Electrochemical C—H phosphorylation of 2-phenylpyridine in the presence of palladium salts

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A new approach was developed to the introduction of the phosphonate group into arylpyridines using 2-phenylpyridine as an example. The approach is the electrochemical oxidation of a mixture of 2-phenylpyridine, diethyl phosphite, and palladium acetate at room temperature. An intermediate dipalladium cyclic complex was isolated that is formed by the *ortho*-palladation of 2-phenylpyridine and substitution of acetate ions by phosphonate ions. The preparative oxidation of this complex selectively results in the product of the phosphorylation of the C—H bond in 2-phenylpyridine.

Key words: C—H phosphorylation, H-phosphonate, electrooxidation, 2-phenylpyridine, palladium complexes.

Direct functionalization of compounds containing C—H bonds provides the most efficient route of transformation of molecules, which attracts vast attention to the problem.[1] Although a wide set of such reactions, including those catalyzed by transition metals, was accomplished to the present time, examples of C—P bond formation are very restricted, most likely, due to the strong coordinating influence of phosphorus reagents.[2] Chemical and electrochemical methods of hydrogen atom substitution by phosphorus-containing nucleophiles are few. Successful examples are mainly described only for the functionalization of nitroaromatic substrates.[3] The routes for C—P bond formation remain to be an urgent field of studies. Special attention is given to the synthesis of phosphonic acid derivatives, since the phosphonate group is in the composition of many natural molecules variable in structure and involved in biological processes. Many potential drugs, which exhibit anticancer or antibacterial properties or act as anti-AIDS agents, also contain phosphonic acid fragments. There are numerous methods in synthetic chemistry for introducing phosphorus groups into various structures, and enantioselective results were obtained in some cases. However, the first catalytic methods that are especially important due to requirements of green chemistry have been developed quite recently, and there are only few successful examples.[4,5]

One of the most difficult problems of performing C—H substitution, including that with participation of P-nucleophiles, is the necessary presence of an oxidant. Each pair of substrates needs preliminary experiments with allowance for the ability of reactants to oxidation, first of all, of nucleophile, which necessarily affects the result of the reaction. For the σ^H-adduct and other intermediates it is very difficult (and sometimes impossible) to estimate the oxidation potential as a measure of the ability of the substance to donate electrons. Therefore, one has to select the oxidant guiding by experience, intuition, and some empirical rules that make it possible to judge only tentatively about the efficiency of the oxidant.

Another problem is that the used cooxidants are expensive (for example, salts of metals of the platinum and silver groups) and organic oxidants with a high molecular weight are hardly separable from the reaction mixture. In addition, all of them are often insufficiently selective.[1f,6,7]

Several different strategies are applied for the solution of the problem of selective C—H functionalization. The most popular strategies assume the use of substrates containing coordinating ligands. These ligands (often named "directing groups") are bound to the metal center and selectively direct the catalyst to the nearest C—H bond. Many transition metals, including Pd, enter into ligand-directed reactions of C—H bond activation (also known as cyclometallation reactions).

The successful examples of the phosphorylation of the C—H bond of the aromatic substrate with the directing pyridyl or other heterocyclic group to the *ortho*-palladation reaction have recently been described.[4,5] The method used[4] makes it possible to obtain the product of phosphorylation of 2-phenylpyridine bearing the $(EtO)_2P(O)$ group in 66% yield (Scheme 1) and with the $(Pr^iO)_2P(O)$ group in 78% yield.

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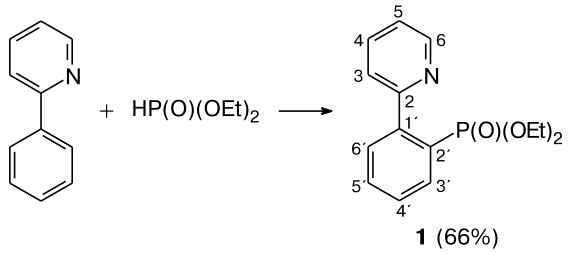
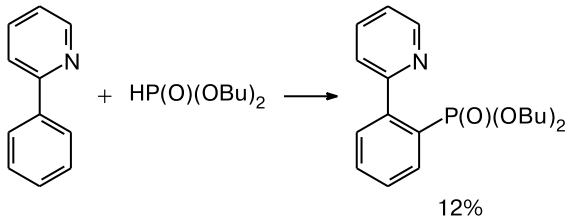
Scheme 1



Reagents and conditions: *tert*-$C_5H_{11}OH$, 120 °C, 13 h. Catalyst $Pd(OAc)_2$ (10 mol.%), base NaOAc (2 equiv.), oxidant AgOAc, benzoquinone for the facilitation of the reductive elimination stage.

