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Electrochemical approaches to the generation of (arylphosphinidene)pentacarbonyltungsten

Yu. G. Budnikova,* T. V. Gryaznova, A. R. Yagfarov, and O. G. Sinyashin

A. E. Arbuzov Institute of Organic and Physical Chemistry,
Kazan Research Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.
E-mail: yulia@iopc.knc.ru

The possibility of formation of arylphosphinidene complexes with tungsten pentacarbonyl ArP=W(CO)$_5$ upon the nucleophilic substitution of the chlorine atoms in aryldichlorophosphines ArPCl$_2$ by the electrochemically generated [W(CO)$_5$]$^{2-}$ anion is demonstrated.

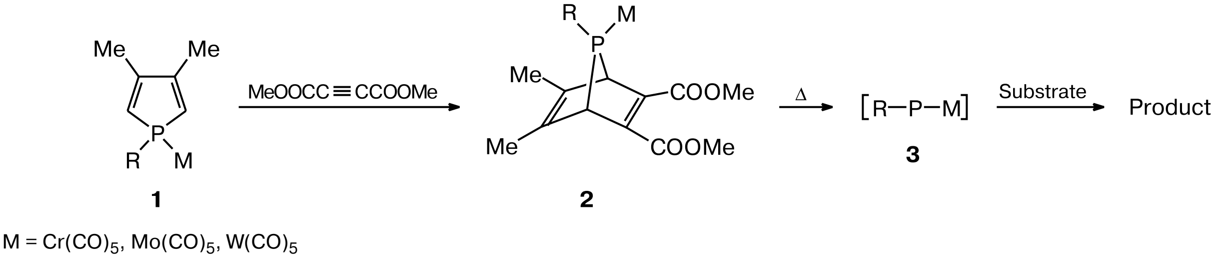
Key words: tungsten pentacarbonyl, electrosynthesis, phosphinidene complexes, phosphirene complexes, cyclic voltammetry.

The synthesis and stabilization of organoelement carbene analogs has become significant in recent years for both theoretical and practical reasons. It is known[1,2] that many organic reactions proceed through these highly reactive intermediates. Phosphinidenes RP, which are phosphorus analogs of carbenes, refer to low-coordinate phosphorus compounds[3] and are similar to nitrenes, silylenes, and germylenes. Although the formation of phosphinidene intermediates is postulated in many reactions, free stable phosphinidenes are still unknown,[3] their existence being proved only by indirect methods. Only in one study,[4] was the formation of mesitylphosphinidene detected by EPR spectroscopy at −196 °C. Phosphinidenes are highly reactive and condense with various substrates.[4,5] Meanwhile, the stabilization of short-lived intermediates of this type in the coordination sphere of transition metals is a way to prove their existence. Depending on the nature of the metal and the ligands attached to it, the phosphorus atom in the terminal phosphinidene metal complexes can possess either nucleophilic or electrophilic properties.[6] Nucleophilic terminal phosphinidene complexes have been thoroughly studied; their structure was determined[7] by X-ray diffraction. However, stable electrophilic terminal complexes have not yet been studied. The key factor that delays the development of the chemistry of these compounds is the lack of methods for generation and stabilization of phosphinidene complexes. The potential of electrochemistry in this field has been barely employed.

The known methods for the generation of terminal phosphinidene complexes are based on thermal or catalytic decomposition of appropriate precursors. An original approach to electrophilic phosphinidene complexes developed previously[8,9] involves the reaction of phospholes **1** with acetylenedicarboxylic acid esters and thermal decomposition of the resulting 7-phosphabicyclo[2.2.1]hepta-2,5-diene complexes **2** (Scheme 1). This is still the principal method for the synthesis of terminal electrophilic phosphinidene complexes with various substituents at phosphorus.

The purpose of the present study is to develop methods for the preparation of terminal phosphinidene complexes of tungsten pentacarbonyl by the reaction of electrochemically generated tungsten pentacarbonyl ion with aryldichlorophosphines.

