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Transformation of white phosphorus in the coordination sphere of nickel complexes with σ-donating ligands

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Oxidation of white phosphorus in the coordination sphere of the nickel(II) complex with 1,1,1-tris(diphenylphosphinomethyl)ethane and 1,1´,5,5´-bis[methylenedi(*p*-phenylene)]di(3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane) was shown to be possible and accompanied by the transformation of P_4 into the σ-P_3 ligand. The change in the nickel state was monitored by cyclic voltammetry, ^{31}P NMR spectroscopy, ESR, and IR spectroscopy.

Key words: white phosphorus, nickel complexes, 1,1,1-tris(diphenylphosphinomethyl)ethane, cyclic voltammetry.

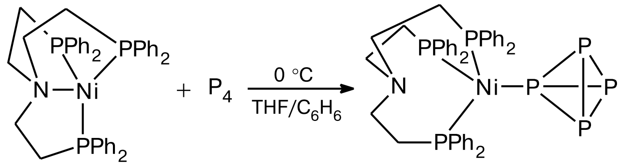
Coordinatively unsaturated organometallic compounds are intermediates in both stoichiometric and catalytic reactions.[1,2] At the first step of catalytic transformation, substrates can act as ligands and thus form a complex with the central metal atom of the metallocomplex. These substrates are, in particular, olefins[3] and white phosphorus.[4] The latter can act as a σ-donating ligand because it contains free unshared electron pairs.

Spectrophotometry and NMR spectroscopy are most widely used for studying such systems. These methods cannot be employed in several cases, for example, when chromophoric or resonant nuclei are absent, the time scale of the spectroscopic method does not coincide with the time scale of the equilibrium reaction, or paramagnetic species present in the system. The broad time scale characteristic of electrochemical methods can be useful for the description of interactions associated with electron transfer processes. In particular, voltammetric methods can provide an information on the dynamics of the systems, which are "frozen" in the time scales of NMR or other spectroscopic methods. In addition, minor amounts of species can be determined and labile organometallic complexes can be studied more reliably using electrochemical methods.

It seems of special interest to study the possibility and mechanism of white phosphorus activation by the nickel complexes, because the latter are catalysts of some reactions of phosphorus functionalization, for example, arylation[5,6] and alkoxylation.[7] It is very important to know the factors determining the routes of transformation of white phosphorus into polyphosphorus cycles. The metal and its ligand environment act as a matrix on which white phosphorus is transformed and the polyphosphorus structures formed are stabilized.

Several stable nickel complexes with polyphosphorus cycles are known.[8—11] White phosphorus is coordinated to Ni^0 in a complex with a ligand of the NP_3 type, retaining its molecular structure[8] (Scheme 1).

Scheme 1



The known η^1-P_4 metal complexes in solutions are mainly characterized using $^{31}P\{^1H\}$ NMR spectroscopy, which is a reliable method for determining the type of coordination of the P_4 molecule.[4] In the coordination sphere of the Ni^{II} complex with 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos), P_4 is transformed, as a rule, into *cyclo*-P_3 to form the $[LNi(P_3)NiL](BF_4)_2$ binuclear three-deck complex (L = triphos),[9,10] whose stabilization is caused by steric hindrances, namely, the presence of three bulky screening PPh_2 groups.

The complex with the P_3 ligand is fairly stable and its structure is confirmed by X-ray diffraction method, although other physicochemical characteristics have been insufficiently studied.[4,9,10]

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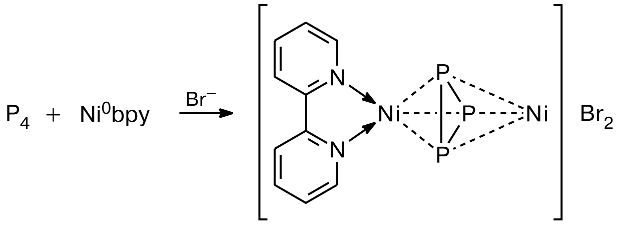
It has recently been shown[6] that P_4 is also transformed into the *cyclo*-P_3 ligand in the coordination sphere of the electrochemically generated Ni^0 complex with bpy (Scheme 2).