The method described[5] is performed under similar conditions (Scheme 2).

Scheme 2



Reagents and conditions: Bu^{t}OH, 120 °C, 48 h. Catalyst $Pd(OAc)_2$ (10 mol.%), base K_2HPO_4 (4.5 equiv.), oxidant AgOAc (2.5 equiv.), 1-methyl-1*H*-pyrrole-2,5-dione (40 mol.%) for the facilitation of the reductive elimination stage.

In this case, the *ortho*-C—H bond in 2-phenylpyridine was subjected to phosphorylation by dibutyl phosphite with the yield of the product only 12%. The best results were achieved[5] when dialkyl phosphite was replaced by the specially prepared α-hydroxyalkyl phosphonate. In this work, we used commercially accessible dialkyl phosphites as phosphorylating agents.

In spite of obvious success of aromatic substrates in C—H phosphorylation,[4,5] many factors (high temperatures, excess of expensive silver-containing oxidant AgOAc and additional agents for the facilitation of the reductive elimination stage, not always satisfactory yields and reaction time) indicate that the search for new simpler and more efficient solutions is important and promising.

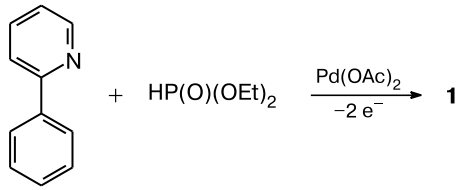
The advantages of electrochemical metal complex catalysis are (1) the possibility of controlled synthesis of active forms of catalysts, *i.e.*, metal complexes with different oxidation states, (2) mild reaction conditions, and (3) the possibility to carry out the reaction in an almost closed system using a minimum amount of the reusable catalyst. It is known that electrochemical processes are ecologically safe and their control can easily be automated.[8]

We have previously shown[9] the possibility of electrochemical C—H acetoxylation and perfluoroalkylation under mild conditions. The purpose of this study is to establish the possibility of the C—H phosphorylation of 2-phenylpyridine under the conditions of electrochemical oxidation involving $Pd(OAc)_2$ and diethyl phosphite as an accessible phosphorus precursor. The application of the electrochemical method would make it possible to carry out the reaction without a specially added oxidant at a controlled potential under milder conditions and to study individual stages of the reaction.

Results and Discussion

The electrochemical oxidation of a mixture of 2-phenylpyridine, diethylphosphorous acid (phosphorous acid diethyl ester) (ratio 1.0 : 1.1), and $Pd(OAc)_2$ (10 mol.%) in a divided electrolyzer gives not only phosphorylated 2-phenylpyridine **1** (Scheme 3) but also a series of other products.

Scheme 3



According to the ^{31}P NMR spectrum of the reaction mixture, the electrolysis affords the dipalladium complex containing phosphonate ligands with δ_P 96.1, phosphorylated 2-phenylpyridine with δ_P 18.1, and probably phosphonium salts (δ_P 27.2) and phosphorous acids. To optimize the electrosynthesis, we carried out experiments under different conditions in the presence of bases and some additives favoring the occurrence of the reductive elimination stage (1-methyl-1*H*-pyrrole-2,5-dione (NMMI), benzoquinone (BQ), bipyridine (bpy)). In the course of the synthesis, diethylphosphorous acid was permanently added dropwise. The results of experiments are presented in Table 1.

It is seen that the target product of C—H phosphorylation **1** is formed under the electrochemical oxidation conditions in satisfactory (in the case of entry *6*, fairly good) yield at both room temperature and 70 °C even in the absence of additives (NMMI or BQ). The best result (see Table 1) was obtained when the electrolysis was carried out in the presence of sodium acetate as a base and benzoquinone facilitating the reductive elimination stage.