Scheme 1



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Results and Discussion

It has been shown previously[10] that electrolysis of $W(CO)_6$ in acetonitrile consumes two electrons per molecule and yields the highly nucleophilic tungsten pentacarbonyl anion **4** (Scheme 2).

Scheme 2

$$W(CO)_6 \xrightarrow[-CO]{+2\,e} \underset{\mathbf{4}}{[W(CO)_5]^{2-}}$$

The reaction of anion **4** with mesityldichlorophosphine was carried out in MeCN at –30 °C (Scheme 3). After mixing the starting reactants, three singlets (δ 766.4, 509.3, and 168.6) appear in the ^{31}P NMR spectrum of the reaction mixture. As the temperature is raised to room temperature, the signal of the starting mesityldichlorophosphine (δ_P 168.6) completely disappears. The low-field signals corresponding to low-coordinate phosphorus were assigned to previously described[11] dimesityldiphosphene MesP=PMes (**6**) (δ_P 509.3) and to the mesitylphosphinidene complex of tungsten pentacarbonyl [Mes—P→W(CO)$_5$] (δ_P 766.4). On keeping the reaction mixture in MeCN under argon for 24 hours, the phosphinidene complexes undergo irreversible changes. After that, the ^{31}P NMR spectrum of the reaction mixture shows the presence of only unidentified decomposition products (δ_P 320.6 and 49.3) and mesitylphosphinic acid (δ_P 29.5).

Scheme 3

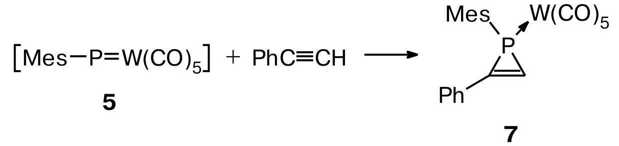
$$MesPCl_2 + \underset{\mathbf{4}}{[W(CO)_5]^{2-}} \xrightarrow[-30\ ^\circ C]{MeCN}$$

$$\longrightarrow \underset{\mathbf{5}}{[Mes{-}P{=}W(CO)_5]} + \underset{\mathbf{6}}{Mes{-}P{=}P{-}Mes}$$

Thus, the reaction of cathodically generated $[W(CO)_5]^{2-}$ anion with mesityldichlorophosphine results in the formation of (mesitylphosphinidene)pentacarbonyltungsten **5** as the major product (see Scheme 3). Dimesityldiphosphene (**6**) may result from either transformations of compound **5** or dimerization of the intermediate phosphinidene MesP species.

To confirm the formation of the terminal electrophilic phosphinidene complex of tungsten pentacarbonyl **5**, we made it to react with phenylacetylene in MeCN by analogy with the reaction described previously.[12] The ^{31}P NMR spectrum of the reaction mixture recorded immediately after mixing the reactants exhibits one signal at δ_P –120.06 ($J_{P,W}$ = 272.52 Hz), which we ascribed to phosphorus of the mesitylphosphirene complex **7** (Scheme 4).

