Activation of white phosphorus in the coordination sphere of nickel complexes with σ -donor ligands*

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Routes of white phosphorus activation in the coordination sphere of the nickel complexes with different ligands are shown. The first route is based on the coordination of a P₄ molecule with the metal, resulting in the deformation of the P₄ tetrahedron without destruction. This case is characteristic of the NiX₂L complexes, which are reduced at higher cathodic potentials $(|E_{red}| > 0.9 V)$ (X = BF₄, Br, and Cl; L is bpy in DMF, MeCN, and acetone; 2,9-dimethyl-1,10-phenanthroline (phen) and PPh₃ in DMF and acetone). To cleave the P—P bonds in the P₄ molecule, this complex should be reduced on the electrode. The second route is the oxidation of white phosphorus in the coordination sphere of the Ni^{II} complex. It occurs when the complex has a sufficiently high oxidizing ability and is reduced rather easily ($|E_{red}| < 0.9 V$) (X = BF₄, L is 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) in acetone; 1,1',5,5'-bis[methylenedi(*p*-phenylene)]di(3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane) (n²p²) in DMF; phen and PPh₃ in MeCN). The P₄ molecule opening is observed to form a new Ni^I complex containing the (P₃) fragment, for example, [(triphos)Ni(P₃)Ni(triphos)](BF₄)₂.

Key words: white phosphorus, nickel complexes, activation, cyclic voltammetry, electrochemistry.

The electrochemical activation of reagents in processes involving organometallic compounds is very efficient. $^{1-4}$ This approach combines advantages of catalysis by metal complexes and activation by means of electrochemical electron transfer. The activation of white phosphorus is a practically important task because of the necessity to search for new routes of direct syntheses of organophosphorus compounds. Numerous reactions of P₄ tetrahedron transformation were described, which resulted in various polyphosphorus structures among which metal complexes with cyclic P_3 , P_5 , and P_6 ligands,⁴ as well as the P_4 ligand,^{5,6} seem to be most interesting. The P_4 molecule is activated due to the deformation of the P4 tetrahedron and, as a consequence, the P–P bond length changes. In ultimate cases, these bonds can cleave to form new polyphosphorus structures. Until now, P₄ transformation was studied only by NMR spectroscopy, and very stable compounds were examined. Evidently, the more stable these structures, the more difficult is the preparation of

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related basis organophosphorus compounds, *i.e.*, the main task of the elemental phosphorus chemistry is the direct transformation of phosphorus into organophosphorus compounds (OPC), excluding traditional steps of its chlorination. At the same time, metal complexes with polyphosphorus ligands can possess a set of useful properties: semiconductivity, corrosion resistance, and others⁷ and act as stable intermediates in various reactions, which are of independent interest.

In this work, we attempted to estimate the reactivity of several nickel complexes with σ -donor ligands toward white phosphorus using cyclic voltammetry (CV), preparative electrolysis, and ³¹P NMR spectroscopy. The nickel complexes were chosen, because they are catalysts of some reactions of white phosphorus functionalization, for instance, arylation^{8,9} and alkoxylation.¹⁰

To establish the mechanism of activation of the P_4 molecule in the coordination sphere of the nickel complexes, we estimated changes in the electrochemical parameters (reduction potential and current) of the complexes upon the addition of white phosphorus. Compounds capable of stabilizing nickel in low oxidation states (+1, 0),

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such as bpy, PPh₃, phen, 1,1,1-(trisdiphenylphosphinomethyl)ethane (triphos), and n^2p^2 , were chosen as ligands.

Experimental

Stationary disk glassy-carbon electrode with the efficient surface area of 3.14 mm² was used as the working electrode in electrochemical studies (CV). Voltammograms were detected using a PI-50-1 potentiostat with a PR-49 programmer and an electrochemical cell switched-on *via* a three-electrode scheme. Curves were recorded at a linear potential sweep of 50 mV s⁻¹ on a two-coordinate recorder. An Ag/0.01 *M* AgNO₃ system in MeCN served as the reference electrode. A platinum wire 1 mm in diameter was used as the auxiliary electrode. Measurements were carried out in a cell at the temperature kept constant at 25 °C under argon.