In order to establish the mechanism of the process, we synthesized intermediate six-membered binuclear palladium complex **3** similar to $[(PhPy)Pd(BuO)_2P(O)]_2$ de-

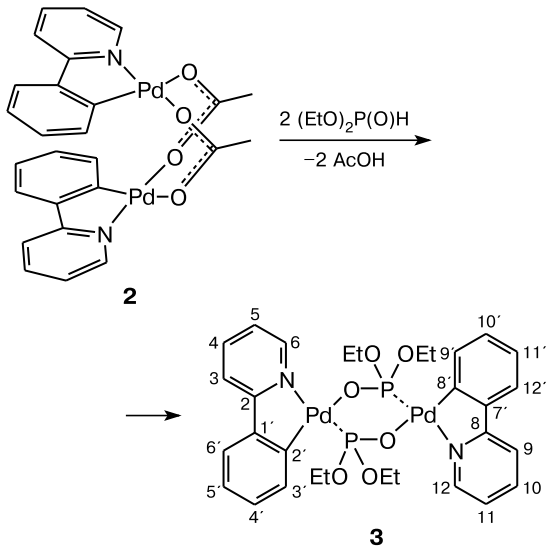
Table 1. Optimization of the electrochemical C—H phosphorylation of 2-phenylpyridine in the presence of 10 mol.% palladium acetate

Entry	Base	Additional reagents	Electrolysis conditions	Yield of product **1** (%)
1	Na_2HPO_4 (excess)	—	MeCN, 20 °C	20
2	$(EtO)_2PONa$ acid/salt = 1 : 2	Maleic anhydride (2 equiv.) and BQ (2 equiv.)	MeCN, 20 °C. Additional reagents were added after electrolysis, 6 h, 80 °C	35
3	$(EtO)_2PONa$ acid/salt = 1 : 1, Na_2HPO_4	BQ	MeCN, 70 °C	43
4	Na_2HPO_4 (excess)	NMMI (40%)	MeCN, 70 °C	42
5	$(EtO)_2PONa$ acid/salt = 1 : 1	—	Amyl alcohol, 80 °C, 4.5 h	15
6	NaOAc (2 equiv.)	BQ (2 equiv.)	MeCN, 20 °C After electrolysis the mixture was heated at 80 °C for 1 h	68
*7**	Lutidine (2 equiv.)	bpy (1 equiv.)	MeCN, 20 °C, $Q = 3$ Φ	52
8	Lutidine (2 equiv.)	bpy (1 equiv.)	MeCN, 20 °C	48

* The equimolar amount of palladium acetate was used.

scribed earlier.[5] For this purpose, we performed the reaction of the acetate dimer of phenylpyridylpalladium **2**, which was obtained using a described procedure,[10] with diethyl phosphite (1 : 2) in acetonitrile (Scheme 4).

Scheme 4

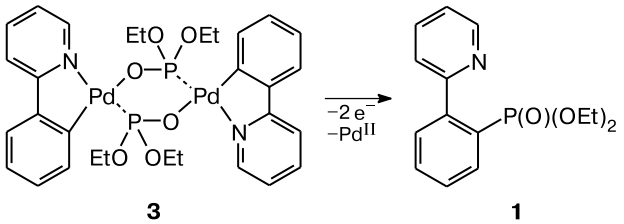


The reaction occurs readily at 20 °C. Complex **3** in 90% yield precipitates from the reaction mixture in 24 h. Earlier,[5] when synthesizing the palladium dibutyl phosphonate complex $[(PhPy)Pd(BuO)_2P(O)]_2$ from α-hydroxybutyl phosphonate and $[(PhPy)Pd(OAc)]_2$, the mixture was heated in dioxane at 120 °C in the presence of 2.2 equiv. K_2HPO_4. Evidently, the ligand exchange is much easy when diethyl phosphite is used.

The binuclear structure was ascribed to complex **3** by analogy to the previously[5] studied relative compound $[(PhPy)Pd(BuO)_2P(O)]_2$.

Then, complex **3** was oxidized at the Pt electrode in MeCN at 20 °C under argon at the potential of the first oxidation peak with the complete conversion to the single product of *ortho*-phosphorylation of 2-phenylpyridine (compound **1**) (Scheme 5) in an almost quantitative yield (the ^{31}P NMR spectrum of the reaction mixture contains the single signal with δ_P 18).

Scheme 5



The electrochemical characteristics of complex **3** were studied by cyclic voltammetry. The cyclic voltammogram of complex **3** (Fig. 1) exhibits two peaks of irreversible oxidation, and their potentials are in a more positive region compared to the potentials of complex **2** ($[(PhPy)Pd(OAc)]_2$).

