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Electrochemical Reduction of Palladium-containing Heteronuclear Complexes

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Abstract—Reduction of a series of palladium-containing complexes with MnPd, Fe_2Pd, and Fe_3Pd skeletons was studied by classical polarography, cyclic voltammetry, and controlled-potential electrolysis in acetonitrile. The electrochemical behavior of these complexes was compared to that of relared platinum complexes.

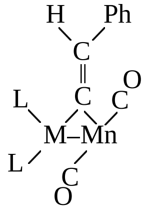
Palladium complexes are widely used as catalysts of redox reactions, for example, oxidation of alkenes into carbonyl compounds and their acetals and ketals, oxidative acetoxylation of alkenes and alkylarenes, reduction of multiple bonds in alkynes and alkenes, etc. [1–3]. The mechanisms of such reactions are not completely clear, which makes difficult selecting optimal conditions and catalysts. To elucidate the mechanism and to develop certain catalytic processes, it is useful to know features of redox transformations of palladium complexes, which are readily established by electrochemical methods.

In the present work we performed electrochemical reduction of three types of palladium intermetallic complexes: binuclear MnPd compounds, such as $Cp(CO)_2MnPd(\mu\text{-}C{=}CHPh)L_2$ [$L_2 = 2PPh_3$ (**Ia**), η^2-$Ph_2P(CH_2)_2PPh_2$(dppe) (**IIa**), η^2-$Ph_2P(CH_2)_3PPh_2\cdot$(dppp) (**IIIa**)], trinuclear Fe_2Pd complex $(CO)_8Fe_2\cdot Pd(dppe)$ (**IVa**), and tetranuclear clusters $(CO)_9Fe_3\cdot Pd(\mu_4\text{-}C{=}CHPh)(\eta^2\text{-}P\text{–}P)$ [P–P = dppe (**Va**), dppp (**VIa**)].

The electrochemical behavior of compounds **Ia**–**VIa** was compared with the behavior of their platinum-containing analogs **Ib**–**VIb** which we studied earlier [4–6] under the same conditions.

The electrochemical characteristics of respective palladium and platinum complexes **Ia**–**VIa** and **Ib**–**VIb** are given in the table. The reduction waves whose parameters are given in the table are diffusion-controlled, as their limiting currents $i_{\lim}$ are proportional to the concentration of complexes c (1×10^{-4}–1×10^{-3} M), $h^{-1/2}$ [h is the height of the mercury column (25–65 cm)], and to $V^{-1/2}$ [V is the potential scan rate (0.01–0.5 V/s)].

The classical polarograms of binuclear complexes **Ia**, **Ib**–**IIIa**, and **IIIb** contain a single one-electron reduction wave (Fig. 1, curve *1* and table).



Ia, Ib–IIIa, IIIb

M = Pd (**Ia, IIa, IIIa**), Pt (**Ib, IIb, IIIb**); LL = 2 PPh_3 (**Ia, Ib**), dppe (**IIa, IIb**), dppp (**IIIa, IIIb**).

As seen from the table, replacement of two monodentate ligands PPh_3 at Pd or P in complexes **Ia** and **Ib** by chelate diphosphine ligands dppe or dppp shifts the reduction potentials of complexes **IIa**, **IIb**, **IIIa**, and **IIIb** to the cathodic region in parallel with the change of the electron-donor power of the new ligands. Complexes **IIa**, **IIb**, **IIIa**, and **IIIb** are reduced reversibly in contrast to compounds **Ia** and **Ib** (the i_{pa}/i_{pc} ratio in cyclic voltammetry on a hanging mercury drop is close to unit).

A feature of the electrochemical behavior of binuclear platinum and palladium complexes with the dppe and dppp ligands is worth noting. The reduction half-wave potentials of both palladium (**IIa**, **IIIa**) and platinum (**IIb**, **IIIb**) complexes do not change as the size of the chelate ring increases by one CH_2 group (see table). Moreover, the half-wave potentials $E_{1/2}$ of all the four platinum and palladium dppe and dppp complexes **IIa, IIb, IIIa**, and **IIIb** are the same (–2.54 eV).