³¹P NMR spectra were obtained with a Bruker MSL-400 NMR Fourier spectrometer (Germany) at a frequency of 161 MHz relatively to the external standard (85% orthophosphoric acid).

ESR spectra were recorded using a Radiopan SE/X-2544 spectrometer (Poland) with diphenylpicrylhydrazyl (DPPH, g = 2.0036) used as the external standard. IR spectra were recorded with a Bruker Vector 22 instrument. UV spectra were obtained using a Specord UV VIS instrument.

X-ray powder diffraction analysis was carried out on a D8 ADVANCE diffractometer with the Cu-K α radiation (wavelength 1.5406 E; 40 kV, 30 mA) and a graphite monochromator. A sample was scanned within $2\theta = 3-70^{\circ}$ with a scan increment of 0.02°. The exposure time in a point was 1 s.

The elemental composition of nickel phosphides was determined using an EMAL 2 laser-ionization mass spectrometer.

Acetonitrile purified by triple fractional distillation above P_2O_5 with an addition of $KMnO_4$ was used. Dimethylformamide was purified by triple vacuum distillation with intermediate drying above molecular sieves. Acetone was distilled above $KMnO_4$ and then above anhydrous $CaCl_2$. To prepare the supporting electrolyte, twice recrystallized salts were used: Et_4NBr , Et_4NCl (from MeCN), and Et_4NBF_4 (from EtOH), which were dried in a vacuum desiccator at 100 °C for 2 days. Benzene was distilled above sodium. White phosphorus was recrystallized from a pyridine—benzene mixture.

A solution of white phosphorus was prepared by the dissolution of the calculated amount of P_4 in benzene in such a way that the addition of 0.1 mL of this solution to the electrochemical cell containing 5 mL of a solution of the studied metal complex provided the P_4 concentration in the cell equal to $5 \cdot 10^{-3}$ mol L⁻¹, *i.e.*, the 1 : 1 stoichiometry with respect to the metal complex concentration.

NiBr₂, NiCl₂, and Ni(BF₄)₂·6 H₂O (reagent grade) and PPh₃, bpy, phen, and triphos were used as received. The n^2p^2 ligand was synthesized by a known procedure.¹¹

Bis[1,1,1-tris(diphenylphosphinomethyl)ethane]phosphiridinonickel(II) bistetrafluoroborate $[Ni_2P_3(triphos)_2](BF_{4})_2$ and 1,1',5,5'-bis[methylenedi(*p*-phenylene)]di(3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane)phosphiridinonickel(II) bistetrafluoroborate $[Ni_2P_3(n^2p^2)](BF_4)_2$ were synthesized by a previously described procedure.¹²

The data of ³¹P NMR spectroscopy of $5 \cdot 10^{-2} M$ solutions of Ni(BF₄)₂L in DMF in the presence of white phosphorus are presented in Table 1.

Table 1. ³¹P NMR chemical shifts for solutions of Ni(BF₄)₂L_n in DMF in the presence of white phosphorus (1 : 1) for L = bpy, phen, and PPh₃ (n = 3) and [NiL(P₃)NiL](BF₄)₂ for L = triphos and n²p²

L _n		δ^{31} P NMR						
	Ι	II	$[LNi(P_3)NiL] (BF_4)_2$	P_4^{free}				
phen	-323.8	-463.4	_					
PPh ₃	-347.2	-487.2	_					
bpy	-363.1	-490	_	-523				
triphos	_	_	-290					
n^2p^2	—	—	-375					
Note. I -	– LNi ^{II} – P	P P, II -	- LNi ^{II-} P-P.					

