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New aspects of the electroreduction of palladium dichloride complex with 1,2-bis(diphenylphosphino)ethane

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The electrochemical reduction of a mono-chelate palladium dichloride complex with 1,2-bis(diphenylphosphino)ethane (dppe) in DMF results in formation of highly reactive mono-chelate palladium(0) complex, which reacts with initial complex by reaction of the ligand abstraction forming stable bischelate complex $[Pd^0(dppe)_2]$ and palladium dichloride.

Catalytic systems based on palladium phosphine complexes attract high practical interest due their high activity in C–C coupling processes.[1,2] The reduction of palladium(II) complexes to the corresponding palladium(0) species is essential at the entrance into the catalytic cycle in order to realize the oxidative addition reaction. The formation of palladium(0) species is also realized in the catalytic cycle as a result of reductive elimination prior to the next oxidative addition reaction. The ways for stabilization of highly reactive coordinatively unsaturated palladium(0) intermediates depend on many factors, including the nature of the used ligand and the reactivity of the reacting substrate.[2] When coordinatively unsaturated palladium(0) complex is not enough stable, it is easily decomposed into inactive palladium black strongly decreasing the catalytic activity of the used system. The use of diphosphine chelating ligands such as 1,2-bis(diphenylphosphino)ethane (dppe), which stabilize both the oxidized and the reduced forms of palladium centre,[2] results in some cases in formation of palladium(0) bischelate complexes inhibiting catalytic activity of the Pd centre.

The mechanism of electrochemical reduction of palladium dichloride complexes bearing chelated 1,2-bis(diphenylphosphino)ethane ligands remains unknown. An electrochemical study may help one to understand the possible ways of stabilization of electrochemically generated highly reactive coordinatively unsaturated Pd-centered species in low oxidation states and to elucidate the nature of the decomposition products.

The aim of this work was to identify the product formed at the first electrochemical reduction process of neutral monochelated palladium dichloride complex formed by 1,2-bis(diphenylphosphino)ethane.

The electrochemical properties of complex $[PdCl_2(dppe)]$ **1** have been already explored. According to Amatore *et al.*,[3] the electroreduction of **1** proceeds *via* a one-electron wave resulting in anionic palladium(I) complexes $[PdCl_x(dppe)]^{(x-1)-}$ **2** [equation (1)]. The absolute overall electron stoichiometry for this process was determined by the combined use of steady state voltammetry and transient chronoamperometry.

$$\underset{\mathbf{1}}{[PdCl_2(dppe)]} + e \longrightarrow \underset{\mathbf{2}}{[PdCl_x(dppe)]^{(x-1)-}} \quad (E_{1/2} = -1.26 \text{ V } \textit{vs.} \text{ SCE}) \qquad (1)$$

More recently, the mechanism of electrochemical synthesis of 1,1′-binaphthyl from 1-naphthyl trifluoromethylsulfonate catalyzed by complex **1** was described postulating two-electron reduction for initial complex **1** into anionic species $[PdCl(dppe)]^-$ **3** in order to be involved in the catalytic cycle:[4]

$$\underset{\mathbf{1}}{[PdCl_2(dppe)]} + 2e \longrightarrow \underset{\mathbf{3}}{[PdCl(dppe)]^-} + Cl^- \qquad (2)$$

It should be noted that the proposed mechanism of electroreduction of complex **1** proceeding *via* Pd^I intermediates seems reasonable because such a dichotomy also exists for the analogous $[NiCl_2(dppe)]$ complex,[5–7] which undergoes reduction in two one-electron steps:

$$[Ni^{II}Cl_2(dppe)] + e \longrightarrow [Ni^{I}Cl(dppe)] + Cl^- \quad (E_{1/2} = -0.77 \text{ V } \textit{vs.} \text{ SCE}) \qquad (3)$$

$$[Ni^{I}Cl(dppe)] + e \longrightarrow [Ni^{0}(dppe)] + Cl^- \quad (E_{1/2} = -1.36 \text{ V } \textit{vs.} \text{ SCE}) \qquad (4)$$

