Electrocatalytic reduction of aryldichlorophosphines with the (2,2⁻-bipyridine)nickel complexes

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The reduction of aryldichlorophosphines in organic solvents was studied by cyclic voltammetry, preparative electrolysis, and chemical reduction. The reaction of the electrochemically generated (2,2'-bipyridine)nickel(0) complexes with aryldichlorophosphines PhPCl₂ and tippPCl₂ (tipp is 2,4,6-triisopropylphenyl) proceeds through the formation of highly reactive organophosphorus intermediates, whose reactions with diphenylacetylene and hex-1-ene afford phosphirene and phosphirane heterocycles, respectively.

Key words: phosphines, nickel complexes, phosphinidenes, cyclic voltammetry, electroreduction, reduction.

The search for new highly efficient synthetic methods is one of the principal trends of the chemistry of organometallic and organophosphorus compounds.¹ The formation of element-carbon bonds, especially phosphorus-carbon bond, is an important goal of the modern organoelement chemistry.^{2,3} In this context, special attention is given to the development of novel approaches to the target synthesis of chemical compounds from highly reactive organophosphorus intermediates. Examples of such intermediates are derivatives of low-coordinate phosphorus, viz., phosphinidenes [RP:] (phosphorus analogs of carbenes), which play a significant role in the synthesis of earlier unknown organophosphorus and heterocyclic compounds.³⁻⁵ In preparative synthesis these short-lived species are used, as a rule, as transition metal complexes. Presently the main and most appropriate method for their generation is the thermal decomposition of the corresponding tungsten and molybdenum 7-phosphanorbornadiene complexes.6

Many publications are focused to the direct synthesis of various stable metal phosphinidene complexes^{7,8} and investigation of their reactivity toward various organic and organoelement compounds.^{8,9} Recently discovered reactions of metal-phosphinidene species of the new type related to the phosphinidene group transfer from the metal

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center attracted attention of researchers to the practical use of the nickel complexes in organic and organophosphorus synthesis^{9–11} and made it possible to improve the methods for synthesis of biologically active compounds and useful ligands. An alternative method using the $[R-P-W(CO)_5]$ intermediates (R = Ar, Alk) and including the step of subsequent demetallation of the obtained organophosphorus product^{4,5,12} is less convenient.

A possibility of the direct synthesis of free phosphiranes and phosphirenes has been demonstrated for the first time using as an example the relatively stable nickelphosphinidene complex⁹ containing the sterically hindered ligand and the substituent at the phosphorus atom.^{10,11} However, the synthesis of this complex is difficult and consists of several steps: the formation of primary phosphine [(dtbpe)Ni(P(H)dmp)] (dtbpe is 1,2-bis(di-*tert*-butylphosphino)ethane, and dmp is 2,6-dimesitylphenyl), its subsequent oxidation with tropilium hexafluorophosphate, and further deprotonation with NaN(SiMe₃)₂.⁹ Thus, this method is more complicated than the known method for synthesis of phosphanorbornadiene, which prevents its wide propagation in the synthetic practice.

In the recent time, we are developing a new approach based on the electrochemical generation of phosphinidene particles in the system containing the nickel complex with 2,2'-bipyridine (bpy) and aryldichlorophosphines. These complexes are known as highly efficient catalysts of various electrochemical coupling processes that allow one to

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synthesize organic and organophosphorus compounds of various types.^{13–15} In some cases, the formation of phosphinidene particles, which act as intermediates of electrocatalytic processes involving organophosphorus reactants and white phosphorus, is detected *in situ*.^{13,14}

In the present work, we describe the reduction of aryldichlorophosphines PhPCl₂ and tippPCl₂ (tipp is 2,4,6-triisopropylphenyl) by the electrochemically generated [Ni(bpy)_n] complexes (n = 1, 2), affording highly reactive phosphorus-containing intermediates that manifest the properties of the phosphinidene complexes.

Results and Discussion

Cyclic voltammetry (CV). The electrochemical reduction (ER) of the [NiCl₂(bpy)] complex occurs *via* a reversible two-step transfer of three electrons (Fig. 1, Table 1, Eqs (1) and (2)).