Electrochemical reduction of the Ni^{II}L_nBr₂ complexes (L = bpy (n = 1), phen (n = 1), and PPh₃ (n = 3)) in the presence of white phosphorus. The working solution (40 mL) was prepared by the dissolution of 10^{-3} moles of the nickel complex (0.36 g of NiBr₂bpy; 0.42 g of NiBr₂phen; or 0.48 g of NiBr₂(PPh₃)₃) and $5 \cdot 10^{-3}$ moles of the supporting electrolyte (1.05 g of Et₄NBr) in DMF. White phosphorus (0.062 g, $5 \cdot 10^{-4}$ mol) was suspended with stirring of the solution under argon at 50 °C. Electrolysis was carried out in a divided cell in the potentiostatic regime (-1.60 V) vs. Ag/0.01 M AgNO₃ in CH₃CN at 50 °C under argon. The catholyte was magnetically stirred during electrolysis. A saturated DMF solution of the supporting electrolyte served as the anolyte. After the end of electrolysis (after the electricity equal to 2e/(nickel atom) corresponding to 27 mAh passed through the solution), a dark precipitate was filtered off, washed with ether, and dried in a vacuum desiccator at 30 °C.

The complexes NiX_2L were synthesized by the mixing of equivalent amounts of a nickel salt and the corresponding ligand in hot ethanol followed by the filtration of the complex and drying *in vacuo* for a day.

The complexes $Ni_3P_2bpy \cdot 3 \cdot H_2O$, $Ni_3P_2phen \cdot 3 H_2O$, and $Ni_3P_2(CH_3)_2NCHO$ were synthesized.

Complex Ni₃P₂bpy·3·H₂O. The yield was 0.35 g (89% calculated based on P), m.p. 154 °C (decomp.). IR (Vaseline), v/cm⁻¹: 769, 1382, 1468, 1662 (bpy). Found (%): C, 26.52; N, 6.43; Ni, 39.64; P, 13.89. Calculated (%): C, 26.73; N, 6.23; Ni, 39.42; P, 13.81. MS (I_{rel} (%)): 449 [M]⁺ (100), 369 (30), 340 (28), 156 (52). XRD: d = 18 E (br.).

Complex Ni₃P₂phen · 3 H₂O. The yield was 0.23 g (46% calculated based on P), m.p. 188 °C (decomp.). IR (Vaseline), v/cm⁻¹: 747, 835, 841, 1417, 1524 (phen). Found (%): C, 28.17; N, 5.72; Ni, 35.11; P, 12.51. $C_{14}H_{18}N_2Ni_3P_2O$. Calculated (%): C, 27.94; N, 5.59; Ni, 35.33; P, 12.37.

Complex $Ni_3P_2(CH_3)_2NCHO$. The yield was 0.21 g (67% calculated based on P), m.p. 258 °C (decomp.). Found (%): C, 11.87; N, 4.57; Ni, 53.18; P, 22.36. $C_3H_7NONi_3P_2$. Calculated (%): C, 11.54; N, 4.49; Ni, 56.73; P, 19.87.

Results and Discussion

Let us consider the electrochemical reduction (CV) of the coordinately unsaturated complexes NiX_2L_n (X = Br,

