Reactions of activated organonickel σ-complexes with elemental (white) phosphorus*

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The reactivity of organonickel σ -complexes of the type [NiBr(Ar)(bpy)] (Ar is 2,4,6-trimethylphenyl (Mes) or 2,4,6-triisopropylphenyl (Tipp); byp is 2,2'-bipyridine) toward elemental (white) phosphorus was studied. For the reaction to occur, the complexes must be activated by removal of the bromide anion from the coordination sphere of nickel. This can be achieved either in the presence of halogen scavengers or by electrochemical reduction. The arylphosphinic acids ArP(O)(OH)H formed by hydrolysis of organic nickel phosphides are the major reaction products of the overall process.

Key words: arylphosphinic acids, white phosphorus, organonickel σ -complexes, organic phosphides, electrochemical activation.

Organometallic σ -complexes (*i.e.*, compounds containing a metal—carbon σ -bond) are key intermediates in various catalytic processes involving organic and organoelement compounds.^{1–5} Compounds of this class are also formed in electrocatalytic reactions of organic halides with complexes of transition metals such as nickel, palladium, and some⁶⁻⁹ other Period IV metals. At this point, however, the world scientific literature provides limited data on the properties and reactivities of organonickel σ-complexes formed in homo- and cross-coupling of organic halides, chlorophosphines, and white phosphorus. Moreover, while the basics of the electrochemical phosphorylation of organic halides with white phosphorus under electrocatalytic conditions in the presence of nickel complexes have been already developed, the mechanism of activation and transformation of the P_4 tetrahedron as well as the mechanism of P–C bond formation remain poorly understood. It should be noted that known techniques for the synthesis of organophosphorus compounds from elemental (white) phosphorus are based on power-consuming and environmentally unsafe "chlorine" procedures involving the formation of phosphorus acid chlorides and large amounts of toxic compounds (HCl, POCl₃, PCl₅, etc.).^{10,11} The use of transition metal complexes^{12,13} and electrochemical methods^{14,15} offers an alternative to the existing routes to organophosphorus compounds.

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The goal of the present work was to study the reactivity of organonickel σ -complexes formed in electrocatalytic dehalogenation of organic halides in the presence of nickel complexes with 2,2'-bipyridine toward elemental (white) phosphorus.

Results and Discussion

We employed the organonickel σ -complexes [NiBr(Ar)(bpy)]¹⁶⁻¹⁸ (Ar is 2,4,6-trimethylphenyl (Mes) (1) and 2,4,6-triisopropylphenyl (Tipp) (2); bpy is 2,2´-bi-pyridine) as model compounds in reactions with white phosphorus (Scheme 1). Note that the use of organonickel σ -complexes containing an unsubstituted phenyl group is not possible due to they low stability.

Direct reactions of organonickel complexes 1 and 2 with white phosphorus were carried out by mixing a solution of either complex with a solution of white phosphorus in different solvents (DMF, benzene, toluene, and THF). However, we found that organonickel σ -complexes are absolutely inert to the P₄ molecule. No reaction occurred when the resulting mixtures were stirred at room temperature or at 60 °C. A ³¹P NMR study of the mixtures revealed that a white phosphorus molecule cannot coordinate to the metal center or displace the ligands from organonickel σ -complexes 1 and 2. Moreover, no products resulting from the coordination or transformation of the P₄ molecule were detected (³¹P NMR data).

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The aforesaid behavior of organonickel σ -complexes can be associated with the absence of vacant coordination site at the Ni atom for the P₄ molecule to be coordinated (this usually occurs in the coordination spheres of metal complexes^{19–21}).

To obtain coordinatively unsaturated organonickel σ -complexes, we removed the bromide anion from the coordination sphere in a reaction with thallium hexa-fluorophosphate. It should be noted that the use of silver salts as halogen scavengers is not possible under the chosen conditions because Ag⁺ ions react with DMF and white phosphorus to give various polyphosphorus oligomers.