At the same time, replacement of platinum in complex **Ib** with terminal PPh_3 ligands by palladium shifts the reduction potential of the resulting complex

Electrochemical characteristics palladium and platinum containing heteronuclear complexes (dropping mercury electrode, MeCN, 0.1 M Et_4NBF_4, c 1×10^{-3} M, Ag/0.1 M $AgNO_3$ in MeCN)

Comp. no.	Compound	First wave		Second wave		Third wave	
		$E_{1/2}$, V	n	$E_{1/2}$, V	n	$E_{1/2}$, V	n
		Binuclear complexes					
Ia	$Cp(CO)_2MnPd(\mu\text{-}C{=}CHPh)(PPh_3)_2$	–2.24	1	–	–	–	–
Ib	$Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(PPh_3)_2$	–2.37	1	–	–	–	–
IIa	$Cp(CO)_2MnPd(\mu\text{-}C{=}CHPh)$(dppe)	-2.54^{a}	1	–	–	–	–
IIb	$Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)$(dppe)	-2.54^{a}	1	–	–	–	–
IIIa	$Cp(CO)_2MnPd(\mu\text{-}C{=}CHPh)$(dppp)	-2.54^{a}	1	–	–	–	–
IIIb	$Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)$(dppp)	-2.54^{a}	1	–	–	–	–
		Trinuclear complexes					
IVa	$(CO)_8Fe_2Pd$(dppe)	-1.40^{a}	2	–2.06	1	–2.30	1
IVb	$(CO)_8Fe_2Pt$(dppe)	-1.64^{a}	2	–1.96	1	-2.72^{b}	2
						–2.66	*1*
						–2.81	*1*
		Tetranuclear complexes					
Va	$(CO)_9Fe_3Pd(\mu_4\text{-}C{=}CHPh)$(dppe)	$-1.14^{a,b}$	2	–2.44	2	–	–
		–1.06	*1*				
		–1.20	*1*				
Vb	$(CO)_9Fe_3Pt(\mu_4\text{-}C{=}CHPh)$(dppe)	-1.43^{a}	2	-2.72^{b}	2	–	–
				–2.66	*1*		
				–2.81	*1*		
VIa	$(CO)_9Fe_3Pd(\mu_4\text{-}C{=}CHPh)$(dppp)	$-1.14^{a,b}$	2	–2.44	2	–	–
		–1.06	*1*				
		–1.20	*1*				
VIb	$(CO)_9Fe_3Pt(\mu_4\text{-}C{=}CHPh)$(dppp)	$-1.43^{a,b}$	2	-2.72^{b}	2	–	–
		–1.33	*1*	*–2.63*			
		–1.55	*1*	*–2.80*			

[a] Reversible stage. [b] At lower potential scan rates, the two-electron wave splits into two one-electron waves whose potentials are printed italic.

Ia to the anodic region, which agrees with the change in the electron-acceptor power of the metal.

In our opinion, the anomalous behavior of palladium and platinum binuclear complexes **IIa**, **IIb**, **IIIa**, and **IIIb** with chelate diphosphine ligands in terms of the electronic effects on their electrochemical characteristics can be explained as follows: Introduction of dppe or dppp ligands results in formation of a stable five- or six-membered ring M–P$(CH_2)_n$–P involving Pd or Pt. Therewith, the nature of one of the CO groups at the Mn atom changes, namely, it becomes semibridging [7]. The formation of such rings gives rise to electron density delocalization in the molecules, which reveals itself in the equality of the $E_{1/2}$ potentials of complexes **IIa**, **IIb**, **IIIa**, and **IIIb** and in the reversibility of their one-electron reduction. It was established by cyclic voltammetry that the reversible reduction of complexes **IIa**, **IIb**, **IIIa**, and **IIIb** points to formation of electron-transfer products, i.e. radical anions stable in the time scale of cyclic voltammetry.