Complex	Ligand	E_{C_1}	E_{C_1}	ΔE	$I_{C_1'}/I_C$
(solvent)		/\	/		
NiBr ₂	_	-1.72	-1.18	0.54	0.1
(DMF)	bpy	-1.35	-1.03	0.32	0.8
	$(PPh_3)_3$	-1.76	-1.13	0.63	1.7
	Phen	-1.12	-0.97	0.15	1.8
	triphos	-1.60	-1.52	0.08	2.0
NiBr ₂	_	-1.10	-0.62	0.48	1.8
(MeCN)	bpy	-1.35	-1.24	0.11	1.3
	$(PPh_3)_3$	-0.48	-0.47	0	1.4
	Phen	-1.01	-0.94	0.07	2.1
	triphos	-0.30	-0.30	0	1.0
$Ni(BF_4)_2$	_	-1.77	-1.14	0.63	1.0
(DMF)	bpy	-1.56	-1.26	0.30	0.8
	$(PPh_3)_3$	-1.75	-1.34	0.41	1.4
	Phen	-1.44	-1.17	0.27	1.0
	triphos	-1.63	-1.40	0.23	1.0
$Ni(BF_4)_2$	_	-1.49	-0.81	0.68	1.4
(MeCN)	bpy	-1.48	-1.36	0.12	1.1
	$(PPh_3)_3$	-0.93	-1.25	-0.32	0.4
	Phen	-0.72	-1.20	-0.48	0.7
	triphos	-0.22	-0.41	-0.19	0.5
NiCl ₂	_	-1.42	-1.03	0.39	1.0
(DMF)	bpy	-1.55	-1.43	0.12	1.0
	$(PPh_3)_3$	-1.59	-1.44	0.15	1.3
	Phen	-1.12	-1.08	0.04	1.0
$Ni(BF_4)_2$	_	-1.10	-0.91	0.19	1.0
(acetone)	bpy	-1.35	-0.87	0.48	1.0
	$(PPh_3)_3$	-1.65	-1.01	0.64	2.0
	Phen	-1.10	-0.91	0.19	0.7
	triphos	-0.32	-0.81	-0.49	1.3

Table 2. Electrochemical characteristics of the reduction of the NiX₂L nickel complexes in the absence (E_{C_1}) and presence (E_{C_1}) of P₄ (Ni : P₄ = 1 : 1)

Cl, BF₄, L = PPh₃ (n = 3), bpy, phen, triphos, and n²p² (n = 1)) in CH₃CN, DMF, and acetone. The reversibility of the process depends on the solvent: in MeCN the ratio of heights of the oxidation to reduction currents (I_a/I_c) is somewhat higher, *i.e.*, Ni⁰L is more stable in solution. The reduction potentials (E_{C1}) of the complexes are presented in Table 2.

The addition of white phosphorus to solutions of the chosen metal complexes shifts the potentials of the observed reduction peaks to the region of less negative potentials or to the more cathodic region, which indicates the formation of new complexes with different electrochemical characteristics. As will be shown further, the change in these characteristics along with the data of preparative electrolysis and ³¹P NMR spectroscopy can suggest the character of interaction of P₄ with the metal complexes under study.

Let us divide all the studied complexes, which behave differently in the presence of white phosphorus, into groups.



Fig. 1. Comparison of the reduction and oxidation potentials of free white phosphorus and white phosphorus in the coordination sphere of the nickel complex.

Nickel complexes NiX₂L_n (L_n is bpy in DMF, MeCN, and acetone; L_n is phen or (PPh₃)₃ in DMF and acetone). A free P₄ molecule is rather poorly polarized: the electrochemical energetic gap ΔG^{13} (the difference between the reduction and oxidation potentials) is significant, being 3.79 V in MeCN and 3.30 V in DMF. The considerable negative reduction potential of white phosphorus contributes greatly to the ΔG value (Fig. 1). Complex formation is accompanied by a sharp decrease in ΔG and, hence, an increase in the polarizability of the P₄ molecule and its ability to accept and donate electrons. The P₄ ligand in the coordination sphere of nickel is reduced and oxidized much more easily, *i.e.*, its reactivity increases.

When P_4 is gradually added to a solution of the chosen metal complex, the [Ni] : P_4 ratio changes from 10 : 1 to 1 : 1 and the initial reduction peak decreases, while at less negative potentials a peak appears. This peak corresponds to the irreversible reduction of a new complex containing the P_4 molecule as a ligand (Fig. 2). For the ratio [Ni] : $P_4 = 1 : 1$, the initial peak disappears, and the new peak reaches a maximum. The observed processes can be described by Scheme 1.