Scheme 4

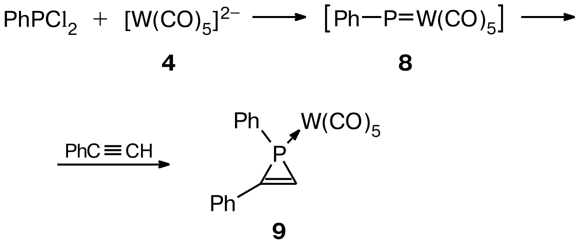


Analysis of the ^1H, ^{13}C, and ^{31}P NMR spectra and the IR spectra of the compound **7** isolated from the reaction mixture confirms the proposed structure. The ^1H NMR spectrum of complex **7** contains two singlets (δ_H 2.28 and 2.54) for the *p*-Me- and *m*-Me-protons of the mesityl group attached to phosphorus in 1 : 2 ratio. The low-field spectral range shows a broadened singlet at δ_H 6.87 (the methine protons of the mesityl), a multiplet at δ_H 7.33 (the Ph-group protons), and a doublet at δ_H 7.47 attributable to the endocyclic proton ($^2J_{P,H}$ = 8.05 Hz). The ^{13}C NMR spectrum of (phosphirene)pentacarbonyltungsten **7** displays signals of the mesityl and phenyl carbon atoms. The endocyclic C atoms (=CH and =$\underline{C}$—Ph) are manifested as doublets (δ_C 121.64, $^1J_{P,C}$ = 32.12 Hz and δ_C 142.32, $^1J_{P,C}$ = 32.16 Hz, respectively). In the far spectral range, two doublets for the carbonyl C atoms are present (δ_C 199.36, $^2J_{P,C}$ = 6.43 Hz (*cis*-CO) and δ_C 201.92, $^2J_{P,C}$ = 24.10 Hz (*trans*-CO)). The IR spectrum also confirms the structure of compound **7**. The spectrum exhibits absorption bands at 2067 and 1905 cm^{-1}, due to the carbonyl groups, and at 1655 and 1605 cm^{-1}, which are characteristic of C=C vibrations.

The mesitylphosphirene complex **7** is hydrolytically unstable.

Using the developed procedure for the synthesis of phosphinidene complexes based on electrochemical generation of the tungsten pentacarbonyl anion, we prepared a similar phenylphosphinidene complex of tungsten pentacarbonyl **8** (Scheme 5).

Scheme 5



After completion of the reaction of phenyldichlorophosphine with the tungsten pentacarbonyl anion, the

^{31}P NMR spectrum of the reaction mixture showed a signal at δ 692.93 due to the phenylphosphinidene complex **8**, which was thus detected for the first time. The synthesis in the presence of a trapping reagent, phenylacetylene, affords (phenylphosphirene)pentacarbonyltungsten **9** (δ_P −157.34), whose physocochemical and spectroscopic characteristics are fully consistent with those described previously[12] (see Scheme 5).

Thus, phenylacetylene condensations with (arylphosphinidene)pentacarbonyltungstens carried out in different ways, by the classical procedure[12] and by the procedure proposed in this study, lead to the same result. In addition, we detected for the first time the intermediate arylphosphinidene complexes of tungsten pentacarbonyl by ^{31}P NMR spectroscopy. In order to confirm the structure of these complexes and rule out another structure of the phosphinidene complex, in particular, the bridging structure, we carried out additional experiments. The reaction of $Na_2W_2(CO)_{10}$ with alkyl(aryl)dichlorophosphines giving rise to bridging phosphinidene complexes, trialkyl(aryl)cyclotriphosphanes, and a range of diphosphene metal complexes has been described.[13] The ratio of the final products depends on the reaction conditions. The ^{31}P NMR spectrum of the bridging phosphinidene complex of tungsten pentacarbonyl obtained by the reaction of $Na_2W_2(CO)_{10}$ with mesityldichlorophosphine contains a singlet at δ 961 (in toluene), which differs from the signal detected for [ArP—W(CO)$_5$]. An attempt to prepare a similar bridging phosphinidene complex by the reaction of 2 equiv. of the pentacarbonyltungsten ions with 1 equiv. of mesityldichlorophosphine in MeCN failed. The ^{31}P NMR spectrum of the reaction mixture showed no signals in the region of δ 800—1000.

The course of the reactions was monitored by cyclic voltammetry. The reduction potential of the starting $W(CO)_6$ occurs in the far cathodic region (−2.35 V). Conversely, mesityldichlorophosphine is reduced at relatively low potentials (−1.25 V). After the addition of $MesPCl_2$ to cathodically generated $[W(CO)_5]^{2-}$, the wave corresponding to dichlorophosphine reduction disappears. This indicates that this compound has been fully consumed, and the reaction products contain no P—Cl bonds. The cyclic voltammogram exhibits one irreversible wave, which is characterized by a reduction potential of −2.25 V. In our opinion, it is the mesitylphosphinidene complex **5** that is reduced irreversibly at −2.25 V consuming two electrons per molecule (Fig. 1). Phenylacetylene is electrochemically inactive in the accessible range of potentials. The phosphinidene reduction wave disappears after the addition of phenylacetylene being replaced by two one-electron irreversible waves for three-membered P-containing heterocycle **7** with a reduction potentials of −2.37 and −2.76 V. Thus, voltammetry is a convenient operative method for monitoring the reactions.