The polarograms of binuclear complexes **Ia**, **Ib**–**IIIa**, and **IIIb** in MeCN solutions subjected to electrolysis on a mercury bottom at controlled potential in the region of the limiting current of one-electron reduction wave show one reduction wave at $E_{1/2}$ ca. –2.80 V (reduction begins at –2.60 V, the limiting current corresponds to addition of more than two electrons). This wave overlaps with the reduction wave of the background electrolyte ($E_{1/2}$ –3.20 V) (Fig. 1, curve *2*). The IR spectra of these solutions, as well as TLC data point to appearance of cymantrene $CpMn(CO)_3$ and phenylacetylene HC≡CPh in these solutions, which are reduced at $E_{1/2}$ –2.70, –2.90 and –2.80, –2.93 V, respectively. Therefore, the reduction

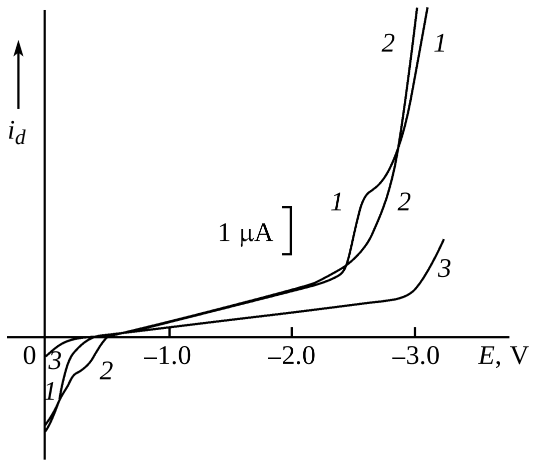


Fig. 1. Current–voltage curves for the $\mathrm{Cp(CO)_2MnPd}\cdot(\mu\mathrm{C{=}CHPh})\mathrm{(dppe)}$ complex (*1*) before electrolysis and (*2*) after electrolysis at E_e –2.60 V; (*3*) background curve (MeCN, 0.1 M $\mathrm{Et_4NBF_4}$, *c* 1×10^{-3} M, Ag/0.1 M $\mathrm{AgNO_3}$ in MeCN).

waves at $E_{1/2}$ ~–2.80 V in the polarograms of solutions of complexes **Ia**, **Ib**–**IIIa**, and **IIIb** after electrolysis can be considered as overlapping reduction waves of cymantrene and phenylacetylene formed by electrolysis.

Thus, combined results of classical polarography and electrolysis of binuclear platinum and palladium complexes **Ia**, **Ib**–**IIIa**, and **IIIb** allow the following assumptions as to the mechanism of the corresponding reactions. The one-electron reduction of the complexes gives radical anions.

$$\mathrm{Cp(CO)_2MnM(\mu\text{-}C{=}CHPh)L_2} + 1\bar{e}$$

Ia, Ib–IIIa, IIIb

$$\longrightarrow [\mathrm{Cp(CO)_2MnM(\mu\text{-}C{=}CHPh)L_2}]^{\overline{\cdot}}$$

The radical anions of the complexes with chelate dppe and dppp ligands are more stable than those of the complexes with terminal triphenylphosphine ligands, which is evidenced by the reversible reduction of the former. Our results agree with the conclusions in [8–10]: Binuclear complexes containing a metal–metal bond and bridging ligands are reduced reversibly to give products whose stability varies over a wide range.

The electrolysis of all the binuclear complexes results in rupture of the Mn–M bonds (M = Pd, Pt) and formation of cymantrene, phenylacetylene, and palladium- or platinum-containing fragments.

$$\mathrm{Cp(CO)_2MnM(\mu\text{-}C{=}CHPh)L_2} + \bar{e}$$
$$\longrightarrow [\mathrm{Cp(CO)_2MnM(\mu\text{-}C{=}CHPh)L_2}]^{\overline{\cdot}}$$
$$\longrightarrow \mathrm{CpMn(CO)_3} + \mathrm{HC{\equiv}CPh} + \text{M-containing fragments.}$$