Scheme 2



These transformations can conveniently be monitored by ^{31}P NMR spectroscopy, which detects the change in the shift of P_4 (−523 ppm) to the region of polyphosphorus P_3 cycles (−100—−380 ppm), where all atoms are equivalent, or to the region of η^1- or η^2-coordinated P_4 (with nonequivalent P atoms).[4,8—10]

The purpose of the present work is to study possible routes of P_4 transformation and stabilization of polyphosphorus cycles in the coordination sphere of the nickel complexes with the 1,1´,5,5´-bis[methylenedi(*p*-phenylene)]di(3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane) (N_2P_2) or triphos ligand (for comparison) using cyclic voltammetry, NMR, ESR, and elemental analysis.

Experimental

Cyclic voltammograms (CV curves) were detected on a two-coordinate recorder using a PI-50-1 potentiostat and a PR-49 programmer, connecting an electrochemical cell through a three-electrode scheme. The linear sweep rate was 50 mV s^{-1}. A stationary disk glassy-carbon electrode with a working surface area of 3.14 mm^2 served as the working electrode. A Pt wire was used as the auxiliary electrode. The reference electrode was the system Ag/0.01 *M* solution of $AgNO_3$ in MeCN. Measurements were carried out in a cell, whose temperature was maintained at 25 °C, in an argon atmosphere.

ESR signals were detected on an SE/X-2544 X-range electronic spectrometer (Radiopan, Poland) using diphenylpicrylhydrazyl as the external standard (g = 2.0036). IR spectra were recorded on a Vector 22 Bruker instrument. UV spectra were recorded on a Specord UV-VIS instrument with a working interval of 50000—13000 cm^{-1}.

^{31}P NMR spectra were obtained on an MSL-400 high-resolution spectrometer (Bruker, Germany) with a working frequency of 161 MHz using 85% H_3PO_4 as the external standard.

Dimethylformamide was purified by triple fractional distillation over calcined K_2CO_3 and molecular sieves, and MeCN was purified by triple fractional distillation over P_2O_5 with addition of $KMnO_4$. The Et_4NBF_4 salt was doubly recrystallized from EtOH and dried *in vacuo* for 2 days at 100 °C.

The $[NiL]X_2$ complexes (L = triphos; X = Br, BF_4) were obtained from $NiX_2 \cdot 3H_2O$ and the triphos ligand (1 equiv.) in EtOH. The precipitate was filtered off, washed with EtOH, and dried for 24 h at 70 °C *in vacuo*. The N_2P_2 ligand was synthesized according to a known procedure.[12]

Bis[1,1,1-tris(diphenylphosphinomethyl)ethane]phosphiridinedinickel(II) bis(tetrafluoroborate), $[Ni_2P_3(triphos)_2](BF_4)_2$. The complex was synthesized according to a known procedure,[13] m.p. 260 °C, decomp.p. 285 °C. Found (%): C, 60.58; H, 4.23; Ni, 7.41; P, 16.88. $C_{82}H_{78}B_2F_8Ni_2P_9$. Calculated (%): C, 60.26; H, 4.78; Ni, 7.22; P, 17.08. ^{31}P NMR (acetone-d_6), δ: 17 (triphos), −373 (P_3). UV (acetone, $C = 1 \cdot 10^{-4}$ mol L^{-1}), λ_{max}/nm: 443 and 523 s (η^3-P_3 derivatives)[14], 634 m. ESR (powder): g = 2.125 (*cf.* Ref. 13: g = 2.1), ΔH ~500 Oe (isotropic symmetrical signal). IR spectrum (Nujol), ν/cm^{-1}: 1657, 1160, 1117, 998, 932, 835, 695.

1,1´,5,5´-Bis[methylenedi(*p*-phenylene)]di(3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane)phosphiridinedinickel(II) bis(tetrafluoroborate), $[Ni_2P_3(N_2P_2)](BF_4)_2$. Solutions of the ligand, $Ni(BF_4)_2 \cdot 6H_2O$, and white phosphorus (2 : 1 : 1) in DMF were mixed in an argon atmosphere. The resulting cherry-colored solution was concentrated *in vacuo*, and the precipitate was filtered off, washed with ether, and dried *in vacuo*. The yield with respect to the ligand was 85%. ESR (powder): $g_{\|}$ = 2.55, $g_{\perp}$ = 2.00 (anisotropic signal). ^{31}P NMR (DMF-d_7), δ: −52 (N_2P_2), −330 (P_3). IR (Nujol), ν/cm^{-1}: 1657, 1612, 1515, 1377, 1253, 1189, 1146, 985, 866, 795, 744, 700.