Attempts were made for proving that the first step of the electrochemical reduction of **1** is a one-electron process. However, the species containing Pd^I have never been isolated or fixed in electrochemical process. Moreover, according to the published data[8] on comparison of the possible ways for stabilization of nickel(I) and palladium(I) complexes using diphosphine ligands, in case when the bischelate complex $[Ni(dppe)_2](BF_4)_2$ is reduced in two one-electron steps *via* ESR detectable Ni^I intermediate ($g = 2.07$), the electroreduction of $[Pd(dppe)_2](BF_4)_2$ is realized as one two-electron process without formation of any paramagnetic species. Note that the nature of the chelating bidentate phosphorus ligand has a strong influence on the electroreductive process of corresponding palladium(II) complexes, including also the P–Pd–P bite angle.[4] It was postulated that palladium dichloride complex **4** with one molecule of bis(diphenylphosphino)methane (dppm) as the ligand exhibits one two-electron reduction process[9] leading to anionic Pd^0 complexes **5**:

$$\underset{\mathbf{4}}{[PdCl_2(dppm)]} + 2e \longrightarrow \underset{\mathbf{5}}{[PdCl_x(dppm)]^{x-}} + (2-x)Cl^- \qquad (5)$$

Thus, the published data have several limitations in understanding the mechanism of electroreduction of monochelated palladium(II) complexes bearing diphosphine ligands and the nature of electrogenerated palladium containing species. We investigated the electrochemical reduction of monochelated palladium(II) dichloride complex $[PdCl_2(dppe)]$ using cyclic voltammetry (CV), macroscale electrolysis, ^{31}P NMR spectroscopy and mass spectrometry.†

Two irreversible peaks C_1 and C_2 are observed in the CV curve of complex **1** in DMF (Figure 1, Table 1), that is in agreement with previously reported data.[3] The peak C_1 corresponds to the first step of electroreduction of **1**. It is attributed to the one-electron process that is based on the comparison of the peak currents of the first wave of electroreduction of related $[NiCl_2(dppe)]$ complex under the same electrochemical conditions (Table 1). However, electrochemical macroscale electrolysis (electroreduction) of complex **1** at the potentials C_1 in the electrochemical ESR microcell does not confirm the formation of stable palladium(I) species in solution.

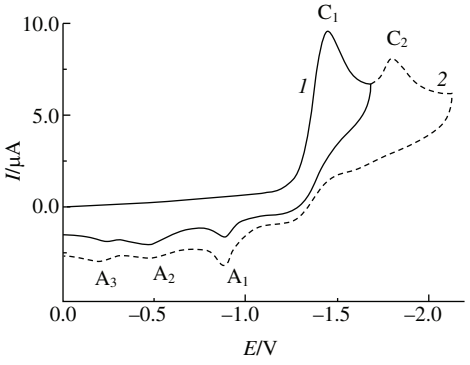

Figure 1 CV curves of complex **1** (5×10^{-3} M) on GC electrode in DMF in the presence of Bu_4NBF_4 (0.1 M). CV curves were recorded at the first scan (*1*) from 0.00 to –1.70 V and back to 0.00 V and (*2*) from 0.00 to –2.10 V and back to 0.00 V.

The second peak C_2 observed in the CV curve of complex **1** (Figure 1, Table 1) is attributed to the reduction of the palladium species formed in electrochemical process at C_1. The ratio I_p^{C1}/I_p^{C2} is 4.97, 4.50, 4.36, 4.25 or 4.18 for 50, 100, 200, 500 or 2000 mV s^{-1}, respectively. At the same time, in a separate experiment, it was established that electroreduction of binary palladium salt $PdCl_2$ under the same electrochemical conditions is irreversible at –0.96 V (*vs.* $Ag/AgNO_3$, 0.01 M in MeCN) (Table 1). Note that the addition of Bu_4NCl to the solution containing $PdCl_2$ and following increase in Cl^- concentration up to a 10:1 (Cl^-:Pd) molar ratio results in appearing new cathodic irreversible peak at –1.62 V (*vs.* $Ag/AgNO_3$, 0.01 M in MeCN) (Table 1). According to published data,[9] this peak is attributed to the reduction of $[PdCl_4]^{2-}$ dianionic species displaying the same morphology of the CV curve as it was recorded for $PdCl_2$ in the presence of Bu_4NCl. A potential scanning of this solution to the anodic region (from 0.00 to +1.40 V and back to 0.00 V) allows one to observe high-intensity oxidation peak A_1 (E_p^{red} = +1.03 V *vs.* $Ag/AgNO_3$, 0.01 M in MeCN) (Table 1) corresponding to the oxidation of free Cl^- added to the solution. No oxidation peaks were observed in the CV curves of both $[PdCl_2(dppe)]$ and $PdCl_2$ species at the anodic potential scanning displaying that Cl^- are not dissociated in these solutions.