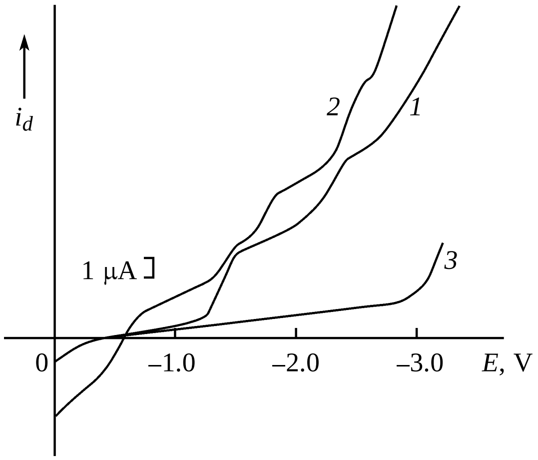
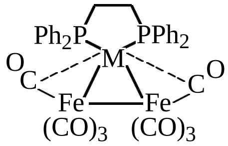


Fig. 2. Polarograms of the $\mathrm{(CO)_8Fe_2Pd(dppe)}$ cluster (*1*) before electrolysis and (*2*) after electrolysis at E_e –1.50 V; (*3*) background curve (MeCN, 0.1 M $\mathrm{Et_4NBF_4}$, *c* 1×10^{-3} M, Ag/0.1 M $\mathrm{AgNO_3}$ in MeCN).

Trinuclear cluster **IVa** is reduced in three stages at $E_{1/2}$ –1.40, –2.06, and –2.30 V (Fig. 2, curve *1*; see table) with addition of two electrons in the first stage and of one electron in the two subsequent stages. The first two-electron stage is reversible, as shown by cyclic voltammetry.



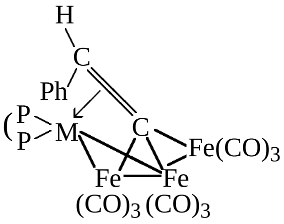
IVa, IVb

M = Pd (**IVa**), Pt (**IVb**).

Unlike complex **IVa**, its platinum analog **IVb** takes up two electrons in the third stage (see table) [5]. The presence of a two-electron reduction wave indicates that the difference in the potentials of the first and second electron transfers is small. At low potential scan rates, the third two-electron reduction wave of complex **IVb** splits into two one-electron waves, and thus four waves appear in the polarogram (see table).

The $E_{1/2}$ value for the first reduction wave of complex **IVa** is shifted to the anodic region, and that for the second wave, to the cathodic region compared to respective values for complex **IVb**. This fact may imply that further reduction of the dianions of complexes **IVa** and **IVb**, formed in the first two-electron reduction stage, occurs differently.

The polarograms of tetranuclear clusters **Va** and **VIa** are identical and contain two two-electron reduction waves at $E_{1/2}$ –1.14 and –2.44 V (Fig. 3, curve *1*;



Va, Vb, VIa, VIb

M = Pd (**Va, VIb**), Pt (**Vb, VIb**). P–P = dppe (**Va, Vb**), dppp (**VIa, VIb**).

see table), the first of them being reversible, as shown by cyclic voltammetry. Their platinum analogs **Vb** and **VIb**, too, are reduced in two two-electron stages at equal potentials of respective waves ($E_{1/2}$ –1.43 and –2.72 V). In certain cases, at low potential scan rates, the two-electron waves split into two one-electron waves (their potentials are given in the table under the values for corresponding two-electron waves and printed italic).

The $E_{1/2}$ values for the reduction of palladium-containing clusters **Va** and **VIa** are shifted to the anodic region compared to those for platinum-containing clusters **Vb** and **Vb**. Therewith, the differences between the $E_{1/2}$ values for the first and second two-electron reduction waves of both clusters **Va**, **VIa**, and **Vb**, **VIb** are equal and make ~1.3 V.

