y. Rollin, M. Troupel, D.G. Tuck, J. Perichon, J.Organomet. Chem. 303 (1986) 131.
[9] M. Durandetti, M. Devaud, J. Perichon, New J. Chem. 20 (1996) 659.
[10] E.C. Constable, Homoleptic complexes of 2,2′-bipyridine, in: A.G. Sykes (Ed.), Advances in Inorganic Chemistry, vol. 34, Academic Press, New York, 1989, p. 1.
[11] A.G. Lappin, A. McAuley, Adv. Inorg. Chem. 32 (1988) 241.
[12] C. Gosmini, S. Lasry, J.-Y. Nedelec, J. Perichon, Tetrahedron 54 (1998) 1289.
[13] C. Gosmini, J.-Y. Nedelec, J. Perichon, Tetrahedron 41 (2000) 201.
[14] Y.H. Budnikova, Yu.M. Kargin, O.G. Sinyashin, Zh. Obshch. Chim. (Russ.) 70 (2000) 123.
[15] G. Meyer, M. Troupel, J. Perichon, J. Organomet. Chem. 393 (1990) 137.
[16] M. Durandetti, J.Y. Nedelec, J. Perichon, J. Org. Chem. 61 (1996) 1748.
[17] Y.H. Budnikova, Y.M. Kargin, J. Perichon, J.-Y. Nedelec, J.Organomet. Chem. 575 (1999) 63.
[18] Y.H. Budnikova, Y.M. Kargin, O.G. Sinyashin, Mendeleev Commun. (1999) 193.
[19] Y.H. Budnikova, J. Perichon, J.-Y. Nedelec, Y.M. Kargin, Phosphorus Sulfur 144–146 (1999) 53.
[20] Y.H. Budnikova, Y.M. Kargin, O.G. Sinyashin, Zh. Obshch. Chim. (Russ.) 70 (2000) 562.
[21] Y.H. Budnikova, Y.M. Kargin, O.G. Sinyashin, Phosphorus Sulfur 144–146 (1999) 565.
[22] Y.H. Budnikova, D.G. Yakhvarov, Yu.M. Kargin, Mendeleev Commun. (1997) 67.
[23] M. Di Vaira, C.A. Ghilardi, S. Midollini, L. Sacconi, J. Am. Chem. Soc. 100 (1978) 2550.
[24] Y.M. Kargin, V.Z. Kondranina, N.I. Semahina, Izv. Akad. Nauk. Ser. Khim. (Russ.) (1971) 278.
[25] M. Troupel, Y. Rollin, O. Sock, G. Meyer, J. Perichon, Nouv. J. Chim. 10 (1986) 593.
[26] S.Ya. Pshegeckii, A.G. Kotov, V.K. Milinchuk, V.A. Roginskii, V.I. Tupikov, ESR of Free Radicals in Radiating Chemistry, Himiya, Moscow, 1972.