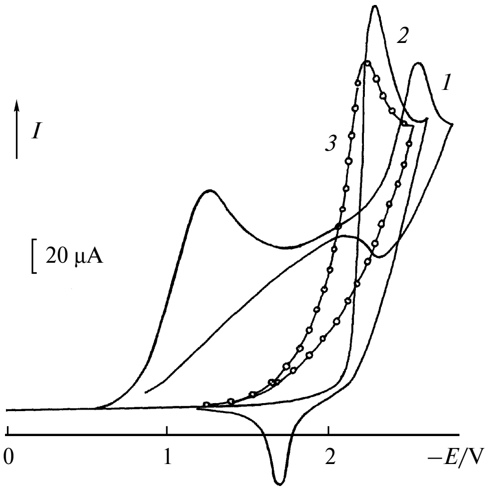


Fig. 1. Cyclic voltammograms of $3 \cdot 10^{-2}$ *M* solutions in MeCN (with Et_4NBF_4): $W(CO)_6$ (*1*), $MesPCl_2$ (*2*) and $MesP{=}W(CO)_5$ (*3*) prepared *in situ* by the addition of $MesPCl_2$ to the product of reduction of $W(CO)_6$.

The method for the generation of (phosphinidene)pentacarbonyltungsten proposed in this work has a number of advantages over the known methods. It is based on readily available starting compounds, includes few steps, and is implemented under mild conditions. Using this method, we obtained the first spectroscopic characteristics of the phosphinidene complexes.

Experimental

Cyclic voltammograms were recorded using an XY-recorder with a PI-50-1 potentiostat and a PR-49 programming device with a three-electrode electrochemical cell. The potential sweep rate was 50 mV s^{-1}. A stationary glass carbon disk electrode with a working area of 3.14 mm^2 was used as a working electrode and a Pt wire was a counter electrode. The Ag/0.01 *M* $AgNO_3$ system in MeCN served as the reference electrode. The measurements were carried out in a cell maintained at a constant temperature (25 °C) in MeCN with Et_4NBF_4 as the supporting electrolyte ($C = 5 \cdot 10^{-3}$ mol L^{-1}) under argon. The complex $Ni(bpy)_3(BF_4)_2$ was used as the standard to determine the number of electrons involved in the electrochemical reaction (I_p = 36 μA at $C = 1 \cdot 10^{-2}$ mol L^{-1}).

The preparative electrolysis was carried out using a B5-49 DC source in a 40-mL three-electrode cell. The working electrode potential was determined using a Shch50-1 DC voltmeter *vs.* the reference electrode, Ag/0.01 *M* $AgNO_3$, in the appropriate solvent. The working surface of the cylindrical platinum cathode used as the working electrode was 20.0 cm^2. The diaphragm was made of paper; a glass carbon plate with a working area of 4 cm^2 was used as the anode, and a saturated solution of Et_4NBF_4 in MeCN was the anolyte.

^{1}H NMR spectra were recorded on a Bruker WM-250 spectrometer (250.132 MHz) and referenced to the residual protons of the deuterated solvent as the internal standard. The ^{31}P NMR spectra were run on a Bruker CXP-100 spectrometer (36.47 MHz) relative to external 85% orthophosphoric acid. ^{13}C NMR spectra were recorded on a Bruker MSL-400 spectrometer relative to an internal standard, the signal of the C atom of deuterated solvent. The IR spectra were measured on a Bruker Vector-22 instrument in the 400—3600 cm^{-1} range in mineral oil in thin films.

Acetonitrile was purified by fractional distillation over phosphorus pentoxide and potassium permanganate; Et_4NBF_4 was recrystallized from ethanol.