1,1´,5,5´-Bis[methylenedi(*p*-phenylene)]di(3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane)phosphiridinedinickel(II) dibromide, $[Ni_2P_3(N_2P_2)]Br_2$. Solutions of the ligand, $NiBr_2 \cdot 6H_2O$, and white phosphorus (2 : 1 : 1) in a THF—acetone (1 : 1) system were mixed and heated for 5 h at 50 °C in an argon atmosphere. The resulting cherry-colored solution was concentrated *in vacuo*, and the precipitate was filtered off, washed with ether, and dried *in vacuo*. The yield with respect to the ligand was 88%. ESR (powder): $g_{\|}$ = 2.55, $g_{\perp}$ = 2.00 (anisotropic signal). ^{31}P NMR (acetone-d_6), δ: −375 (P_3).* IR (Nujol), ν/cm^{-1}: 1657 (P—P), 1612, 1515, 1377, 1253, 1189, 1146, 985, 866, 795, 744, 700. Found (%): C, 53.22; H, 4.60; Br, 12.89; N, 4.78; Ni, 8.46; P, 16.05. $C_{58}H_{56}Br_2N_4Ni_2P_7$. Calculated (%): C, 53.42; H, 4.30; Br, 12.28; N, 4.30; Ni, 9.05; P, 16.65.

Results and Discussion

The CV curves of the nickel complexes with the triphos ligand contain (Figs. 1 and 2) the first reversible reduction peak that by analogy to the reduction of the nickel complexes with PPh_3, bpy, and phenanthroline[14—16] can be ascribed to the $[Ni^{II}L]X_2/Ni^0L$ redox transition (X = BF_4, Br). The reversible redox transitions are observed at the potentials of the first step in MeCN and acetone. When white phosphorus is added (saturated solution in toluene) to a solution of the $[Ni^{II}L]X_2$ complex, the height of the peak at the potentials from −0.2 to

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* The signal of the ligand is broadened.