 $[NiCl_2(bpy)] + 2 e \implies [Ni(bpy)] + 2 Cl^-$ (1)

$$[Ni(bpy)] + e \implies [Ni(bpy)]^{-}$$
(2)

The first reversible reduction peak (C_1) corresponds to the two-electron reduction step of transformation of the [NiCl₂(bpy)] complex into the [Ni(bpy)] complex (see Eq. (1)). The second peak (C_2) is attributed to the one-electron reversible reduction of [Ni(bpy)] to the [Ni(bpy)]^{•-} radical anion complex (see Eq. (2)). The data obtained by ESR spectroscopy (g = 2.007)¹⁶ show that in this particle the electron is predominantly localized on the ligand. As a whole, the electrochemical behavior of this complex is similar to that of the earlier described¹⁶ [NiBr₂(bpy)] complex under similar electrochemical conditions.

As can be seen from the presented results (see Table 1), the ER of the aryldichlorophosphines considered occurs at more negative potentials (see Fig. 1) than the potential of the Ni^{II}/Ni^0 system and is an irreversible two-electron



Fig. 1. CV curve of the [NiCl₂(bpy)] complex $(5 \cdot 10^{-3} \text{ mol } L^{-1})$ in DMF in the presence of Bu₄NBF₄ ($10^{-1} \text{ mol } L^{-1}$); dash line shows the CV curve of PhPCl₂ ($5 \cdot 10^{-3} \text{ mol } L^{-1}$) in the same solution.

Table 1. Potentials (E_p) and currents (I_p) of the reduction (C) and re-oxidation (A) peaks in the CV curves of the [NiCl₂(bpy)] complex and dichlorophosphines (GC electrode, DMF/0.1 *M* Bu₄NBF₄)

Com- pound	Peak	$-E_{\rm p}$ /V	$I_{\rm p}$ / $\mu { m A}$	Theoretical number of electrons
[NiCl ₂ (bpy)]	C_1	1.47	-44	2
	A_1	1.30	41	2
	C_2	2.18	-20	1
	$\bar{A_2}$	2.08	17	1
PhPCl ₂	$\tilde{C_3}$	1.62	-32	2
	A_3	_	_	_
tippPCl ₂	C_4	1.68	-22	2
	A_4	_	_	_

Note. The CV data obtained without *IR*-compensation are presented here and in Table 2.

process, which agrees with published data.¹⁷ Several mechanisms of the ER of substituted phosphines under various conditions have been proposed previously.^{18–20} In some cases, the formation of a free phosphinidene species as an intermediate of the electrochemical process was postulated.^{17,18} It was also shown¹⁹ that the cathodic reduction can generate cyclic polyphosphines of the (RP)_n type (R = Ar, Alk; n = 4-6).

The CV curve of a mixture of the [NiCl₂(bpy)] complex with PhPCl₂ (1 : 1 molar ratio) exhibits the appearance of a new irreversible reduction peak (C_3) at more anodic values than the potential of the first reduction peak of the starting nickel complex (Fig. 2, Table 2). In this case, based on the CV data (appearance of the pre-peak C_3) and earlier conclusions,²⁰ one can judge about the interaction of phenyldichlorophosphine with the nickel(II) complex. The absence of the reduction peak of the free ligand (see Table 1, $E_p(C_3) = -1.62$ V) and unchanged C_1/A_1 and C_2/A_2 peaks indicate the quantitative reduction of coordinated PhPCl₂ at potentials of the C_3 pre-peak (see Fig. 2). In addition, it can be assumed



Fig. 2. CV curve of the [NiCl₂(bpy)] complex $(5 \cdot 10^{-3} \text{ mol } L^{-1})$ in DMF in the presence of PhPCl₂ $(5 \cdot 10^{-3} \text{ mol } L^{-1})$ and Bu₄NBF₄ $(10^{-1} \text{ mol } L^{-1})$.