In the re-oxidation process, a falling of the current is observed at C_1 and three anodic peaks A_1, A_2 and A_3 corresponding to the oxidation of electrochemically formed intermediates are observed (Figure 1, Table 1). Such a morphology of the CV curve is analogous to the reported electrochemical behaviour of the related $[PdCl_2(dppm)]$ complex.[10] According to published

Table 1 Potentials[a] and currents of the reduction (C) and re-oxidation (A) peaks in the CV curves of the investigated complexes (reference electrode $Ag/AgNO_3$, 0.01 M in MeCN).

Complex	Peaks	E_p/V	I_p/μA
$[PdCl_2(dppe)]$	C_1	–1.44	8.75
	C_2	–1.79	1.75
	A_1	–0.89	1.75
	A_2	–0.47	0.50
	A_3	–0.20	0.30
$[NiCl_2(dppe)]$	C_1	–1.17	12.40
	C_2	–1.81	6.20
	A_1	–0.75	8.40
	A_2	–0.43	3.40
$[PdCl_2]$	C_1	–0.96	3.50
	no oxidation peaks	—	—
$[PdCl_2] + 10Bu_4NCl$	C_1	–0.94	2.30
	C_2	–1.62	9.20
	A_1	+1.03	102.50

[a]The CV data were obtained without IR compensation.

† All manipulations and reactions were carried out under an atmosphere of dry nitrogen. Cyclic voltammograms (CV curves) were recorded in DMF on a glassy carbon (GC) electrode (working surface of 3.14 mm^2) in a thermostatically controlled (20 °C) three-electrode electrochemical cell in the presence of Bu_4NBF_4 (0.1 M). CV curves were recorded at a constant potential scan rate of 50 mV s^{-1} using a Model PI-50-1 potentiostate/galvanostate supplied with a PR-8 programmator. A silver electrode $Ag/AgNO_3$ {0.01 M solution in MeCN [E^0(Fc/Fc$^+$) = +0.20 V]} was used as the reference electrode and a Pt wire (1.0 mm in diameter) served as an auxiliary electrode.

The macroscale electrolysis was performed in DMF in the presence of Bu_4NBF_4 (0.1 M) in a 40 ml three-electrode electrochemical cell with separation of anodic and cathodic compartments supplied with GC electrode (60 cm^2) referred as the cathode using a B5-49 DC device. Paper was used as a diaphragm and GC with the working surface area of 4 cm^2 was used as the anode, the anolite was 0.1 M solution of Bu_4NBF_4 in DMF.

DMF was dried with calcium hydride and purified by distillation. The electrolyte Bu_4NBF_4 was dried by melting in a vacuum and stored under nitrogen. $[PdCl_2(dppe)]$ was synthesized from a corresponding palladium salt and an equivalent amount of dppe according to the described method.[11] Solvents were purified by distillation before use.

The ^{31}P NMR spectra were recorded using a Bruker 400 instrument (161.9 MHz). The ESR spectra were recorded with a Radiopan electronic spectrometer of the X-range SE/X-2544 from solution in three-electrode electrochemical ESR microcell. The construction of the ESR microcell was identical to described one[12] used for investigation of the short-lived radicals in which instead of the mercury electrode Pt plate (5 mm^2 working surface) was used. The mass spectra of electronic ionization (EI) were recorded on a ThermoQuest TRACE MS quadrupole mass spectrometer. The insertion of the sample was performed using direct injection combined with a water cooling system (DIP).