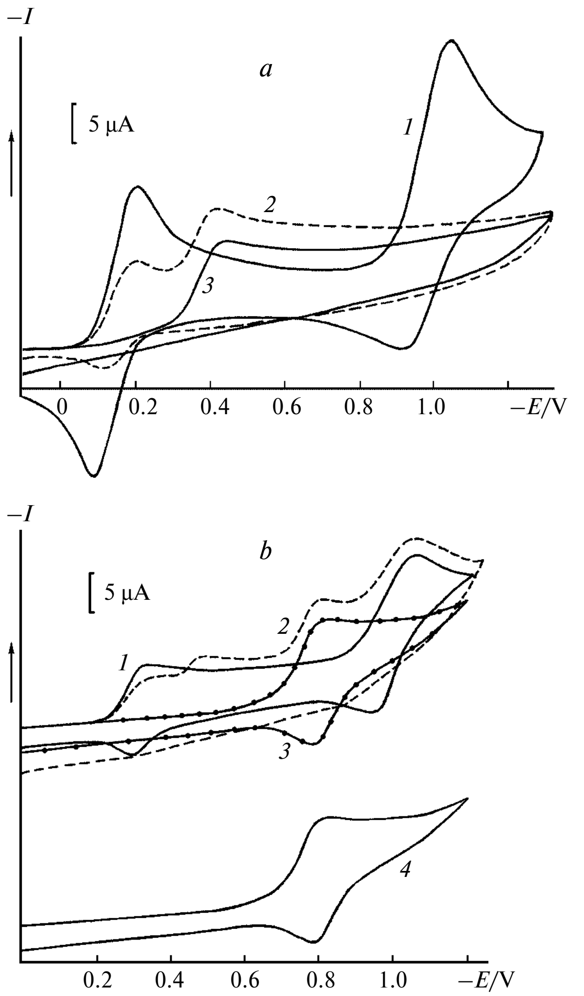


Fig. 1. Cyclic voltammograms of the $Ni(BF_4)_2$triphos ($5\cdot10^{-3}$ mol L^{-1}) (*1*), $Ni(BF_4)_2$triphos + P_4 (1 : 1) (*2*), and $Ni(BF_4)_2$triphos + P_4 (1 : 3) (*3*) systems and the preliminarily synthesized $[Ni_2P_3(triphos)_2](BF_4)_2$ complex ($5\cdot10^{-3}$ mol L^{-1}) (*4*) in MeCN (*a*) and in acetone (*b*).

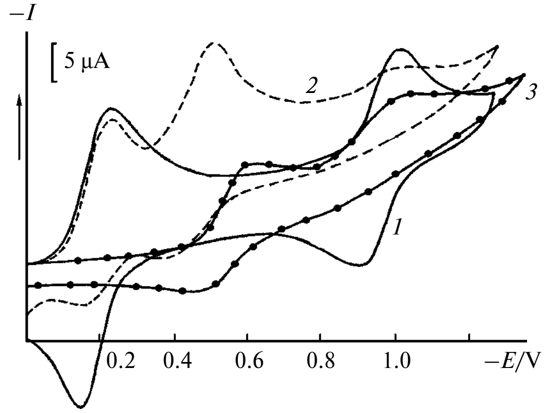
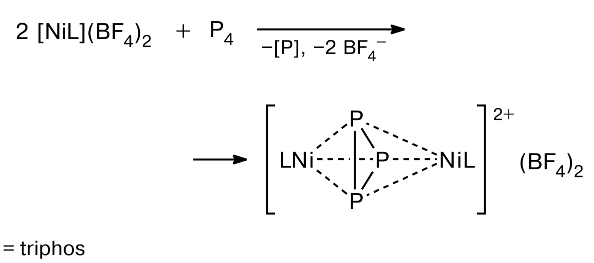


Fig. 2. Cyclic voltammograms of the $NiBr_2$triphos ($5\cdot10^{-3}$ mol L^{-1}) (*1*), $NiBr_2$triphos + P_4 (1 : 1) (*2*) and $NiBr_2$triphos + + P_4 (1 : 3) (*3*) systems in MeCN.

−0.3 V decreases gradually until it disappears, and a new peak appears at more negative potentials (−0.6—−0.8 V) (see Figs. 1 and 2). The qualitative changes observed in the CV curves can be attributed to a change in the oxidation state of nickel due to the interaction of phosphorus with the starting $[Ni^{II}L]X_2$ complex accompanied by the appearance of the more cathodic peak corresponding to Ni^{I} (see Figs. 1 and 2, curves *3*). As known,[9,10] in the coordination sphere of the nickel complex white phosphorus is transformed into the *cyclo*-P_3 ligand (Scheme 3). The CV curve of the preliminarily synthesized $[Ni_2P_3(triphos)_2](BF_4)_2$ complex corresponds qualitatively to curve *3* (see Fig. 1, *b*). It is possible that white phosphorus suffers transformations according to Scheme 3.

Scheme 3



The reversibility of the new peak depends on the nature of the solvent and is most pronounced in acetone, which agrees with the known published data on the higher stability of the *cyclo*-P_3 complexes in this solvent.[17] The ESR spectrum of the solid nickel δ-P_3 complex is characterized by the isotropic symmetrical signal, indicating that the Ni^+(δ-P_3)Ni^+ paramagnetic fragment is symmetrical. The destiny of the fourth P atom was not specially studied. It is likely that a rearrangement occurs according to the stoichiometry 3 $P_4 \rightarrow 4\ P_3$, although the synthesis in a THF—EtOH mixture affords diethyl ethylphosphonate as a by-product.[13]

The CV method makes it possible to monitor the interaction of white phosphorus with the central Ni^{II} ion in the complex resulting in the transformation of P_4 with the P—P bond cleavage and a change in the oxidation state of the metal *in situ*. The method can be used for studying analogous reactions of nickel complexes with other ligands, *e.g.*, with the macrocyclic ligand 1,1′,5,5′-bis[methylenedi(*p*-phenylene)]di(3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane) (N_2P_2, see above).