ArPCl ₂	Peak	$-E_{\rm p}$ /V	<i>I</i> _p /μΑ	Theoretical number of electrons
PhPCl ₂	C_1	1.47	-41	2
	A_1	1.37	21	_
	$\dot{C_2}$	2.18	-20	1
	$\tilde{A_2}$	2.08	11	_
	$\tilde{C_3}$	1.21	-36	2
	$\tilde{C_4}$	1.88	-4	_
tippPCl ₂	C_1	1.44	-31	2
	A_1	1.36	20	_
	$\dot{C_2}$	2.18	-6	1
	$\tilde{A_2}$	2.09	4	1
	$\bar{C_3}$	1.88	-33	2
	A_3^{J}	0.72	5	_

that the phosphorus-containing product of PhPCl₂ reduction rapidly escapes from the coordination sphere of the metal to regenerate the initial complex. However, it is very difficult to make any conclusions about the mechanism of the process (electron transfer to PhPCl₂ *via* the metal ion or directly from the electrode) and the nature of the formed product (phosphinidene [RP:] or R(Cl)P-P(Cl)R, or other coupling species).

It was established that the ER of PhPCl₂ can occur not only in the coordination sphere of the nickel complex at the potential of the C_3 peak but also as an interaction in the solution bulk with the electrochemically generated [Ni(bpy)] complex at the potential of the C_1 peak (Scheme 1).





Sterically hindered aryldichlorophosphine containing the bulky 2,4,6-triisopropylphenyl substituent at the phosphorus atom has been used in an attempt to stabilize the organophosphorus intermediate in the coordination sphere of the nickel complex. The voltammetric study of the electrochemical behavior of the [NiCl₂(bpy)] complex in



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Fig. 3. CV curve of the [NiCl₂(bpy)] complex $(5 \cdot 10^{-3} \text{ mol } L^{-1})$ in the presence of tippPCl₂ $(5 \cdot 10^{-3} \text{ mol } L^{-1})$ and Bu₄NBF₄ $(10^{-1} \text{ mol } L^{-1})$.

the presence of tippPCl₂ taken in a molar ratio of 1 : 1 showed that the substrates considered reacted according to a mechanism different from that of PhPCl₂. This follows from a comparison of the character of the CV curves (Fig. 3, Table 2). The absence of the pre-peak indicates that no coordination of phosphine with the nickel complex occurs in this case. However, an irreversible reduction peak (C_3) appears at -1.88 V in the CV curve of the nickel complex in the presence of tippPCl₂ (see Figs 2 and 3). In this case, the peaks of reduction and re-oxidation of the [NiCl₂(bpy)] complex are retained but an additional re-oxidation peak A_3 appears ($E_p(A_3) = -0.72$ V). Evidently, the two-electron irreversible reduction of tippPCl₂ occurs at a potential of -1.88 V.

The rise of the C_3 peak (see Fig. 3) can also be due to the reduction of a new compound (probably, an organonickel intermediate) containing the nickel—phosphorus σ -bond, as it was exemplified for some organic halides.^{13,14} This peak corresponds, most likely, to the reduction of σ -organonickel complex 1 formed *via* the oxidative addition of tippPCl₂ to the [Ni(bpy)] complex at one of the P—Cl bonds (Scheme 2).

Scheme 2



tipp is 2,4,6-triisopropylphenyl (2,4,6-Prⁱ₃C₆H₂)

Possibly, the two-electron reduction of species 1 at a potential of -1.88 V or by [Ni(bpy)] could result in the

elimination of two chloride anions to form nickelphosphinidene complex 2 as an intermediate of the process (Scheme 3).



Thus, four electrons per one tipp PCl_2 molecule or two molecules of the [Ni(bpy)] complex should be consumed for the generation of the phosphinidene complex from [NiCl₂(bpy)].

Macroscale electrolysis. The preparative ER of PhPCl₂ and the [NiCl₂(bpy)] complex in a molar ratio of 1 : 1 in DMF in the presence of Bu_4NBF_4 (0.1 *M*) affords primary phosphine PhPH₂ and diphosphene unit coordinated to the nickel center²¹ (3) (Scheme 4).