Preparative electrochemical reduction of complex [$PdCl_2$(dppe)] **1**. A solution for electrolysis was prepared by mixing 0.086 g (0.15 mmol) of complex **1** and 0.987 g (3.0 mmol) Bu_4NBF_4 in 30 ml of DMF. The direct current in amount of 1.0, 2.0, 4.0 and 8.0 mA h corresponding to 0.25, 0.5, 1.0 and 2.0 e/Pd, respectively, has been passed through the working solution under potentiostatic conditions at the controlled working electrode potential of –1.40 V (Ag/0.01 M solution of $AgNO_3$ in MeCN). The colour of the working solution was changed from slightly yellow to dark red-brown during electrolysis. After the electrolysis was completed, the solution was transferred to the flask and concentrated by evaporation of the solvent in a vacuum. The ^{31}P NMR and mass spectra were recorded from the residual samples.

^{31}P NMR (161.9 MHz, DMF, C_6D_6-capillary, 25 °C) δ: +29.2 (s).

Mass spectra after electrolysis (the molecular and characteristic Pd-containing ions are shown in italic, the peaks of fragment ions with intensity of less than 5% are omitted), EI, (1.0 e/Pd), *m/z* (%): *906 (0.09), 905 (0.08), 904 (0.17), 903 (0.12), 902 (0.23), 901 (0.15), 900 (0.06)* [$M^{+\cdot}$], 399 (5), 398 (20), 370 (14), 295 (15), 290 (8), 289 (40), 275 (18), 262 (23), 261 (8), 243 (13), 242 (83), 212 (17), 186 (6), 185 (56), 184 (100), 183 (84), 168 (6), 152 (5), 142 (33), 140 (21), 134 (5), 108 (19), 106 (11), 98 (12), 78 (13), 49 (13).

Mass spectra of the complex $[PdCl_2(dppe)]$ **1**, EI, *m/z* (%): *543 (2.7), 542 (1.2), 541 (4.9), 540 (2.1), 539 (4.7), 538 (3.1), 537 (1.4)* [$M^{+\cdot}$ – Cl], 506 (1.4), 504 (1.9), 503 (1.4), 477 (1.5), 476 (1.1), 475 (2.3), 474 (1.5), 466 (1.8), 463 (3.5), 462 (1.3), 461 (3.5), 460 (2.1), 459 (1.1), 399 (3.3), 398 (10.4), 371 (2), 370 (8), 291 (5), 290 (6), 289 (25), 275 (11), 263 (9), 262 (41), 261 (8), 213 (4), 212 (16), 185 (29), 184 (15), 183 (100), 154 (15), 153 (5), 152 (8), 134 (6), 133 (6), 108 (25), 107 (12), 103 (10).

data,[10] the anodic peaks A_1 and A_3 can be attributed to the oxidation of anionic Pd^0 complex $[PdCl_x(dppe)]^{x-}$ **6** formed at the potentials C_1 *via* two consecutive steps giving Pd^I intermediate $[PdCl_x(dppe)]^{(x-1)-}$ **2**. On the cyclic voltammetry timescale, **6** evolves to give neutral Pd^0 derivative [Pd(dppe)(DMF)] **7**, which is oxidized at the potential of peak A_2. At the same time, taking into account the fact that electroreduction of $[PdCl_2(dppe)]$ complex **1** is postulated as a one-electron process,[3] the formation of Pd^0 derivatives can be described as a EC process involving disproportionation reactions:

$$\underset{\mathbf{1}}{[PdCl_2(dppe)]} \xrightarrow[-Cl^-]{+e} [PdCl(dppe)] \xrightarrow{\times 2} [PdCl(dppe)]_2 \quad (6)$$

$$[PdCl(dppe)]_2 \xrightarrow{DMF} \underset{\mathbf{7}}{[Pd^0(dppe)DMF]} + [PdCl_2(dppe)] \quad (7)$$