On mixing the Ni^{II} salt with the N_2P_2 ligand in DMF, several hours until the reversible peak of the complex (at −1.0 V) can be observed due to the retarded complex formation (Fig. 3). On adding white phosphorus to the resulting solution, as in the case of the triphos ligand,

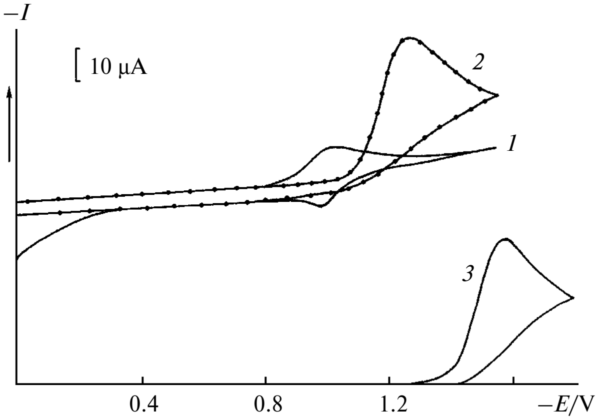


Fig. 3. Cyclic voltammograms of the $NiBr_2$ (10^{-2} mol L^{-1}) + + N_2P_2 ($5\cdot10^{-3}$ mol L^{-1}) (*1*), $NiBr_2$ + N_2P_2 + P_4 ($[P_4] : [N_2P_2] = 1 : 1$, no changes upon the addition of P_4) (*2*) systems and the sample (*3*) preliminarily synthesized by the reaction $Ni(BF_4)_2 + N_2P_2 + P_4$ (10^{-2} mol L^{-1}, 1 : 1 : 1).

the reduction peak of the starting complex disappears and a new peak appears at more negative potentials (−1.25—−1.55 V) (see Fig. 3). The ^{31}P NMR spectrum of the solution shows that white phosphorus (δ −523) is transformed into the δ-P_3 fragment bonded to nickel in which all P atoms are equivalent (characteristic signals at δ −330 and −375 for the $Ni(BF_4)_2$ and $NiBr_2$ complexes, respectively). The ESR spectrum of the powder confirms that the new Ni^I complex is paramagnetic but the molecule with the macrocyclic ligand is asymmetrical. The ESR spectrum in solution cannot be recorded because of signal broadening. Unfortunately, this new complex is insufficiently stable and poorly soluble and is partially decomposed during isolation. However, based on the data of CV and other methods, the transformation of white phosphorus into the *cyclo*-P_3 ligand with a change in the oxidation state of nickel from +2 to +1 might be suggested.

$$Ni^{2+}{}_2L + P_4 \xrightarrow[-[P]]{} Ni^{+}{}_2(P_3)L$$

$L = N_2P_2$

Voltammetry is especially suitable for studying the complexes unstable on isolation, because the process occurred *in situ* can be suggested by analogy to the already proved cases.

Thus, white phosphorus in the coordination sphere of the Ni^{II} complexes with the triphos or N_2P_2 ligands undergoes oxidation accompanied by the transformation of P_4 into the δ-P_3 ligand.

Based on the X-ray diffraction analysis data[12] for the N_2P_2 ligand, we can assume that the P_3 cycle, which is perpendicular to the N_2P_2 plane, can be accomodated inside the macrocycle cavity. In fact, the distance between the P atoms of the opposite diazadiphosphacyclooctane groups is 9.4 Å, the N atoms lie apart at least 10.32 Å along the diagonal of the cavity, and the distance between the ultimate P atoms in the P—Ni—P_3—Ni—P chain should not exceed 9.2 Å.[9,10] Exocyclic coordination can be assumed that favors polymeric forms of the product in which the macrocycle stabilizes the nickel—P_3—nickel fragment at the external rim of the macrocycle. However, non-macrocyclic ligands of the diazadiphosphaoctane type, which can be visualized on imaginary halving the macrocycle along the methylene bridge, are inefficient in the reactions studied. Therefore, white phosphorus undergoes no changes in the presence of the nickel(II) complexes with such ligands, confirming the suppositions made for the product structure.

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