Scheme 4



Perhaps, primary phosphine is formed by the reaction of the product of two-electron reduction of PhPCl₂, namely, phosphinidene particle [PhP:] (Eq. (3)), with the cations of the supporting electrolyte or proton-donor admixtures (Eq. (4)), as it has been described earlier.¹⁸

$$PhPCl_2 + 2 e \longrightarrow [PhP:] + 2 Cl^{-}$$
(3)

$$[PhP:] + 2 NBu_4^+ \longrightarrow 2 Bu_3N + PhPH_2 + 2 EtCH=CH_2$$
(4)

The presence of but-1-ene and tributylamine in the reaction medium was found by GLC.

It should be mentioned that diphosphene complex 3 can be formed by the dimerization of the phosphinidene complexes. Similar examples have also been described earlier.²¹

The four-electron preparative ER of tippPCl₂ was carried out at the controlled potential of the working electrode from -1.3 to -1.4 V (Ag/AgNO₃ (0.01 mol L⁻¹)) in the galvanostatic regime. When 4 F electricity were passed, the reaction mixture contained primary phosphine tippPH₂ and compound 4 containing coordinated diphosphene, whose yield was 46 and 21%, respectively. Probably, primary phosphine is also the reaction product of the organophosphorus intermediate with molecules of the supporting electrolyte and proton-donor admixtures. The formation of complex 4 can be presented as a result of the interaction of two nickelphosphinidene particles of 2 (see Scheme 3) followed by the elimination of the [Ni(bpy)] complex (Scheme 5) by analogy to the formation and dimerization of similar electrophilic phosphinidene iron complexes formed by the reduction of the corresponding dichlorophosphines.²²



Chemical reduction. We carried out the chemical reduction of tippPCl₂ with the $[Ni(bpy)_2]$ complex, and the results obtained were compared with those for the ER (*i.e.*, in the presence of the supporting electrolyte). As shown above, the ER of dichlorophosphine tippPCl₂ requires two equivalents of the [Ni(bpy)] complex generated *in situ* (see Schemes 2 and 3). The $[Ni(bpy)_2]$ complex was synthesized using the electrochemical technique to perform chemical reduction (Scheme 6).

Scheme 6

Cathode: $[NiCl_2(bpy)] + bpy + 2 e \implies [Ni(bpy)_2] + 2 Cl^{-1}$

Anode:
$$2 \text{ Cl}^- - 2 \text{ e} \longrightarrow \text{ Cl}_2$$

The electrochemical method makes it possible to synthesize and isolate in good yield the highly reactive $[Ni(bpy)_2]$ complex from the simple nickel salts (for example, NiCl₂). This method is efficient and convenient and finely supplements the earlier described procedures of synthesis of the nickel(0) complexes with 2,2'-bipyridine including the use of K₄Ni(CN)₄ in liquid nitrogen²³ or the ligand exchange reaction in the corresponding [Ni(cod)₂] complex (cod is cycloocta-1,5diene).²⁴ The use of two equivalents of bipyridine is necessary to stabilize the nickel atom in the low oxidation state in order to level the possible disproportionation between two [Ni(bpy)] complexes coordinately unsaturated with respect to bipyridine¹⁶ (Eq. (5)).

$$2 [Ni(bpy)] \longrightarrow [Ni(bpy)_2] + Ni$$
 (5)

After tippPCl₂ was added to a solution of the $[Ni(bpy)_2]$ complex in toluene at -70 °C in the absence of ions of the supporting electrolyte, the reaction mixture was slowly warmed to ~20 °C with continuous stirring. In this case, virtually no primary phosphine is formed and only small amounts of diphosphine (tippHP)₂ and three-membered phosphorus cyclic compound (tippP)₃ were found (Scheme 7).

Scheme 7



The presence of small amounts of the homocoupling product, namely 1,2-dichlorodiphosphine, compound 5, can be due to the intermediate formation of complex 1 by oxidative addition and its subsequent reaction with tippPCl₂ (Scheme 8).