The electrochemical behavior of complex **2** has been studied previously.[9b] It was shown that complex **2** is oxi-

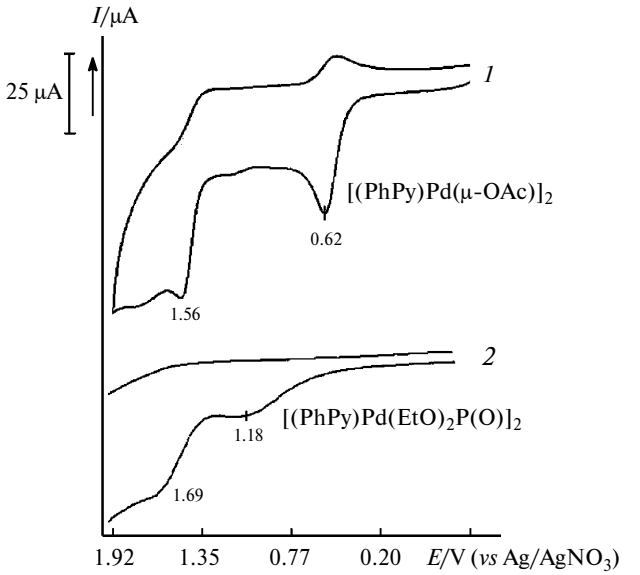


Fig. 1. Cyclic votammograms of 0.005 *M* solutions of complexes $[(PhPy)Pd(\mu\text{-}OAc)]_2$ (**2**) (curve *1*) and $[(PhPy)Pd(EtO)_2P(O)]_2$ (**3**) (curve *2*) in MeCN. The concentration of the complexes is $5 \cdot 10^{-3}$ mol L^{-1}, and the potential sweep is 100 mV s^{-1}.

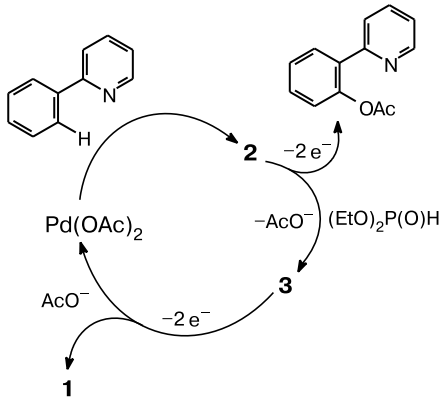
dized in two stages with the transfer of two electrons at each stage. The first peak characterizes the reversible oxidation and is due to the metal-centered electron transfer and conversion $Pd^{II} \rightarrow Pd^{III}$. Two electrons are also transferred at the second stage, but the oxidation $Pd^{III} \rightarrow Pd^{IV}$ is irreversible. The formation of intermediate Pd^{III} was earlier detected in the oxidation of compound **2**, whereas no paramagnetic intermediates were observed in the case of complex **3**. However, two oxidation stages (two peaks but at more positive potentials) are also observed for this complex.

Thus, the substitution of hydrogen in the *ortho*-position of 2-phenylpyridine by the phosphonate group proceeds selectively under the electrochemical oxidation conditions and does not require additional reagents (NMMI, BQ, PPh_3, *etc.*) promoting the reductive elimination stage, which are always present in all earlier published works.[4,5] It can be assumed that in the chemical variant of C—H phosphorylation the role of AgOAc as an oxidant was not only to participate in the regeneration of the palladium catalyst by the oxidation of presumably formed Pd^0 to Pd^{II}, as it is suggested by the authors.[4,5] Perhaps, Ag^+ can act as an oxidant of the intermediately formed phosphorus-containing diphenylpyridinepalladium complex $[(PhPy)Pd(BuO)_2P(O)]_2$ affording the target product $PhPy(BuO)_2P(O)$.

We reproduced the reductive eliminations stage[5] by heating complex **3** in MeCN (at the temperature of the bath 120 °C) in the presence of 2 equiv. NMMI for 4 h. However, only half an initial complex decomposed to the product of *ortho*-phosphorylation of 2-phenylpyridine **1**. Thus, the electrochemical oxidation favors the reductive elimination of intermediate **3** to occur much more efficiently.

According to the oxidation potentials of the key intermediates complexes $[(PhPy)Pd(\mu\text{-}OAc)]_2$ **2** and $[(PhPy)Pd(EtO)_2P(O)]_2$ **3**, phosphorus complex **3** is more difficultly oxidized than acetate complex **2**. A comparison of the chemical (AgOAc as an oxidant (see Refs 4 and 5)) and electrochemical oxidations shows that the acetate complex would be oxidized first. The latter undesirable reaction results in the *ortho*-acetoxylation of 2-phenylpyridine.[9b] To obtain target product **1** in good yield, it is necessary to provide conditions for the predominant oxidation of the phosphorus complex, *i.e.*, to perform electrolysis at the oxidation potential of complex **3**. The presumable scheme of the electrochemical C—H phosphorylation of 2-phenylpyridine can be presented as Scheme 6.