Scheme 1

NiX₂LS + 2e

$$\stackrel{-2X^{-}}{\longrightarrow}$$
 Ni⁰LS
 $\stackrel{+P_4}{\uparrow}$
 $\stackrel{+P_4}{\uparrow}$
 $\stackrel{+P_4}{\uparrow}$
NiX₂(P₄)L + 2e
 $\stackrel{-2X^{-}}{\longrightarrow}$ Ni⁰L(P₄) $\stackrel{i}{\longrightarrow}$ Niⁿ⁺(P₄)ⁿ⁻L



Fig. 2. Schematic cyclic voltammograms of the NiX₂L nickel complex with the σ -donor ligand in the absence (*I*) and presence of white phosphorus (2–4): P₄ : Ni 1 : 2 (2), 1 : 1 (3), 2 : 1 and (4); 5, CV of solution 3 after passing 2 F electricity.

The decrease in the reduction potential of the $NiX_2(P_4)L$ complex formed (see Fig. 2) as compared to the initial one indicates a decrease in the LUMO due to the donor-acceptor interaction in the NiL_nX₂ $-P_4$ pair, where unoccupied d-orbitals of phosphorus can withdraw a part of the electron density of the metal complex. It is known that the addition of some substrates capable of coordinating with metal to solutions of metal complexes results in a change in the shape of the voltammetric curve, namely, the disappearance of the reduction peak of the initial metal complex and the appearance of and a gradual increase in a new peak at less negative potentials. This is observed, for instance, when acrylonitrile was added to Ni^{II}-PPh₃¹⁴ or different phosphine ligands were added to the nickel salt.¹⁵ The saturation of the coordination sphere of Ni^{II} with high-field ligands (for example, compounds of tricoordinated phosphorus P^{III}) increases the electron density on the metal atom. As a result, the HOMO of Ni^{II} and LUMO of the ligand are brought together, thus facilitating the removal of the ligand as an anion. Due to the intramolecular one-electron transfer, the hexacoordinated complex is completely ionized¹⁵

$$NiX_2L_3L' = NiL_3L'^{2+} + 2X^{-}.$$

The shift of equilibrium toward the cationic $[NiL_3L']^{2+}$ complexes depends on the basicity of the σ -donor and its volume and the nickel—ligand binding strength. The cationic $[NiL_3L']^{2+}$ complexes are isostructural analogs of coordinately saturated complexes of zero-valence nickel $[NiL_3L']^0$ with close bond lengths and bond angles. In this pair of complexes, the activation energy of electron transfer is very low, because no rearrangement of the coordination sphere is required and the electron transfer is strictly reversible and occurs at a potential close to the standard value for the Ni^{II}/Ni⁰ pair (with the corresponding ligands). If white phosphorus is a usual stable P^{III} ligand, then the nickel(II) complex with P_4 would be characterized by the reversible reduction peak, whose potential is somewhat shifted relatively to that of the initial complex. The observed irreversibility is related to the fast subsequent transformation of white phosphorus in the coordination sphere of the Ni⁰ complex.

The data of ³¹P NMR spectroscopy indicate that in polar aprotic solvents, *e.g.*, DMF, white phosphorus exists as both the free P₄ molecule ($\delta_P = -523$) and the η^1 -coordinated complex with the nickel atom. A similar situation is observed for the Ni complexes with bpy, PPh₃, and phen (see Table 1). The broad signals with $\delta_P = -320$ —-365 are attributed to the phosphorus atom linked to nickel.⁴ The signals with δ_P at -460—-490 correspond to three other phosphorus atoms in the coordinated P₄ molecule. ⁴

When P_4 is added, the reduction of Ni^{II} to Ni⁰ becomes irreversible, which can be explained by the fast subsequent chemical transformation of phosphorus (route *i*, Scheme 1) in the coordination sphere of the Ni⁰ complex. A new C₂ peak appears in the CV (see Fig. 2) at more negative potentials with respect to the C₁ peaks and corresponds, most likely, to the reduction of the product of the reaction between Ni⁰ and P₄. Thus, P₄ acts as both the ligand and a substrate (reactant). The reduction potentials of the nickel salts and complexes in the presence and absence of white phosphorus are presented in Table 2.

An increase in the P₄ concentration over the stoichiometric value, the reduction peak (C₃) of the P₄ itself (E = -2.20 V in DMF) appears in the voltammogram, and its height is proportional to the P₄ concentration (see Fig. 2).