When solid TlPF₆ is added to a solution of white phosphorus and nickel complex 1, the originally red (due to [NiBr(Mes)(bpy)]) reaction mixture turns orange-yellow. This color is characteristic of oligophosphorus intermediates formed by transformations of the coordinated P_4 molecule (complex 3) in the coordination sphere of nickel (Scheme 2).



The reaction mixture contains only residual amounts of white phosphorus (³¹P NMR, δ 525.8). Upon 24-h stirring, the reaction mixture turns black and, in agreement with published data²² on activation of nickel bromide complexes, a large amount of TlBr is formed as a colorless crystalline precipitate (the bromide anions are bound to the thallium cations). The ³¹P NMR spectrum of a super-

natant sample shows a weak signal at $\delta - 87.9$ (d, ${}^{1}J_{PH} =$ 233 Hz) corresponding to the secondary phosphine Mes₂PH. This suggests that white phosphorus tetrahedron undergoes opening to form a P–C bond. Note that the primary phosphine MesPH₂, which is also formed, has the stronger ability to coordinate with transition metals because of its less pronounced (compared to Mes₂PH) steric effects and is completely bound in nickel phosphide complexes, so free MesPH₂ is not detected in the ³¹P NMR spectrum.

Stirring of the reaction mixture with a small amount of degassed water for 6 h does not make changes in the ³¹P NMR spectrum. Addition of a small amount of concentrated HCl (37% w/w) was also not effective. However, paramagnetic nickel(II) can be detected in the solution after five days, which is reflected in the morphology of the ³¹P NMR spectrum. As a result, the sixth-day spectrum contains two very broad signals at δ 6.2 and 22.9. Subsequent concentration of the reaction mixture and extraction of organophosphorus products with toluene gave mesitylphosphinic acid (MesP(O)(OH)H) as a major reaction product in moderate yield (32%).

It should be noted that the precipitate containing insoluble nickel complexes can be dissolved by addition of concentrated HNO_3 . This procedure allows recovering the major part of nickel involved in the reaction.

A similar reaction procedure with complex 2 gave 2,4,6-triisopropylphenylphosphinic acid (TippP(O)(OH)H), though in a lower yield (24%). The secondary phosphine Tipp₂PH was not detected in the reaction mixture. Apparently, its formation is limited by steric hindrances, which make it difficult to attach a second sterically hindered aromatic fragment to the phosphorus atom during the opening of the P₄ tetrahedron.

To obtain reactive species from organonickel σ -complexes without using toxic thallium salts as halogen scavengers, we applied electrochemical activation. Klein *et al.*²³ have demonstrated, with the organonickel σ -complex [NiBr(Mes)(bpy)] as an example, that transfer of an electron to the complex molecule is accompanied by elimination of the bromide anion from the coordination sphere of nickel, thus producing coordinatively unsaturated neutral complex radical **4** (Scheme 3).





The sign " \Box " stands for a vacant coordination site.

Complex	Reduction peaks			Reoxidation peaks		
	Peak	-E/V	Ι/μΑ	Peak	-E/V	<i>Ι</i> /μΑ
[NiBr(Mes)(bpy)] (1)	C ₁	1.80	4.8	A ₁	1.64	1.2
	C_2^1	2.15	4.7	A_2	2.05	4.6
	$\tilde{C_3}$	2.62	0.4	A_3^2	2.50	0.4
[NiBr(Tipp)(bpy)] (2)	C_1	1.75	5.9	A_1	1.54	0.6
	$\dot{C_2}$	2.03	2.0	A_2	1.97	4.2
	$\tilde{C_3}$	2.33	1.3	A_3^2	2.20	1.0

Table 1. Peak potentials* and currents on the cyclic voltammograms of organonickel σ -complexes 1 and 2 at glassy carbon electrode (cathodic potential scan)

* The CV curves were recorded without *IR*-compensation; the potentials are given versus the reference electrode Ag/AgNO₃, 0.01 *M* in MeCN ($E^{\circ}(Fc/Fc^{+}) = 0.20$ V).