Scheme 8



Reactions of the phosphorus intermediates with scavengers. It has been found rather recently¹⁰ for the unique nickelphosphinidene complex [(dtbpe)Ni=P(dmp)] that this type of complexes is prone to the phosphinidene group transfer in the reactions with various reactants. The reactions of this complex with carbon monoxide, ethylene,

and acetylene afford phosphaketene, phosphiranes, and phosphirenes, respectively, and the nickel(0) complexes.^{10,11} However, the chemical properties of the nickelphosphinidene complex considered and the mechanism of interaction have been studied only partially up to presently.¹¹

It seemed of interest to study the formation of phosphinidene species in the coordination sphere of the nickel complexes using scavengers. In the experiments carried out, the phosphorus-containing intermediates were generated *in situ* by the reaction of the electrochemically synthesized $[Ni(bpy)_2]$ complex with tippPCl₂ (molar ratio 2 : 1) in the presence of 10-fold excess diphenylacetylene as the scavenger. As a result, products **6** and **7** were obtained in a molar ratio of ~1 : 1 (Scheme 9).

Scheme 9



Minor amounts of $(tippPCl)_2$ and $(tippP)_3$ were also found. The formation of diphosphetene 7 can be due to the insertion of the phosphinidene fragment at one of the P-C bonds of primarily formed phosphirene 6. This type of interaction is possible for the electrophilic phosphinidene complexes. It is known^{25,26} that similar 1,2-diphosphetenes can be obtained according to the mechanism including the insertion of the phosphinidene intermediate into the phosphirene heterocycle.

The formation of phosphirane 8 is observed under similar conditions for the reaction in the presence of hex-1-ene (Scheme 10).

Scheme 10



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It should be mentioned that the phosphorus-containing intermediates formed in the reaction medium are absolutely inert toward electrophilic reagents (DMF, acetone). Only the (tippP)₃ triphosphorus cycle is formed in the reaction mixture, whereas no products of the Wittig reaction or [2+2]-cycloaddition characteristic of the nucleophilic phosphinidene complexes are observed.

It should be emphasized that the formation of phosphiranes, phosphirenes, and triphosphorus cycles can be a result of the interaction of a free phosphinidene species with unsaturated organic substrates. Similar intermediates were proposed earlier²⁷ for the reactions of aryldichlorophosphines bearing substituents in the *ortho*-position of the aromatic ring. We performed the chemical reduction of tippPCl₂ with sodium or magnesium to prove the formation of the phosphinidene intermediate in the coordination sphere of nickel. The major product was (tippP)₃. There were several attempts to trap and introduce the free phosphinidene species into the reaction using chemical reagents, including unsaturated compounds.^{27,28} However, no formation of phosphiranes and phosphirenes was observed under these conditions.

In summary, the results obtained and respective conclusions illustrate new possibilities for using the electrochemical methods to generate highly reactive phosphorus-containing intermediates. The formation of the phosphirane and phosphirene heterocycles as the reaction products of these intermediates with scavengers can be highly valuable from the viewpoint of development of new methods for the synthesis of organophosphorus compounds.

Experimental

All experiments were carried out under dry nitrogen. Solvents were purified by distillation prior to use. Dimethylformamide was dried over calcium hydride followed by distillation *in vacuo*. The supporting electrolyte salt Bu_4NBF_4 was dried by melting *in vacuo* and stored under dry nitrogen. Phenyldichlorophosphine and 2,2'-bipyridine were purchased from Aldrich.

In CV studies, a stationary glassy carbon (GC) disc electrode with a working surface of 3.14 mm² was used as the working electrode. The CV curves were recorded with switching on the electrochemical cell according to the three-electrode scheme. The curves were detected in DMF against a 0.1 *M* solution of Bu₄NBF₄ on an EG&G Princeton Applied Research, model 273A potentiostat and a LINSEIS LY 1400 two-coordinate recorder with a potential sweep of 50 mV s⁻¹. The reference electrode was an Ag/0.01 *M* AgNO₃ system in MeCN ($E^{\circ}(Fc/Fc^+) = +0.20$ V). A Pt wire with a diameter of 1 mm served as the auxiliary electrode. Measurements were carried out in a temperature-controlled (20 °C) cell under nitrogen. Preparative electrolysis was carried out at 20 °C on the same electrochemical setup in a 30-mL three-electrode cell under divided electrolysis conditions in DMF containing a 0.1 *M* solution of Bu₄NBF₄.