Thus, the electrochemical characteristics of clusters $(CO)_9Fe_3M(\mu_4\text{-C=CHPh})(\eta^2\text{-P–P})$ **Va**, **Vb**, **VIa**, and **VIb** depend on the nature of metal M, but do not depend on the nature of the chelate ligand at this atom.

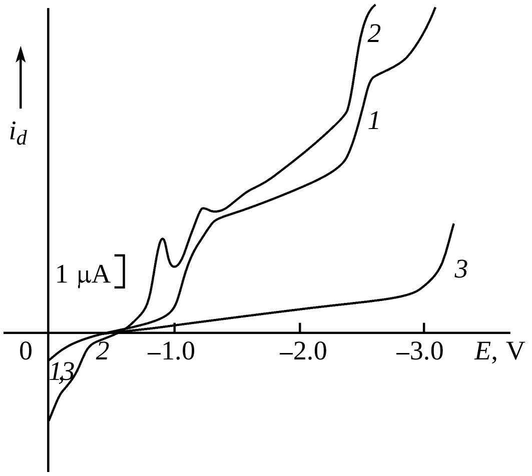


Fig. 3. Polarograms of the $(CO)_9Fe_3Pd(\mu_4\text{-C=CHPh})\cdot$(dppe) cluster (*1*) before and (*2*) after electrolysis at E_e –1.30 V; (*3*) background curve (MeCN, 0.1 M Et_4NBF_4, *c* 1×10^{-3} M, Ag/0.1 M $AgNO_3$ in MeCN).

As noted above, not only the reduction characteristics (reversibility and equal number of electrons added, *n* = 1) of binuclear complexes **Ia**, **Ib**–**IIIa**, and **IIIb**, but also the $E_{1/2}$ values are independent of the nature of the diphosphine ligand and metal M. This can be caused by the presence of a chelate ring formed by the dppe or dppp ligand and M and of the semibridging CO group, which results in electron density delocalization in the molecule. The tetranuclear platinum clusters comprise, along with the dppe and dppp chelates, two semibridging CO groups [11], in contrast to the palladium compounds where the semibridging M–CO bond is weak [12]. This is a probable reason for the different effect of the metals on the reduction potentials of complexes **Va**, **VIa** and **Vb**, **VIb**.

To elucidate the mechanisms of the electrochemical reduction of the tri- and tetranuclear clusters, we performed electrolysis of solutions of complexes **IVa**, **IVb**–**VIa**, and **VIb** in acetonitrile on a mercury bottom at controlled potential of the limiting current of the first two-electron reduction wave.

The polarogram of a solution of trinuclear cluster **IVa** subjected to electrolysis (Fig. 2, curve *2*) contains a reduction wave at $E_{1/2}$ –2.44. This wave is present in the classical polarograms of the tetranuclear palladium clusters (see table), but it was not detected in the polarograms of similar platinum compounds. At the same time, the reduction wave at $E_{1/2}$ –2.72 V, which is absent from the polarograms of solutions of the palladium clusters, is observed for the tri- and tetranuclear platinum clusters (see table). This suggests that the reduction wave at $E_{1/2}$ –2.44 V belongs to a palladium-containing fragment, and that at $E_{1/2}$ –2.72 V, to a platinum-containing fragment, which are formed after two-electron reduction of clusters **IVa** and **IVb**, respectively.

Except for the reduction waves of palladium- and platinum-containing fragments ($E_{1/2}$ –2.44 and –2.72 V, respectively), new reduction waves were detected at $E_{1/2}$ –0.81 and –1.12 V in the polarograms of the solutions of both palladium and platinum-containing tetranuclear clusters **Va**, **VIa** and **Vb**, **VIb** after electrolysis. These waves have the same $E_{1/2}$ values as the reduction waves of the trinuclear cluster $(CO)_9Fe_3(\mu_3\text{-C=CHPh})$ (**VII**) [13]. This fact suggests formation of cluster **VII** after two-electron reduction of compounds **Va**, **VIa** and **Vb**, **VIb**. Cluster **VII** is reduced at higher positive potentials than clusters **Va**, **Vb**, **VIa**, and **VIb** (see table). Therefore, no reduction waves of of cluster **VII** were found in the polarograms of the solutions of clusters **Va**, **Vb**, **VIa**, and **VIb** after electrolysis.