In all cases considered for the NiX₂L_n complexes with bpy in DMF, MeCN, and acetone and with phen and PPh₃ in DMF and acetone, the P₄ molecule is coordinated with the nickel atom acting as a ligand. White phosphorus can be regenerated, most likely, in the unchanged state from these systems.

In these cases, the only coordination of the phosphorus atom with metal is insufficient to cleave one or several P—P bonds in P₄. The Ni^{II}L—P₄ complex should be reduced electrochemically to Ni⁰L—P₄. It has previously⁹ been shown for NiBr₂bpy that the P₄ molecule is transformed into the *cyclo*-P₃ ligand under the action of electrochemically generated Ni⁰. The reduction potential of the [bpyNi(P₃)Ni]Br₂ complex formed by electrolysis $(E_{C_2} = -1.72 \text{ V})$ (see Fig. 2, curve 5) corresponds to the potential of the new peak, which was observed in the voltammograms upon the addition of P₄ to Ni^{II}bpy $(E_{C_2} = -1.73 \text{ V})$ (see Fig. 2, curve 3).

It can be assumed that the formation of a black precipitate due to electrolysis is a consequence of a low stability of the primarily formed *cyclo*- P_3 complex, which undergoes subsequent transformation into a more stable form. On keeping the solution for 1 day after electrolysis, the black colloidal solution coagulates gradually, and nickel phosphide including bipyridine precipitates.¹⁶

Similar results are observed in the case of the electrochemical reduction of the nickel complexes with phen and PPh_3 in the presence of white phosphorus.

It is of interest that in DMF the reduction current of the nickel(II) complex with white phosphorus almost corresponds to the current of the initial NiX₂L complex, whereas in MeCN the height of the peak of the $[Ni-P_4]$ complex often increases. This fact indicates an important role of the solvent in the studied complexation and transformation processes involving P₄.

It can be expected that the reduction potential of the Ni complex determines its reactivity toward white phosphorus (as the ligand and substrate) and certain regularities will be found. We analyzed the dependence of the shift of the reduction potential of the nickel complex upon white phosphorus addition ($\Delta E = E_{\text{Red}}^{[\text{NiL}-P_4]}$ – $E_{\text{Red}}^{[\text{NiL}]}$) on the reduction potential of the initial nickel complex. The results are presented in Fig. 3. In several cases, a satisfactory correlation between ΔE and $E_{\rm Red}^{\rm [NiL]}$ is observed. The more negative the reduction potential of the initial nickel complex $(E_{\text{Red}}^{[\text{NiL}]})$, the higher is the potential shift in the presence of white phosphorus (ΔE). Although there is a certain scatter of points, we can estimate E_{Red} at $\Delta E = 0$ as a value close, in most cases, to -0.8—-0.9 V. Although this regularity is approximate, it indicates the determining role of white phosphorus as a ligand, because its presence aligns the difference in the redox properties of the initial NiX_2L_n complexes. The preliminary quantum-chemical calculations of the Ni^{II}bpy, Ni⁰bpy, Ni^{II}bpy–P₄, and Ni⁰bpy–P₄ complexes showed¹⁷ that their coordination with white phosphorus decreases the HOMO energy of the complexes and affects, correspondingly, their reduction potentials, which shift to less negative values compared to that of Ni^{II}bpy. The nonpolar P₄ molecule is activated due to coordination, which is also confirmed by the quantum-chemical



Fig. 3. Shifts of the reduction potential of Ni^{II}L upon the addition of white phosphorus $\Delta E = E_{\text{Red}}^{[\text{NiL}-\text{P4}]} - E_{\text{Red}}^{[\text{NiL}]}$ at different reduction potentials of the initial nickel complex $E_{\text{Red}}^{[\text{NiL}]}$: *1*, bpy; *2*, phen; and *3*, PPh₃.

calculations¹⁸: the P—P bond energies change nonuniformly and effective charges appear on the P atoms. It can be assumed that a similar pattern would be observed for several other nickel complexes with σ -donor ligands when P₄ is incorporated into the coordination sphere of the metal. The results of quantum-chemical calculations will be considered in more detail elsewhere.