The working electrode for preparative syntheses was the GC electrode with a working surface of 60 cm². NMR spectra were recorded on a Bruker 400 high-resolution spectrometer. ESR spectra were measured on an SE/X-2544 X-range electron spectrometer (RADIOPAN). Melting points were determined on an Electrothermal IA9000 SERIES Digital Melting Point Apparatus instrument in capillaries under nitrogen. The nickel content in selected samples was determined by atomic adsorption analysis on a Carl Zeiss AAS1 spectrometer.

Synthesis of [NiCl₂(bpy)] complex. A solution of bpy (1.97 g, 12.6 mmol) in EtOH (15 mL) was added to a solution of NiCl₂·6H₂O (3 g, 12.6 mmol) in EtOH (25 mL) at ~20 °C. After stirring for 6 h, a pale green precipitate formed was filtered off, washed with EtOH (3×20 mL), and dried *in vacuo* for 8 h. The yield was 3.02 g (84%). Found (%): C, 41.85; H, 2.63; Cl, 24.54; N, 9.58; Ni, 21.02. $C_{10}H_8Cl_2N_2Ni$. Calculated (%): C, 41.97; H, 2.79; Cl, 24.83; N, 9.79; Ni, 20.64.

2,4,6-Triisopropylphenyldichlorophosphine. Magnesium turnings (11.4 g, 0.45 mol) were placed in a round-bottom flask (1000 mL), and the content of the flask was three times evacuated on heating followed by filling with argon. Then freshly distilled diethyl ether (350 mL) was poured and 1-bromo-2,4,6triisopropylbenzene (120 g, 0.42 mol) was dropped at ~20 °C. The reaction start was determined from boiling of the ether on the surface of the magnesium turnings. Several drops of 1,2-dibromoethane were added to the reaction medium to activate magnesium. The mixture was stirred for 14 h, after which it became turbid and gray. The resulting solution was carefully filtered and transferred to a dropping funnel and then added dropwise to a solution of PCl₃ (62 g, 0.45 mol) in diethyl ether (100 mL). After stirring for 14 h, the precipitate formed was filtered off and the filtrate was left for 10 h at -4 °C. The obtained yellowish needle-like crystals of tippPCl₂ were filtered off and dried in vacuo. The yield was 97.4 g (76%), m.p. 85–95 °C (cf. Ref. 29: m.p. 90–100 °C). ³¹P NMR (C_6D_6), δ : 165.2. The spectrum also contained an admixture signal at 8 160.0 corresponding to tippPClBr.

Electrochemical reduction of [NiCl₂(bpy)] in the presence of ArPCl₂. Solutions containing the [NiCl₂(bpy)] complex (65 mg, 0.23 mmol), ArPCl₂ (0.23 mmol) (70 mg of tippPCl₂ or 41 mg of PhPCl₂), and Bu₄NBF₄ as the supporting electrolyte (659 mg, 2.0 mmol) in DMF (20 mL) were prepared for electrolysis. Electrochemical reduction was carried out in the galvanostatic regime in a divided cell at ~ 20 °C. The potential of the working electrode ranged from -1.3 to -1.4 V (Ag/0.01 M AgNO₃). A direct current of 24.7 mA was passed through the working solution for 1 h. After the end of electrolysis, the solvent was removed in vacuo and the reaction products were extracted from the residue with toluene (5×20 mL). Toluene was evaporated in part from the extract, and the toluene layer was decanted from the residues of DMF and the supporting electrolyte. After the toluene extract was concentrated, organophosphorus products were extracted from the residue with pentane. As a result, PhPH₂ (³¹P NMR (C₆D₆), δ : -124.8 (t, ¹J_{P,H} = 200 Hz)) and diphosphene complex 3 (³¹P NMR (C_6D_6), δ : +14.0 (s)) were obtained in 52 and 17% yields, respectively.