Commercial $W(CO)_6$ (DalKhim, Nizhny Novgorod) was used. Mesityldichlorophosphine was obtained by a known procedure.[14]

Electrolysis of tungsten hexacarbonyl. Tungsten hexacarbonyl (0.3591 g, 10^{-3} mol) and Et_4NBF_4 (0.0325 g) in MeCN (30 mL) were placed in an electrochemical cell and electricity (2 F per mole of $W(CO)_6$, $I = 53.8$ mA) was passed, while the solution was stirred on a magnetic stirrer under a constant flow of argon.

(1-Aryl-2-phenylphosphirene)pentacarbonyltungstens (general procedure). Aryldichlorophosphine (10^{-3} mol) was added dropwise at −30 °C to a freshly prepared solution of the tungsten pentacarbonyl anion **4**. The reaction mixture was stirred for 30 min, and phenylacetylene ($7 \cdot 10^{-3}$ mol) was added dropwise. The reaction mixture was warmed up to room temperature and then heated for 3 h at 50 °C. After cooling, the solvent was removed and the remaining crystalline mass was extracted with benzene. The resulting extract was concentrated to remove benzene and the crystalline residue was washed with diethyl ether to give compounds **7** and **9**.

(1-Mesityl-2-phenylphosphirene)pentacarbonyltungsten (7). Yield 0.26 g (45.1%), m.p. 128—130 °C. ^{31}P NMR (MeCN), δ: −120.06 ($^1J_{P,W}$ = 272.52 Hz). ^{1}H NMR ($CDCl_3$), δ: 2.28 (s, 3 H, p-Me$_{Mes}$); 2.54 (s, 6 H, m-Me$_{Mes}$); 6.87 (br.s, 2 H, H$_{Mes}$); 7.33 (m, 5 H, Ph); 7.47 (d, 1 H, =CH, $^2J_{P,H}$ = 8.05 Hz). ^{13}C NMR ($CDCl_3$), δ: 20.96 (s, p-Me); 21.17 (d, m-Me, $^3J_{P,C}$ = 8.03 Hz); 121.64 (d, *cyclo*-CH, $^1J_{P,C}$ = 32.12 Hz); 125.85 (d, i-C$_{Ph}$, $^2J_{P,C}$ = 8.57 Hz); 127.73 (d, o-C$_{Mes}$, $^2J_{P,C}$ = 14.45 Hz); 127.99 (s, m-C$_{Ph}$); 128.17 (s, o-C$_{Ph}$); 128.32 (d, i-C$_{Mes}$, $^1J_{P,C}$ = 29.72 Hz); 128.47 (s, p-C$_{Mes}$); 129.90 (s, m-C$_{Mes}$); 131.75 (s, p-C$_{Ph}$); 142.32 (d, $\underline{C}$—Ph, $^1J_{P,C}$ = 32.16 Hz); 199.36 (d, *cis*-CO, $^2J_{P,C}$ = 6.43 Hz); 201.92 (d, *trans*-CO, $^2J_{P,C}$ = 24.10 Hz). IR (mineral oil), ν/cm^{-1}: 2067 (CO), 1905 (CO), 1655 (C=C), 1605 (C=C arom.).

(1,2-Diphenylphosphirene)pentacarbonyltungsten (9). Yield 0.21 g (39.3%), m.p. 85—87 °C. ^{31}P NMR (MeCN), δ: −157.34 ($^1J_{P,W}$ = 288.53 Hz). ^{1}H NMR ($CDCl_3$), δ: 6.65 (m, 5 H, Ph); 7.48 (m, 5 H, =CPh); 8.04 (d, 1 H, =CH, $^2J_{P,H}$ = 10.45 Hz). ^{13}C NMR ($CDCl_3$), δ: 121.36 (d, CH, $^1J_{P,C}$ = 31.51 Hz); 139.22 (d, C—Ph, $^1J_{P,C}$ = 32.16 Hz); 199.53 (d, *cis*-CO, $^2J_{P,C}$ = 7.04 Hz); 201.02 (d, *trans*-CO, $^2J_{P,C}$ = 28.14 Hz). IR (mineral oil), ν/cm^{-1}: 2076 (CO), 1949 (CO), 1653 (C=C), 1602 (C=C arom.).

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