Following this approach, we tried to activate organonickel σ -complexes **1** and **2** for the preparation of organometallic species that would be reactive toward a white phosphorus molecule. We found that electron transfer to the molecules of organonickel complexes **1** and **2** produces reactive species capable of transforming a white phosphorus molecule into organic nickel phosphides. Note that the organonickel σ -complexes can be activated *in situ* in the presence of white phosphorus because the first cathodic reduction potentials C₁ of the organonickel σ -complexes (Table 1) are less negative than the electrochemical reduction of P₄ molecule (E = -2.25 V (*vs.* Ag/AgNO₃, 0.01 *M* in MeCN).^{15,16}

Electrochemical activation of organonickel σ-complexes 1 and 2 was carried out in a divided electrochemical cell in DMF in the presence of 0.1 M Bu₄NBF₄ as a supporting electrolyte. After an electricity quantity of 1 F (1 e per Ni atom) was passed through the working solution, its originally red color turned black. This was accompanied by the formation of black precipitate of organic nickel phosphides. The ³¹P NMR spectrum of the supernatant is featureless, thus suggesting that the consumed phosphorus and derived phosphorus-containing products are bound in organic phosphides. After vigorous stirring of the reaction mixture for 6 h, its ³¹P NMR spectrum shows a signal at $\delta - 87.5$ (d, ${}^{1}J_{PH} = 233$ Hz) for the secondary phosphine Mes₂PH. The ³¹P NMR spectrum of the reaction mixture obtained from organonickel complex 2 under the same electrochemical conditions bears no evidence for the presence of a secondary phosphine. This nicely fits the data we obtained with $TlPF_6$ as a halogen scavenger.

Acid hydrolysis and concentration of the resulting reaction mixtures followed by extraction of the electrolysis products with toluene gave mesitylphosphinic and 2,4,6-triisopropylphenylphosphinic acids in moderate yields (53 and 42%, respectively). This confirms that the P–C bond formation under electrochemical conditions involves the reactions of the activated organonickel σ -complexes with white phosphorus (Scheme 4).





Ar = Mes, Tipp

Interestingly, when the organonickel σ -complexes are activated in the absence of white phosphorus, coordinatively unsaturated intermediate organonickel σ -complexes dimerize to give di- and polynuclear organometallic compounds and clusters. Our investigations of their structures are in progress.

To sum up, we experimentally proved that the reactions of coordinatively unsaturated organonickel σ -complexes with white phosphorus yield organophosphorus compounds, *viz.*, the arylphosphinic acids ArP(O)(OH)H, which can be widely used in magnetochemistry as efficient exchange channels²⁴ for novel electronic devices based on molecular magnetics.

Experimental

All experiments were carried out under dry nitrogen using standard Schlenk equipment. Solvents were purified by distillation prior to use. Dimethylformamide was purified by threefold vacuum distillation with intervening desiccation over calcined K_2CO_3 and molecular sieves. White phosphorus was treated with a solution of $K_2Cr_2O_7$ in conc. H_2SO_4 and recrystallized from DMF; then phosphorus was melted (50 °C), rolled into beads while stirring it with a magnetic bar, and cooled. The complexes [NiBr(Mes)(bpy)] and [NiBr(Tipp)(bpy)] were prepared as described earlier.^{16,17} The salt Bu_4NBF_4 (Acros Organics) used as a supporting electrolyte and TIPF₆ (Alfa Aesar) were used as purchased.

For CV measurements, a stationary glassy carbon disk electrode (active surface area 3.14 mm²) was used as a working electrode. Cyclic voltammograms were recorded on an Epsilon Electrochemical Workstation analytical unit (BASi, USA) in a temperature-controlled (20 °C) three-electrode cell (linear scan rate 50 mV s⁻¹) in DMF with 0.1 *M* Bu₄NBF₄ as a supporting electrolyte. The system Ag/AgNO₃, 0.01 *M* in MeCN ($E^{\circ}(Fc/Fc^+) = 0.20$ V) served as a reference electrode. A platinum wire 1 mm in diameter was used as an auxiliary electrode. The concentration of the substrate was 5 · 10⁻³ mol L⁻¹.