Thus, tetranuclear clusters **Va** and **VIa** are reduced with reversible addition of two electrons to give corresponding dianions whose decomposition is likely to provide trinuclear cluster **VII** and palladium-containing fragments. Further these fragments are reduced at $E_{1/2}$ –2.44 V to Pd(0) which precipitates on the electrode, as evidenced by the observation of a gray palladium film on the mercury surface.

On the basis of the aforesaid we can propose the following scheme of the electrochemical reduction of tetranuclear clusters **Va**, **Vb**, **VIa**, and **VIb**.

$$\underset{\textbf{Va, Vb, VIa, VIb}}{(CO)_9Fe_3M(\mu_4\text{-C=CHPh})(\eta^2\text{-P–P})} + 2\bar{e}$$

$$\longrightarrow [(CO)_9Fe_3M(\mu_4\text{-C=CHPh})(\eta^2\text{-P–P})]^{2-}$$

$$\begin{tikzcd}
{} \arrow[r] & \underset{\textbf{VII}}{(CO)_9Fe_3(\mu_3\text{-C=CHPh})} \arrow[d, "\bar{e}"] & + & \text{M-containing fragments} \arrow[d, "2\bar{e}"] \\
& {[(CO)_9Fe_3(\mu_3\text{-C=CHPh})]^{\overline{\cdot}}} \arrow[d, "\bar{e}"] & & M(0) + \text{fragments} \\
& {[(CO)_9Fe_3(\mu_3\text{-C=CHPh})]^{2-}} & &
\end{tikzcd}$$

The electrochemical study of bi-, tri, and tetranuclear palladium-containing compounds and comparison of their behavior with the behavior of their platinum-containing analogs showed that introduction of chelate dppe or dppp ligands instead of two mononuclear PPh_3 ligands at the Pd or Pt atom in binuclear complexes makes reduction of the resulting complexes reversible, i.e. increases stability of species formed by reduction. Increase in the number of metal atoms facilitates reduction and increases stability of tri- and tetranuclear clusters, compared to binuclear clusters, in redox reactions, which leads to reversibility of their two-electron reduction. The difference in the electrochemical characteristics of platinum and palladium tetranuclear clusters with the dppe and dppp ligands is apparently connected with the presence of two semi-bridging CO groups in the platinum-containing clusters and weak M–CO bonds in the palladium-containing analogs.

EXPERIMENTAL

Compounds **Ia**–**VIa** were obtained by the procedures in [14, 15].

Electrochemical measurements were carried out in freshly prepared solutions of compounds **Ia**–**VIa** in acetonitrile purified as described in [16], under argon at room temperature. The background electrolyte was 0.1 M Et_4NBF_4. The polarograms and cyclic voltammograms were recorded on a PA-2 polarograph operated in the three-electrode mode. The potential scan rate was varied within 0.01–0.50 V/s. The working electrodes were a dropping mercury electrode with forced dropping (m 3.6 mg/s, τ 0.23 s) or a stationary platinum electrode (diameter 1 mm) embedded in a Teflon housing (10 mm). For reproducible operation the platinum working electrode was polished before each measurement with a wet aluminum oxide powder (chromatographic grade) applied on a felt support.

The reference electrode was Ag/0.1 M $AgNO_3$ in MeCN, connected with the cell by an electrolytic bridge filled with the background electrolyte. The auxiliary electrode was a platinum spiral placed in a glass tube with a porous filter.

The number of electrons participating in each reduction stage was determined by polarographic coulometry [17].

Controlled-potential electrolysis was carried out on a PA-3 polarograph operated in the three-electrode mode. The working electrode was bottom mercury (4 cm^2) located on the bottom of the electrochemical cell. Other experimental conditions were the same as above-described. Electrolysis was carried out with vigorous stirring and bubbling argon.

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