In order to identify the products generated at the potential C_1, the macroscale electrolysis of complex **1** combined with the monitoring of the reaction mixture by ^{31}P NMR spectroscopy and mass spectrometry was realized under potentiostatic conditions. In the ^{31}P NMR spectrum of the reaction mixture after exhaustive electrolysis (1 F mol^{-1}) at the potential of the working electrode of –1.44 V, a new complex resonated at δ_P +29.2 ppm (s). This chemical shift is attributed to bischelate Pd^0 complex $[Pd(dppe)_2]$ **8**.[11] At the same time, the ^{31}P NMR signal of the initial complex **1** [δ_P +65.0 ppm (s)][11] completely disappeared proving absolute conversion of the starting material into new complex **8** under conditions of one-electron reduction process. In the mass spectra of the initial complex **1**, before electrochemical reduction, the characteristic ion with *m*/*z* 541 is present.‡ This ion is formed as the result of the chloride-anion abstraction from the molecular ion of complex **1**. In the present electrochemical macroscale electrolysis (after passing electricity of 1 F mol^{-1}), the ion with *m*/*z* 541 corresponding to complex **1** was not present in the mass spectra of the resulted solution and only complex **8** was found in the reaction medium that is confirmed by occurrence of the ion with *m*/*z* 902 in the mass spectra and by ^{31}P NMR spectroscopy [δ_P +29.2 ppm (s)].

At the same time, when 0.25 and 0.5 F mol^{-1} of electricity (0.25 e/Pd and 0.5 e/Pd) are passed through the working mixture, both complexes **1** and **8** are present in the reaction mixture displaying the ions with *m*/*z* 541 and 902 in the mass spectra. Our attempts to run the electrolysis consuming 2 F mol^{-1} of electricity under potentiostatic conditions failed due to the absence in solution electrochemical depolarizator reduced at C_1 (the potential of the working electrode was moved to the cathode values).

As it has been already mentioned based on the obtained by the combined use of steady-state voltammetry and transient chronoamperometry results,[3] the absolute overall electron stoichiometry for the electrochemical reductions of complex $[PdCl_2(dppe)]$ is a one-electron step. However, the product obtained in electrochemical reduction at the potential of the first wave is the complex containing palladium(0) metal centre. The formation of bischelate palladium(0) complex **8** can be a result of a complex series of disproportionation and the ligand exchange reactions taking place in the reaction medium. The mechanism of the overall process can involve a stage of a bridging Pd^I complex formation and its disproportionation to Pd^0 and Pd^{II} species accompanied by the ligand abstraction initiated by the coordinatively unsaturated [Pd(dppe)(DMF)] complex with formation of stable bischelate complex **8**. Moreover, it should be noted that electrochemically formed in the reaction medium $PdCl_2$ rapidly reacts with generated in the same reaction free chloride anions to result in dianionic palladium tetrachloride species $[PdCl_2]^{2-}$, which are reduced at the potentials of peak C_2 (Figure 1). The overall scheme of the electroreduction process of complex **1** proceeding at the potentials of peaks C_1 and C_2 can be described as follows:

$$\underset{\mathbf{1}}{2[PdCl_2(dppe)]} + 2e \xrightarrow{C_1} \underset{\mathbf{8}}{[Pd(dppe)_2]} + PdCl_2 + 2Cl^- \quad (8)$$

$$PdCl_2 + 2Cl^- \longrightarrow [PdCl_4]^{2-} \quad (9)$$

$$[PdCl_4]^{2-} + 2e \xrightarrow{C_2} Pd + 4Cl^- \quad (10)$$

Thus, the complete conversion of the $[PdCl_2(dppe)]$ complex in electrochemical reduction is a one-electron process, which is realized in the reaction medium by interaction of electrochemically generated palladium(0) species with initial form of the starting complex (1:1 molar ratio) accompanied by the ligand abstraction reaction to form the stable bischelate complex $[Pd(dppe)_2]$ and palladium dichloride.

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‡ Hereinafter, the main peak from the multiplet of Pd-containing ions is shown.

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