Scheme 6



Electrolysis at the oxidation potential of phosphorus complex **3** favors the catalytic process and increases the yield. The addition of other substances (BQ, NMMI, PPh_3), which facilitate, as a rule, reductive elimination, can probably shift the oxidation potentials of complexes **2** and **3** to different extents, which increases the yield of the target product. As can be seen from Table 1, the best result was achieved upon the addition of benzoquinone.

Thus, the new approach was developed to the introduction of the phosphonate group into arylpyridines using 2-phenylpyridine as an example. The approach is based on the electrochemical oxidation of a mixture of 2-phenylpyridine and diethyl phosphite at room temperature in the presence of palladium acetate. The intermediate six-membered binuclear palladium cycle linked to the phosphonate ligand through the oxygen and phosphorus atoms $[(PhPy)Pd(EtO)_2P(O)]_2$ (**3**) was isolated, and its redox properties were determined. The preparative oxidation of complex **3** selectively gives the target product of C—H bond phosphorylation in quantitative yield.

When considering the mechanism of C—H phosphorylation, one should take into account the dual role of the metal salt (in particular, AgOAg) introduced into the reaction mixture as a regenerator of the active form of the catalyst and an oxidant of the key intermediate of the reactions.

Experimental

Acetonitrile was distilled over P_2O_5 and $KMnO_4$ and then over molecular sieves. Benzene was distilled over sodium. After purification, the solvents were kept under dry argon. Supporting salt Et_4NBF_4 was recrystallized from ethanol and dried in a vacuum desiccator at 100 °C for 48 h. Diethylphosphorous acid was obtained by an earlier described procedure.[11] The palladium complexes were synthesized according to known procedures.[12,13] 2-Phenylpyridine (Acros) was used. All syntheses were carried out under dry argon.

Preparative electrolysis was carried out using a B5-49 constant current source in a 40-mL three-electrode cell with divided anodic and cathodic spaces in the presence of Et_4NBF_4 as a supporting electrolyte. The potential of the working electrode was measured with a V7-27 constant current voltmeter relative to the reference electrode Ag/0.01 *M* $AgNO_3$ in acetonitrile. The working surface of the platinum cylindrical cathode used as a working electrode was 20.0 cm^2. A ceramic plate with a pore size of 900 nm served as a membrane. The anode was a platinum wire, and the catholyte was a saturated solution of $PyHBF_4$ in MeCN. The electrolyte was magnetically stirred at a permanent argon flow passing through the drying system.

NMR spectra were recorded on Bruker AVANCE-400 multinuclear spectrometers (400.1 (^{1}H) and 162.0 MHz (^{31}P)). The ^{1}H chemical shifts were detected relative to the signal of the deuterated solvent used as an internal standard, and the ^{31}P shifts were measured relative to the signal of phosphoric acid as an external standard.

Cyclic voltammograms were detected on a BASi Epsilon potentiostat at a linear potential sweep of 100 mV s^{-1}. The glassy carbon stationary disc electrode with the working surface area 8 mm^2 was used as a working electrode. The Ag/0.01 *M* $AgNO_3$ system in MeCN served as reference electrode, and an auxiliary electrode was a platinum wire with a diameter of 1 mm and a length of 10 mm. The measurements were performed in a temperature-controlled (25 °C) cell in argon. The cyclic voltammograms of the complexes were detected in MeCN at a concentration of the substrate of $5 \cdot 10^{-3}$ mol L^{-1} in a 0.01 *M* solution of Bu_4NBF_4.