Preparative electrolyses were carried out under potentiostatic conditions using a B5-71/1 U dc power supply. The potential of the working electrode (cathode) was measured with a Shch50-1 dc voltmeter versus the reference electrode Ag/AgNO₃, 0.01 *M* in MeCN ($E^{\circ}(Fc/Fc^+) = 0.20$ V). The working surface of the cathode (glassy carbon, Pt) was 32 cm². After the electrolysis was completed, the resulting solution was concentrated and organophosphorus products were extracted with toluene and dried *in vacuo* at room temperature for 3 h.

³¹P NMR spectra were recorded on a high-resolution Avance 400 spectrometer (Bruker, 161.9 MHz) in DMF at room temperature. IR spectra (KBr pellets) were recorded on a Vector-22 spectrometer (Bruker) in the 4000–400 cm⁻¹ range (resolution 4 cm⁻¹). A GC-MS study (EI, 70 eV, ion source temperature 290 °C) was carried out on a DFS Thermo Electron Corporation instrument (Germany). The GC facilities included an ID-BP5X capillary column (50 m × 0.32 mm × 0.25 µm; an analog of DB-5MS) and helium as a carrier gas. The data obtained were processed with the Xcalibur program. Test samples (the starting compounds) were infused into the instrument as solutions (~10⁻³ g µL⁻¹) in HPLC-grade acetonitrile.

Reactions of the complexes [NiBr(Ar)(bpy)] with white phosphorus in the presence of TIPF₆ (general procedure). Thallium hexafluorophosphate (0.349 g, 1.0 mmol) was added to a vigorously stirred solution of an organonickel σ -complex (1.0 mmol, 0.414 (1) or 0.498 g (2)) and white phosphorus (0.124 g) in DMF (40 mL). The originally red (due to the starting organonickel complex) reaction mixture turned orange-yellow. This was accompanied by the formation of white precipitate of TlBr. The resulting suspension was treated with 2 M HCl (10 mL), and the reaction mixture was stirred at room temperature for 120 h. The precipitate was filtered off, the filtrate was concentrated. and organophosphorus products were extracted with toluene (3×50 mL) and recrystallized. The yields of mesitylphosphinic (MesP(O)(OH)H) and 2,4,6-triisopropylphenylphosphinic acids (TippP(O)(OH)H) were 0.059 (32%) and 0.064 g (24%), respectively. Their physicochemical characteristics are in full agreement with the literature data.24,25

Electrochemical reactions of the complexes [NiBr(Ar)(bpy)] with white phosphorus (general procedure). A working solution for electrolysis was prepared by dissolving an organonickel σ -complex (1.0 mmol, 0.414 (1) or 0.498 g (2)), white phosphorus (0.124 g, 1.0 mmol), and Bu₄NBF₄ (0.987 g, 3.0 mmol) in DMF (30 mL). The resulting solution was placed in the cathodic compartment of a divided cell. The anodic compartment was charged with a 0.1 *M* solution (10 mL) of Bu₄NBF₄ in DMF. Then a constant voltage was applied to this system, and an electric current (I = 26.8 mA, electrolysis time 1 h) was passed at the working electrode potential varying from -1.6 to -1.8 V (*vs.* Ag/AgNO₃, 0.01 *M* in MeCN). After the electrolysis was completed, the resulting suspension was treated with 2 *M* HCl (10 mL) and the reaction mixture was stirred at room temperature for 120 h and concentrated. The organophosphorus products were extracted with toluene (3×50 mL) and recrystallized. The yields of mesitylphosphinic (MesP(O)(OH)H) and 2,4,6-triisopropylphenylphosphinic acids (TippP(O)(OH)H) were 0.098 (53%) and 0.112 g (42%). Their physicochemical characteristics are in full agreement with the literature data.^{24,25}

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