Complexes Ni(BF₄)₂(triphos) in acetone, $Ni(BF_4)_2(n^2p^2)$ in DMF, and $Ni(BF_4)_2$ phen and $NiX_2(PPh_3)_3$ in MeCN (X = BF₄, Br). The dynamics of slow chemical transformations can be studied by a change in the morphology of cyclic voltammograms of the Ni^{II} complexes in the presence of P₄. When the activation and transformation of P₄ in the coordination sphere of the Ni^{II}L complex occur easily in the absence of electrochemical action, a gradual decrease in the concentration of the initial Ni^{II}L in solution is detected in the CV. This process can be caused by a change in the oxidation state of nickel due to phosphorus oxidation with Ni^{II}, which is accompanied by the appearance of a more cathodic $Ni^{I}C_{3}$ peak (Fig. 4). In the general form, the oxidation of white phosphorus in the coordination sphere of nickel(II) can be presented by Scheme 2.

Scheme 2

$$NiX_2LS + P_4 \implies NiX_2(P_4)L \longrightarrow Ni^+[(P_4)^+]X_2L$$

The products of the reactions of P_4 with Ni^{II}triphos and Ni^{II}(n²p²), which are binuclear Ni^I complexes with the *cyclo*-P₃ ligand (Scheme 3), were isolated in the individual state. Their structures were determined by NMR and ESR spectroscopies, elemental analysis, and cyclic voltammetry.¹²

The cyclic voltammograms of complexes **1** and **2** show reversible reduction corresponding to the Ni^{1}/Ni^{0} redox transition (see Fig. 4, curve 2).

It is of interest that the reduction potential of the nickel(Π) complexes involved in the transformation of the P₄ molecules without electroreduction lies below the potential region in which the straight lines reflecting the



Fig. 4. Schematic cyclic voltammograms of the NiX₂L nickel complex with the σ -donor ligand in the absence (*I*) and presence (*2*) of white phosphorus (1 : 1) after 1–2 h (at different ligands).

Scheme 3



L = triphos (1), n^2p^2 (2)

dependence of ΔE on $E_{\text{Red}}^{[\text{NiL}]}$ converge (see Fig. 3) upon their extrapolation to $\Delta E = 0$. It can be assumed that this potential region is boundary, and at less negative $E_{\text{p}}^{\text{NiL}}$ white phosphorus can be transformed in the coordination sphere of the metal without electricity, *i.e.*, it can spontaneously be oxidized to the *cyclo*-P₃ ligands reducing Ni^{II} to Ni^I.

Thus, the CV method is convenient for (1) the detection of white phosphorus coordination with the nickel(II) complexes by a change in the current and reduction potential of the latter and (2) the study of the inner-sphere interaction between Ni⁰ and a white phosphorus molecule resulting in P₄ transformation with the P—P bond cleavage.

Thus, two routes of white phosphorus activation are possible. The first route is the coordination with metal resulting in the retention of the structure of the P₄ molecule. As a result, the white phosphorus tetrahedron is only deformed without its destruction. Donor-acceptor interactions between the metal and ligands decrease the LUMO energy of the complex and, correspondingly, the reduction potential of Ni^{II}. This case is characteristic of the complexes reducible at high negative potentials $|E_{red}| > ~0.9$ V (L = bpy in DMF, MeCN, and acetone; phen and PPh₃ in DMF and acetone). This complex should be reduced on the electrode to cleave the P–P bonds.

The second route is the oxidation of white phosphorus in the coordination sphere of the Ni^{II} complex. This process occurs when the nickel(II) complex has a sufficiently high oxidizing ability and is rather easily reduced (~0-0.9 V) (X = BF₄, L = triphos in acetone; n^2p^2 in DMF; phen and PPh₃ in MeCN). This route produces a new Ni^I complex, for example, Ni₂triphos₂(P₃)(BF₄)₂.

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