General procedure of electrolysis. The electrochemical cell was loaded with palladium acetate (0.7 mmol, 0.16 g), 2-phenylpyridine (7 mmol, 1.104 g), and the corresponding base in acetonitrile (30 mL). Electricity (2 *F*) was passed through the electrolyte based on 1 mole of the initial 2-phenylpyridine (375.5 mA h^{-1}). Electrolysis was carried out at the potential E_p = 1.2 V. Diethylphosphorous acid (7 mmol, 0.983 g) in acetonitrile (5 mL) was added dropwise in the course of the synthesis. After the end of electrolysis, the reaction mixture was evaporated on a rotary evaporator, washed with a saturated aqueous solution of ammonium chloride (3×50 mL), and extracted with benzene (3×40 mL). The organic layer was dried over $MgSO_4$ for 24 h, and the solvent was removed. The residue was purified by passing through a chromatographic column packed with silica gel (hexane—dichloromethane (1 : 3) as an eluent). 2-(Pyridin-2′-yl)phenyldiethyl phosphonate (**1**) was obtained (see Table 1, entry *6*) in a yield of 1.4 g (68%). ^{1}H NMR ($CDCl_3$), δ: 8.81 (d, 1 H, H(6), Py, $^3J_{H,H}$ = = 5.85 Hz); 8.10 (dt, 1 H, H(3′), Ph, $^3J_{H,H}$ = 7.98 Hz, $^4J_{H,H}$ = 1.25 Hz); 7.86 (d, 2 H, H(3), Py and H(6′), Ph, $^3J_{H,H}$ = 7.28 Hz); 7.65 (d, 1 H, H(5′), Ph, $^3J_{H,H}$ = 7.54 Hz); 7.42 (t, 2 H, H(4), Py and H(4′), Ph, $^3J_{H,H}$ = 7.89 Hz); 7.34 (m, 1 H, H(5), Py); 4.05 (dq, 4 H, C$\underline{H}_2$CH$_3$, $^3J_{H,H}$ = 7.09 Hz, $^3J_{P,H}$ = 7.95 Hz); 1.23 (t, 6 H, CH$_2$C$\underline{H}_3$, $^3J_{H,H}$ = 7.01 Hz). ^{31}P NMR ($CDCl_3$), δ: 18.1. Found (%): C, 60.93; H, 5.81; N, 4.63; P, 10.34. $C_{15}H_{18}NO_3P$. Calculated (%): C, 61.85; H, 6.18; N, 4.81; P, 10.65.

Synthesis of the dimer of phenylpyridylpalladium diethyl phosphonate (3). Diethylphosphorous acid (2 mmol, 0.28 g) was added to $[PhPyPdOAc]_2$ (**2**) (1 mmol, 0.64 g) in MeCN (15 mL). The reaction mixture was stirred for 24 h at 20 °C. Precipitated transparent crystals were filtered off and dried, and complex **3** was obtained in a yield of 0.71 g (90%). ^{1}H NMR ($CDCl_3$), δ: 8.98 and 8.97 (both d, 2 H, H(6), H(12), Py, $^3J_{H,H}$ = 4.57 Hz); 7.91 (m, 2 H, H(3′), H(9′), Ph); 7.86 and 7.84 (both dd, 2 H, H(6′), H(12′), Ph, $^3J_{H,H}$ = 7.48 Hz, $^4J_{H,H}$ = 1.75 Hz, $^3J_{H,H}$ = = 7.44 Hz, $^4J_{H,H}$ = 1.73 Hz); 7.76 (br.d, 2 H, H(3), H(9), Py, $^3J_{H,H}$ = 7.93 Hz); 7.57 (m, 2 H, H(5′), H(11′), Py); 7.28 (t, 2 H, H(4), H(10), Py, $^3J_{H,H}$ = 6.40 Hz); 7.12 (m, 4 H, H(5), H(11), Py and H(4), H(10), Ph); 4.33 (dq, 8 H, C$\underline{H}_2$CH$_3$, $^3J_{H,H}$ = 7.52 Hz, $^3J_{H,H}$ = 14.65 Hz); 1.26 (t, 12 H, CH$_2$C$\underline{H}_3$, $^3J_{H,H}$ = 7.03 Hz). ^{31}P NMR ($CDCl_3$), δ: 97.5.

Electrochemical oxidation of complex 3. Dipalladium complex **3** (0.5 mmol, 0.40 g) in MeCN (30 mL) was placed in an electrochemical cell. Electrolysis was carried out with divided anodic and cathodic spaces in the supporting electrolyte Et_4NBF_4. Electricity (2 *F*) was passed through the electrolyte based on 1 mole of the initial complex (268.0 mA h^{-1}). After the end of electrolysis, the reaction mixture was evaporated on a rotary evaporator, washed with a saturated aqueous solution of ammonium chloride (3×50 mL), and extracted with benzene (3×40 mL). The organic layer was dried over $MgSO_4$ for 24 h, and the solvent was removed. The residue was purified by passing through a chromatographic column packed with silica gel (hexane—dichloromethane (1 : 3) as an eluent). 2-(Pyridin-2′-yl)phenyl diethyl phosphonate (**1**) was obtained in a yield of 0.23 g (79%). ^{31}P NMR ($CDCl_3$), δ: 18.1.

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