Electrochemical synthesis of the $[Ni(bpy)_2]$ complex. The $[NiCl_2(bpy)]$ complex (338 mg, 1 mmol), bpy (156 mg, 1 mmol), and the Bu₄NBF₄ supporting electrolyte (659 mg, 2.0 mmol) were dissolved in DMF (20 mL). The electrolysis of the resulting solution was carried out in the divided cell at the potential of the

working electrode from -1.48 to -1.52 V (Ag/0.01 *M* AgNO₃). A direct current of 26.8 mA was passed through the solution for 2 h. After the end of electrolysis, the solvent was evaporated *in vacuo* and a product, which crystallized from the solution on cooling to -35 °C, was extracted from the dark violet residue with toluene (5×20 mL). The crystals were filtered off and dried *in vacuo*. The yield was 237 mg (64%), m.p. 154 °C (*cf.* Ref. 24: m.p. 155 °C). Found (%): C, 64.68; H, 4.43; N, 15.14; Ni, 15.68. C₂₀H₁₆N₄Ni. Calculated (%): C, 64.74; H, 4.35; N, 15.09; Ni, 15.90.

Reaction of [Ni(bpy)₂] with tippPCl₂. A solution of tippPCl₂ (76 mg, 0.25 mmol) in toluene (15 mL) was added to a solution of [Ni(bpy)₂] (186 mg, 0.5 mmol) in toluene (25 mL) at -70 °C (liquid nitrogen with EtOH was used as the cooling mixture). The resulting mixture was slowly heated to $\sim 20 \text{ °C}$ with continuous stirring. At -40 °C the working solution became slightly red, and at 0 °C the dark green color was observed. A lot of a yellowish precipitate was formed upon stirring of the reaction mixture for 4 h. The precipitate was filtered off, and the solvent was removed *in vacuo*. The resulting mixture of the products was identified by ³¹P NMR spectroscopy: (tippP)₃ (³¹P NMR (C₆D₆), δ : -158.9 (t, ¹*J*_{P,H} = 178 Hz)), tippPH₂ (³¹P NMR (C₆D₆), δ : -111.9 (dd, ¹*J*_{P,H} = 149 Hz, ²*J*_{P,H} = 70 Hz); -116.4 (dd, ¹*J*_{P,H} = 149 Hz, ²*J*_{P,H} = 70 Hz)), and (tippPCl)₂ (³¹P NMR (C₆D₆), δ : +77.7, +75.4 (both s)).

Reaction of [Ni(bpy)₂] with tippPCl₂ in the presence of scavengers. A solution containing tippPCl₂ (76 mg, 0.25 mmol) and 2.5 mmoles of the scavenger (444 mg of diphenylacetylene, 210 mg of hex-1-ene, and 183 mg of DMF or 145 mg of acetone) in toluene (15 mL) was added dropwise to a solution of the [Ni(bpy)₂] complex (186 mg, 0.5 mmol) in toluene (15 mL) cooled to -70 °C. The solution was slowly heated to ~ 20 °C. The precipitate formed was filtered off, and the solvent was removed *in vacuo*. The following products were obtained: 1-(2,4,6-triisopropylphenyl)-2,3-diphenylphosphirene (6) (³¹P NMR (C₆D₆), δ : -172.1 (s)), 1,2-bis(2,4,6-triisopropylphenyl)-3,4-diphenyl-1,2-diphosphetene (7) (³¹P NMR (C₆D₆), δ : -42.6 (s)), and 1-(2,4,6-triisopropylphenyl)-2-butylphosphirane (8) (³¹P NMR (C₆D₆), δ : -222.4 (s)).

Reduction of tippPCl₂ using sodium or magnesium as reducing agents. A solution containing tippPCl₂ (153 mg, 0.5 mmol) and diphenylacetylene (890 mg, 5 mmol) in toluene (15 mL) was added to a suspension containing metallic sodium (23 mg, 1 mmol) or magnesium turnings (24 mg, 1 mmol) in toluene (15 mL) cooled to -70 °C. Then the mixture was slowly heated to ~20 °C and stirred for ~6 h. In the case of using magnesium, the reaction mixture was additionally refluxed for 3 h. The precipitate formed was filtered off, and the filtrate was concentrated *in vacuo*. The residue was analyzed by ³¹P NMR. ³¹P NMR (C₆D₆), δ : -99.6 (d, ¹J_{P,P} = 178 Hz); -132.9 (t, ¹J_{P,P} = 178 Hz) ((tippP)₃).

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